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Studies on Zeolite-Supported Mo and Re Catalysts
—Catalytic Performance in Methane Aromatization Reaction and Their Structural Characterization—

ゼオライト担持モリブデンおよびレニウム触媒の研究
—メタンの芳香族化反応の触媒特性と構造キャラクタリセーション—

BY

Linsheng Wang
王　林勝

DS Thesis
Submitted to the Graduate School of Sciences
Hokkaido University

December, 1998

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PREFACE

This is a thesis for a doctorate of Hokkaido University on sciences. This thesis comprise several chapters which have been published and will be published.

I express my thanks for the supervision of Prof. M. Ichikawa by his enlightening research guidance and for preparing my DS thesis submitting to Hokkaido University. Additionally, I acknowledge Prof. Y. Xu , Prof. L. Tao and Prof. X. Guo in Dalian Institute of Chemical Physics, Chinese Academy of Sciences for their supervision of my research works on catalytic conversion of alkanes on zeolite catalysts as the former contribution in my DS thesis.

Many helps and discussions from Dr. R. Ohnishi and Dr. A. Fukuoka are greatly appreciated. I also appreciate the helps from Mr. Suziki, Mr. Zama, Ms. Yamamoto, Ms. Fujishima, Dr. Sasahara, Mr. Higashimoto in Advanced Catalyst Design Laboratory of Catalysis Research Center.

Linsheng Wang

Sapporo
January, 1999

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学位論文内容の要旨

博士の専攻分野の名称　博士（理学）　氏名　王　林勝

学　位　論　文　題　名

Studies on HZSM-5-Supported Mo and Re Catalysts— Catalytic Performances in Methane Aromatization Reaction and Their Structural Characterization
（ゼオライト担持 Mo 及び Re 触媒の研究
－メタンの芳香族化反応の触媒特性と構造キャラクタリゼーション）

触媒作用を分子レベルで詳細に理解し、より高活性な触媒を分子設計するためには、より良く構造規定された活性中心を固体表面に精密合成するとともに、活性サイト周辺の反応場をも精密制御することが重要である。金属担持触媒は石油化学原料の酸化反応、異性化反応及び重合反応などの触媒反応に用いられる工業的に有用な固体触媒であり、その触媒活性構造や触媒メカニズムに関して基本的な理解を得ることは学術的意義のみならず、工業的にも重要な研究課題である。天然ガス及び CO_2 のエネルギー化や資源化は炭素資源エネルギー体系の改革と関連して２１世紀にむけての重要な研究課題である。本研究において、申請者はゼオライト担持の Mo 及び Re 触媒メタンの脱水素縮合化反応でベンゼン、ナフタレンの芳香族原料と水素を合成し、高効率で安定な触媒性能を示すことをはじめて見出した。新規なゼオライト担持 Mo 及び Re 触媒についてメタンの芳香族化反応の触媒特性と触媒活性構造のキャラクタリゼーションを XAFS/TEM/XPS などの物理化学的手法により明らかにした。また本研究において、Mo カーバイド粒子とゼオライトのブレンステット酸点からなる複合触媒作用に関するメタンの脱水素芳香化反応の新しいメカニズムを提出した。

本論文では十章から構成されている。

第一章では本研究の位置づけを示した後、第二章から三章において、Mo/HZSM-5 を触媒とし、600~800 ℃の温度域でメタンからベンゼンなどの芳香族化合物と水素を直接合成するメタンの芳香族化反応について述べる。まず、HZSM-5 ゼオライトを担体に用いて２０種以上の異なる遷移金属元素の担持触媒を調整しメタンの芳香族化反応に対する触媒特性を調べた。この結果、Mo,Re,W といったオレフィンのメタセシス反応に有効な触媒金属においてのみ、高いメタン酸化率で、また高い選択率でベンゼンを生成することを見出した。さらに様々なミクロ及びメソ細孔多孔質担体を用いて調整した Mo 担持触媒についてメタンの芳香族化反応を調べた。その結果、HZSM-5 以外の１０Å以上の細孔径を有する MOR や FAU や FSM-16 などのゼオライトやシリカやアルミナ担体を用いた場合、コーク生成が著しくベンゼンへの転化率が著しく低いことが判った。最適な SiO_2/Al_2O=20-70 を有する HZSM-5 に Mo を担持すると特異的に高活性と高選択率でベンゼン、ナフタレン等の芳香族化合物を生成する事を見いだした。HZSM-5 上の B 酸がベンゼン生成のためのメタンの縮合反応に効果的であると考えた。

第三章において Mo/HZSM-5 とメタンとの反応について SEM、TEM および XAFS 解析に

よって調べた。その結果、Mo 酸化物は HZSM-5 上に均一平坦にに分布しすること、メタンと反応することで、その粒子が Mo_2C であることが解った。EXAFS 解析によると生成した Mo_2C の Mo-Mo 配位数は 2 ～ 3 であり、Mo2C 結晶での C,N,=12 に比べて、著しく小さい値を Mo2C は ZSM-5 ゼオライト細孔チャンネル（6 Å径）に高分散されていると考えた。

第四章では第三章での研究結果をいかして、メタンへの CO あるいは CO_2 の添加効果と作用メカニズムについて調べた。

メタン反応率は反応時間とともに低下するが、CO あるいは CO_2 をメタン中に数%添加すると、ベンゼンの生成速度の増大とともに、活性低下の度合が著しく改善されことを見出した。定常状態では、導入した CO_2 の 2 倍量の CO が生成していることが分かった。従って、この条件下で　$CH_4+CO_2=2CO+2H_2$　の反応が進行し、結果的には CO ないし CO_2 から生成した活性酸素が Mo カーバイド表面の不活性なコークと反応し、副生するコークを低減して、触媒活性の安定化が得られると推察した。

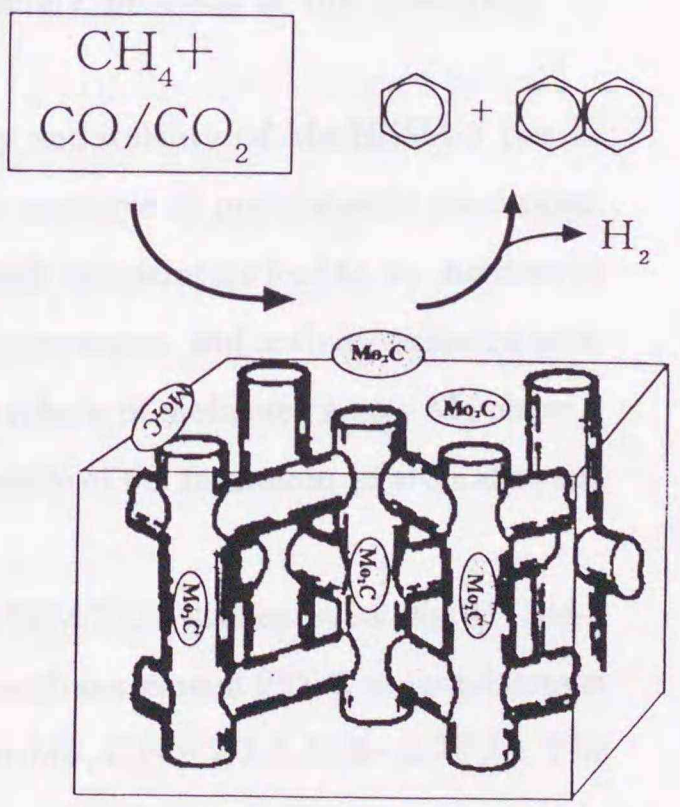
さらに、第五章では反応後、触媒表面にどのような蓄積炭素種があるのかを空気で昇温しながらコーク生成量の解析を行った。その結果、CO や CO_2 添加により触媒上の coke 蓄積量が著しく減少しており、これが活性低下を防ぐ 1 つの要因となっていることが判った。

さらに、第六章においてメタンへの CO や CO_2 の添加効果がどうして起こるのかを調べるために ^{13}CO をメタンに混合して実験した。その結果、反応進行につれてベンゼン中に ^{13}C が均一的に分布しており、ベンゼン 1 分子中に 0.6 から 0.9 個の ^{13}C が含まれていた。以上の結果から、Mo_2C 上で CO は $2CO=CO_2+C$ の反応により活性な炭素と酸素を供給し、この活性炭素がメタンの脱水素によって生成した炭素 2 個を含む中間体を経由してゼオライト表面でベンゼンなどの芳香族化合物へと転化していく。bifunctional な触媒作用のメカニズムを提案した。

第七章において XPS や Mo_2C+HZSM-5 ハイブリッド触媒の研究から Mo_2C が本反応におけるメタンを活性化するサイトであることを見出した。

第八～九章においては、これまで研究をしてきた Mo/HZSM-5 触媒に対してさらに高活性で高選択的なメタンの芳香族化反応に有効な Re/HZSM-5 を発見し、この触媒特性と反応メカニズムについて研究を行った。Re 触媒は、Mo 触媒とほぼ同様のメタン転化率やベンゼンへの高い生成選択性を示した。さらに、メタンに CO_2 を添加すると触媒活性が安定化し長時間一定の活性を保った。コーク生成の抑制が触媒の安定化の要因であることを結論した。

第十章において本研究の総括を行うとともに、メタンの芳香族化反応の反応機構と Mo/HZSM-5 及び Re/HZSM-5 触媒は示す複合触媒作用についてその特徴を明らかにした。



Mo/HZSM-5

Studies on HZSM-5-Supported Mo and Re Catalysts
— Catalytic Performances in Methane Aromatization Reaction and Their Structural Characterization—

Abstract

The main achievements in the present studies are summarized as 4 key points: 1) HZSM-5 supported Mo and Re catalysts are found to be quite active and selective for directly converting methane to benzene, naphthalene and C_2 hydrocarbons. A great progress for methane aromatization has been made because of the discover of the two new catalysts. 2) Coke deposition on the catalyst for non-oxidative conversion of methane is solved by varying methane pressure combined with addition of CO_2 in methane feed. Coke selectivity is about 0 at 3 atm methane and with 1-3% CO_2 addition in methane feed. 3) Two reactions on Re/HZSM-5 catalyst are identified: i) methane with CO at the nearly same consumption rate to produce benzene, naphthalene and C_2 hydrocarbons; ii) an improved reforming reaction of methane with CO_2 to produce aromatics and synthesis gas. 4) MoO_3/HZSM-5 and Re_2O_7/HZSM-5 are first endothermically converted to its reduced state before production of benzene. Mo exists in its carbide and is highly dispersed on the HZSM-5 support. The results are presented in details in 9 chapters.

It was found in chapter 2 that Mo modified ZSM-5 catalysts exhibited excellent catalytic activity and selectivity to benzene for the conversion of methane at 973 K under non-oxidizing conditions. H_2 and ethene may be the primary products in the conversion of methane to benzene.

It was found in chapter 3 that the catalytic activity and stability of Mo/HZSM-5 can be enhanced by the addition of Zr or W and it is also very sensitive to pretreatment conditions. Pretreatment of catalysts under air atmosphere at a high temperature lead to an increase in pore size of the catalysts and a decrease in methane conversion and activity maintenance. However, the catalysts can be stabilized under the atmosphere of methane. A new Mo phase is formed under the methane atmosphere, which is a perquisite of the formation of aromatics and C_2 hydrocarbons.

In chapter 4, the TG/DTA/MS , XANES/EXAFS and SEM/TEM studies reveal that HZSM-5 supported Mo oxide is endothermally converted with methane around 955 K to molybdenum carbide (Mo_2C) cluster (Mo-C, C.N.=1, R= 2.09 Å; Mo-Mo, C.N.= 2.3-3.5; R= 2.98 Å). The

formed Mo carbide exists on HZSM-5 support in the uniform particles. The highly dispersed metal carbide on HZSM-5 support acts as the active center to activate methane primarily to C_2 hydrocarbons, which are secondarily dehydrocondensed towards benzene and naphthalene on HZSM-5 support.

Methane aromatization with addition of C_2 hydrocarbons such as ethane and ethene and acetylene on Mo/HZSM-5 catalyst is studied in chapter 5. Addition of all C_2 hydrocarbons in methane feed lead to an increase of benzene formation rate and ethane addition is most effect to enhance the rate of benzene formation. A much high formation rate and selectivity of benzene is achieved by addition of about 4.3% ethane in methane feed. The formation rate and selectivity of naphthalene is most effectively enhanced by addition of 4.3% acetylene. The increase of benzene formation rate is due to high concentration of $[C_2H_y]$ intermediates for benzene formation by addition of C_2. Addition of acetylene lead to enhancement of the secondary reaction of benzene to produce naphthalene, so the formation rate and selectivity of naphthalene is high.

In chapter 6, catalytic dehydroaromatization of methane with CO and/or CO_2 toward benzene and naphthalene on Mo/HZSM-5 and Fe/Co modified Mo/HZSM-5 in the prolonged time of 100 h is studied. The catalyst stability is enhanced and coke formation is suppressed by adding CO and/or CO_2 to the methane feed and by varying methane pressure. Bifunctional catalysis of Mo/HZSM-5 is discussed by the mechanism that methane is activated on Mo sites to form CHx and C_2-species, and then secondarily to form benzene and naphthalene.

Dependence of activity and selectivity for methane aromatization on Mo/HZSM-5 on the reaction conditions such as pressure and specific velocity of methane, CO_2 addition at high SV and reaction temperature is investigated in chapter 7. A high and stable benzene formation rate of about 1700 nmole/s/g-cat is achieved for methane aromatization on Mo/HZSM-5 by increasing methane pressure from 1 to 3 atm, methane specific velocity from 1440 to 10000 ml/h/g-cat and reaction temperature from 973 to 1073 K, and by adding about 2.1% CO_2 to methane feed. The rate of benzene formation with time on stream is remarkably stabilized by varying methane pressure and addition of 2.1% CO_2 in methane feed and greatly enhanced by increasing methane specific velocity from 1440 to 10000 ml/h/g-cat and reaction temperature from 973 to 1073 K. The selectivity of benzene and naphthalene and coke is also controlled by varying reaction conditions. High methane specific velocity lead to high benzene selectivity and low naphthalene selectivity.

Catalytic features of Re/HZSM-5-based catalyst for aromatization reaction of methane are studied and compared with that of Mo/HZSM-5 in chapter 8. It is found in TPR of Re_2O_7/HZSM-5 in methane flow that methane activation process is initiated by reduction of Re_2O_7/HZSM-5, which is endothermic and company with production of hydrocarbon oxides and loss of catalyst weight. However, the reduction of catalyst in hydrogen stream is a exothermic process and takes place at a much lower temperature. We propose that rhenium carbide is formed by reduction of Re_2O_7/HZSM-5 in methane flow. The carbide is stable in the atmosphere of methane and catalyze the reaction of methane aromatization. The temperature for formation of rhenium carbide is about 100 K lower than that for formation of molybdenum carbide and Re/HZSM-5 shows much better low-temperature activity than Mo/HZSM-5-based catalyst. To compare with Mo/HZSM-5-based catalyst, Re/HZSM-5-based catalyst exhibits a better lower-temperature activity and a higher selectivity to C_2 hydrocarbons.

Catalytic conversion of methane with CO to aromatics on Re/HZSM-5-based catalyst are studied in chapter 9. The CO involves in the catalytic conversion with methane to produce aromatics and the catalytic activity for benzene formation, therefore, is greatly enhanced by adding CO to methane feed. Furthermore, the conversion of CO with methane also lead to formation of some intermediate products such as CO_2 and H_2O, which eliminate coke on the catalyst. Therefore, the coke deposition is decreased and catalyst stability is enhanced by CO addition.

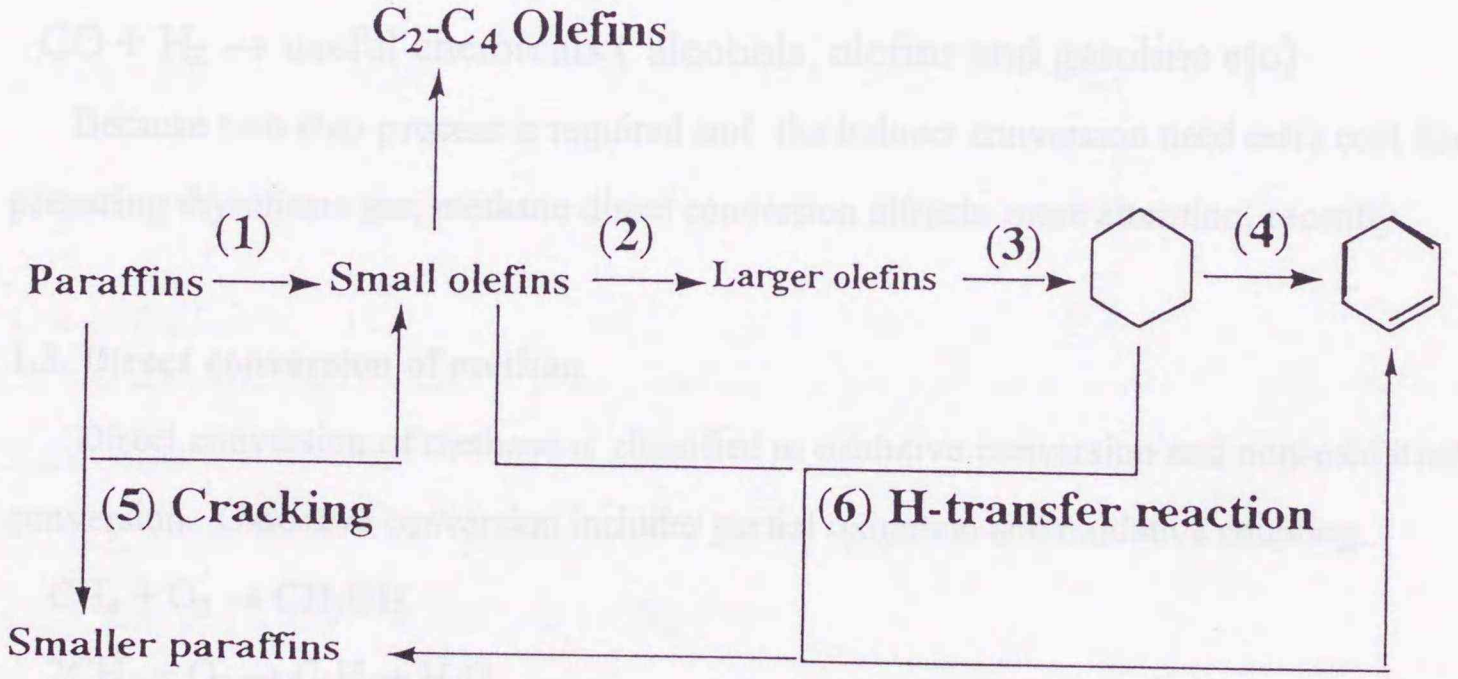
Effect of CO_2 addition on aromatization of methane on Re/HZSM-5-based catalyst are studied in chapter 10. High and stable rate of benzene formation is achieved at a high SV of methane on Re/HZSM-5 type catalyst by addition of about 1-3% CO_2 to methane feed. A little amount of CO_2 in methane feed is very effective to suppress deposition of coke on the catalyst and to enhance selectivity of hydrocarbon products. Selectivity for coke deposition is about 0 at the presence of 1-3% CO_2 in methane feed. The reaction of CO_2 with coke to produce CO and the secondary reaction of produced CO with hydrogen to produce CHx species are responsible for the low coke selectivity and high hydrocarbon selectivity.

Chapter 1. General introduction

1.1. Aromatization of light hydrocarbons

Transformation of light alkans such as propane and butane into aromatics has been extensively studied over the past years because of its significance in both industrial and acedemic points. The aromatic hydrocarbons can be utilized as a booster for high octane number gasoline and are fundamental raw chemicals in petroleum chemistry. The best catalysts for light alkane aromatization is Zn or/and Ga modified ZSM-5 zeolites with bifunction. The acepted mechanism for aromatization of light alkanes is as below,

Conversion routes of light paraffins on ZSM-5 zeolites



(1) Dehydrogenation (2) Oligomerization,
(3) Cyclization (4) dehydrogenation

(1) light alkane activation is initiated by dehydrogenation to produce olefin,

(2) oligomerization of the olefin to produce larger olefins

(3) cyclization of the larger olefins to produce cyclohexanes or cyclohexene

(4) dehydrogenation of cyclohexanes or cyclohexenes to produce benzene

A commerciallized process called as cycolar process has been developed for aromatization of light alkanes. Methane is much more abundant and cheaper raw materials thane propane and butane. However, the catalysts such as Zn or Ga modified ZSM-5 shows only very low activity for aromatization of methane. Therefore, to find new catalysts for methane aromatization is highly disirable and much more siugbifcant from both industrial and acedemic points.

1.2. Indirect conversion of methane

Methane can be converted to usfule chemicals indirectly and directly. For indirect conversion: the first step is to prepare synthesis gas, and the second step is to produce useful chemicals such as alcohols, olefins and gasoline etc from thynthesis gas as below,

$CH_4 \rightarrow CO + H_2$ (to prepare thynthesis gas)

$CO + H_2 \rightarrow$ useful chemicals (alcohols, olefins and gasoline etc)

Because two step process is required and the indirect conversion need extra cost for preparing thynthesis gas, methane direct conversion attracts more attention, recently.

1.3. Direct conversion of methan

Direct conversion of methane is classified as oxidative conversion and non-oxidative conversion. Oxidative conversion includes partial oxidation and oxidative coupling:

$CH_4 + O_2 \rightarrow CH_3OH$

$2CH_4 + O_2 \rightarrow C_2H_4 + H_2O$

Non-oxidative conversion includes:

Homologation (two steps)

step 1: $CH_4 \rightarrow CH_x + H_2$ step 2: $CH_x + H_2 \rightarrow C_{2+}$ hydrocarbons

Thermal pyrolysis and catalytic pyrolysis

$CH_4 \rightarrow C_6H_6 + C_2H_2 + H_2 + C$

Although cost of preparing thynthesis gas is saved for methane direct conversion, the problem is that methane is very stable molecular. For oxidative conversion, the further

oxidation of products is unavaidable. Therefore, the selectivity is low. For non-oxidative conversion, usually high reaction temperature is required. High reaction temperature for methane nonoxidative conversion cause serious coke deposition problem. Some data for methane aromatization by different methods are list in table 1.

Table 1. Comparation of the results for methane dehydroaromatization by different methods

Catalyst	reaction temperature (K)	conversion (%)	selectivity (%) aromatics	aromatics yield C_2	(%)	reference
pyrolysis	1480-1580				6-10	(1)
silica gel	1273				4.2-7.2	(2)
NaCl/MnO2	1223	13.2	23.4	24.2	3.1	(3)
15% Mo/HZSM-5	1073	12.0	91.2	4.6	10.9	*
10% Re/HZSM-5	1073	10.5	88.0	6.5	9.2	*

References:

(1) H.L.Mitchell III, R.H. Waghorne, U. S. Patent, 4 172 810, 1979

(2) J. Oro and J. Han, Science,153 (1966) 1393

(3) J.B. Claridge, M.L.H. Green et al, App. Catal. A, 89 (1992) 103

* The results are achieved in the present work; SV= 10000 ml/h/g-cat, P= 3 atm, with addiotion of 2.1% CO_2 in methane feed

For thermal pyrolysis of methane, 1480-1580 K is required to obtaine about 6-10% benzene. For catalytic pyrolysis of methane on gel, the temperature is 1273 K to obtaine 4.2-7.2% aromatics. Methane mixture with oxigen pass through $NaCl/MnO_2$ at high

temperature of 1223 K, about 3.1% aromatics can be obtained. The above methods, both selectivity and yield of aromatics is low, and reaction temperature is quite high.

However recently, HZSM-5 supported Mo and Re two type catalysts are developed by us. The data we have achieved on this two catalysts for methane dehydroaromatization are compared with the data in reference. 9.2-10.9% aromatics yiel is obtained at a temperature of 1073 K and aromatics selectivity is quite high (about 90%). We will discuss those two type catalysts and the catalytic reaction of methane on the catalysts in the following 9 chapters.

Chapter 2

HZSM-5 Zeolite-Supported Mo Catalyst for Methane Aromatization Reaction

Abstract

It has been found that Mo modified ZSM-5 catalysts exhibited excellent catalytic activity and selectivity for methane aromatization reaction at 973 K without oxygen. Benzene is the main aromatic product for methane conversion on Mo/HZSM-5 catalyst. H_2 and ethene may be the primary products in the conversion of methane to benzene. Medium pore structure of HZSM-5 play a important role for selective conversion of methane to benzene. In addition, HZSM-5 supported Mo catalyst is the most active and selective for methane aromatization reaction among the more thane 10 tested transition metals.

1 Introduction

In the chemical industries concerning the utilization of the different carbon resources, a left difficult problem is the chemical utilization of natural gas by methane direct conversion, which has challenged many minds because methane is a too stable molecule. Over the past years, methane conversion with oxygen to ethylene or methanol has been extensively studied. However, for the oxidative methane coupling process, the C_2-hydrocarbon selectivity is substantially suppressed by increasing the methane conversion on Sm_2O_3 and Li/Sm_2O_3, as shown in table 1. The situation for methane partial oxidation to methanol on Mo/SiO_2 has no change. Product selectivity at high methane conversion is low. Therefore, the industry interests in these processes have been limited so far.

Recently, increasing attention has been shifted to the methane conversion without oxygen. The free energy for methane conversion without oxygen is positive. To avoid

the limitation in thermodynamics, two-step homologation reaction of methane was designed as shown in fig. 1. Methane is first dehydrogenated to CHx species (x=0-3) on the catalyst at a high temperature, which are hydrogenated to higher hydrocarbon such as ethane at a lower temperature. This is not feasible to industry because of its low productivity. Recently, we are interested in the direct conversion of methane to benzene, which become quite feasible by increasing temperature. However, the carbon production is thermodynamically much more favorable than hydrocarbon production at high temperature. The purpose of the present work is to convert methane to benzene selectively with inhibition of carbon deposition. This is a big challenge not only to the catalyst designer but also to all the chemists.

2 Experiments

Mo/HZSM-5 was prepared by impregnating NH_4ZSM-5 (SiO_2/AI_2O_3=40, Toso Co.) with $NH_4)_6Mo_7O_{24}4H_2O$ (Kanto Chem. Co.) aqueous solution, followed by drying at 383 K for 4 h and calcination at 773 K for 4 h. The final ratio of Mo/HZSM-5 in weight was set to be about 3%. HZSM-5 supported other transition metal catalysts were prepared by the same method. The sample was finally pressed, crushed and sorted into 20-40 mesh.

Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow straight type quartz reactor. After catalyst was pretreated by air stream at 873 K for 30 min and then by He stream at 873 K for 30 min, the stream was switched to feed gas and catalyst bed was brought to a selected temperature for 30 min and it finally was brought to the reaction temperature. The catalytic test was performed at a methane partial pressure of 100-500 kPa (1 -5 atm) and a methane space velocity of

1440 ml/g/h at NTP. The raw materials of methane is over 99.99% pure. All the flow rate of gas was controlled with mass flow controllers (ASAHI Keiki Co. LTD). The products were withdraw periodically from the outlet of reactor and analyzed by two on-line gas chromatography of Shimadazu GC-9A and GC-8A equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) respectively. Hydrocarbon products were separated by a 4mm ×1m Porapak P column and Ar , CH_4, CO, CO_2, H_2 were analyzed by a 4mm×1m active carbon column. 2.2% Ar in methane was employed as internal standard. Formation rate of products, methane conversion and product selectivity were calculated by an internal standard analyzing method]. Below, the method is presented briefly. Even if the total flow rate changed at outlet from inlet of reactor (F_{Total}^{intlet}, F_{Total}^{outlet}). Flow rate of internal standard gas (F_{st}) doses not change.

$$F_{st} = F_{Total}^{outlet} \times X_{st}^{outlet} = F_{Total}^{inlet} \times X_{st}^{inlet}$$

Here, X_{st} refer to concentration of the internal standard gas.

Formation rate of i product (F_i) can be calculated as,

$$F_i = F_{Total}^{outlet} \times X_i^{outlet} = F_{st} \times X_i^{outlet} / X_{st}^{outlet}$$

By the same way, methane conversion ($C_{methane}$) can be calculated as,

$$C_{methane} = (F_{methane}^{inlet} - F_{methane}^{outlet}) / F_{methane}^{inlet} = 1 - F_{methane}^{outlet} / F_{methane}^{inlet}$$

$$= 1 - F_{Ar} \times X_{methane}^{outlet} / X_{Ar}^{outlet} \times F_{methane}^{inlet}$$

TPSR (Temperature Programmed Surface Reaction) experiments was performed with about 200mg catalyst placed in a U-shape quartz reactor. Fig 1 shows a scheme of setup used in this work for TPAR experiments. The catalyst zone was heated in a He stream to 873 K and held at 873 K for 30 min then cooled to room temperature.

At room temperature the stream was switched to methane feed. Temperature-programmed methane reaction was started from room temperature to 973 K at 10 K/min and then held at 973 K for 30 min. The products such as H_2 (m/e=2), CO(m/e=28), CO_2(m/e=44), C_2H_4 (m/e=26), C_2H_6 (m/e=30), C_6H_6 (m/e=78) was monitored with TE-150 multiple channel mass spectrometer and the spectra was recorded at the same time. Reaction pressure is 34 kPa.

3 Results and discussion

It is well known that the Zn or Ga modified HZSM-5 have been employed to the aromatization of C_2-C_4 hydrocarbons. However, they are limited if applying to methane feed. We try to seek the catalyst which is active for methane aromatization reaction, therefore we combine the transition metals with HZSM-5 zeolite and test its catalytic performance. We have found that Mo/HZSM-5 is quite active and selective for methane aromatization But the other tested metals such as Nb, W, Fe, Co, Ni, Cu, V, Zr, Ti, Pt, Ru, etc. have no or only a little activity for methane aromatization .

The catalytic performance of HZSM-5 supported Mo catalyst and HZSM-5 supported other metal such as Nb is compared in table 3. For HZSM-5 supported Mo catalyst, hydrocarbons are main products and rate of benzene formation is quite high. However, for Nb/HZSM-5 and HZSM-5 support only exhibit a little activity for this reaction and the main product is carbon. The contribution of Nb to the catalytic activity can be neglected.

The effect of the supporting materials on the catalytic performance is also studied and the results are shown in this table. 3%Mo was supported on the different supporting materials such as HZSM-5, Al_2O_3, Mordenite, FSM-16, SiO_2, USY. We found that only Mo/HZSM-5 is active and selective for methane aromatization. This is due to that

HZSM-5 zeolite has a straight channel and medium pore structure. The pore size is about 5.5 A, which is very similar to the molecule size of aromatics. Therefore, it has a good shape-selectivity for aromatics formation. Other supporting materials such as Al_2O_3, Mordenite, FSM-16, SiO_2, USY have a macropore structure and their pore size is much larger than that of ZSM-5 zeolite. The larger pore size easily lead to serious coke disposition.

A Study by Temperature Programmed Aromatization Reaction (TPAR) over Mo/HZSM-5, Zn/HZSM-5 and HZSM-5 gave further information on the methane aromatization reaction as shown in figs. 3-5. Two important observations can be made from the results: 1) the starting temperature for benzene formation over Mo/HZSM-5 is about 973 K, which is about 50 K lower than that over Zn/HZSM-5. HZSM-5 zeolite did not exhibit any activity for the aromatization under the given experiment conditions. 2) Ethene and H2 can be directly detected from TPAR and both evolved over Mo/HZSM-5 at about 973 K, Which is the same temperature at which benzene evolved.

4 Conclusion

1. Catalytic dehydrocondensation of methane towards aromatics such as benzene and naphthalene with bulky hydrogen production was found to proceed by the HZSM-5 zeolite supported Mo catalyst.

2. Benzene is the main aromatic product for methane conversion on Mo/HZSM-5 catalyst. H_2 and ethene may be the primary products in the conversion of methane to benzene.

3. Medium pore structure of HZSM-5 play a important role for selective conversion of methane to benzene. HZSM-5 supported Mo catalyst is the most active and selective for methane aromatization reaction among the more thane 10 tested transition metals.

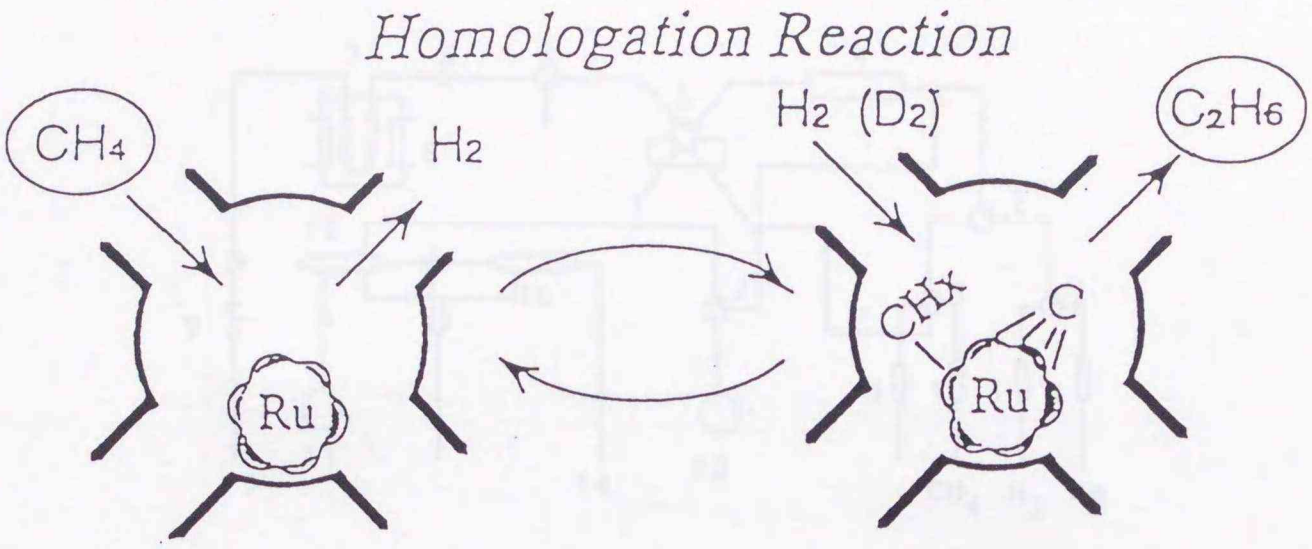
Table 1
Thermodynamics of CH_4 conversion with O_2

Reaction	ΔG° at 298K (kJ/mol)	ΔG° at 1000K (kJ/mol)
$CH_4 + 1/2O_2 \rightarrow 1/2C_2H_4 + H_2O$	- 143.7	- 152.7
$CH_4 + O_2 \rightarrow CH_3OH$	- 115.4	-75.8
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	- 800.8	- 800.8

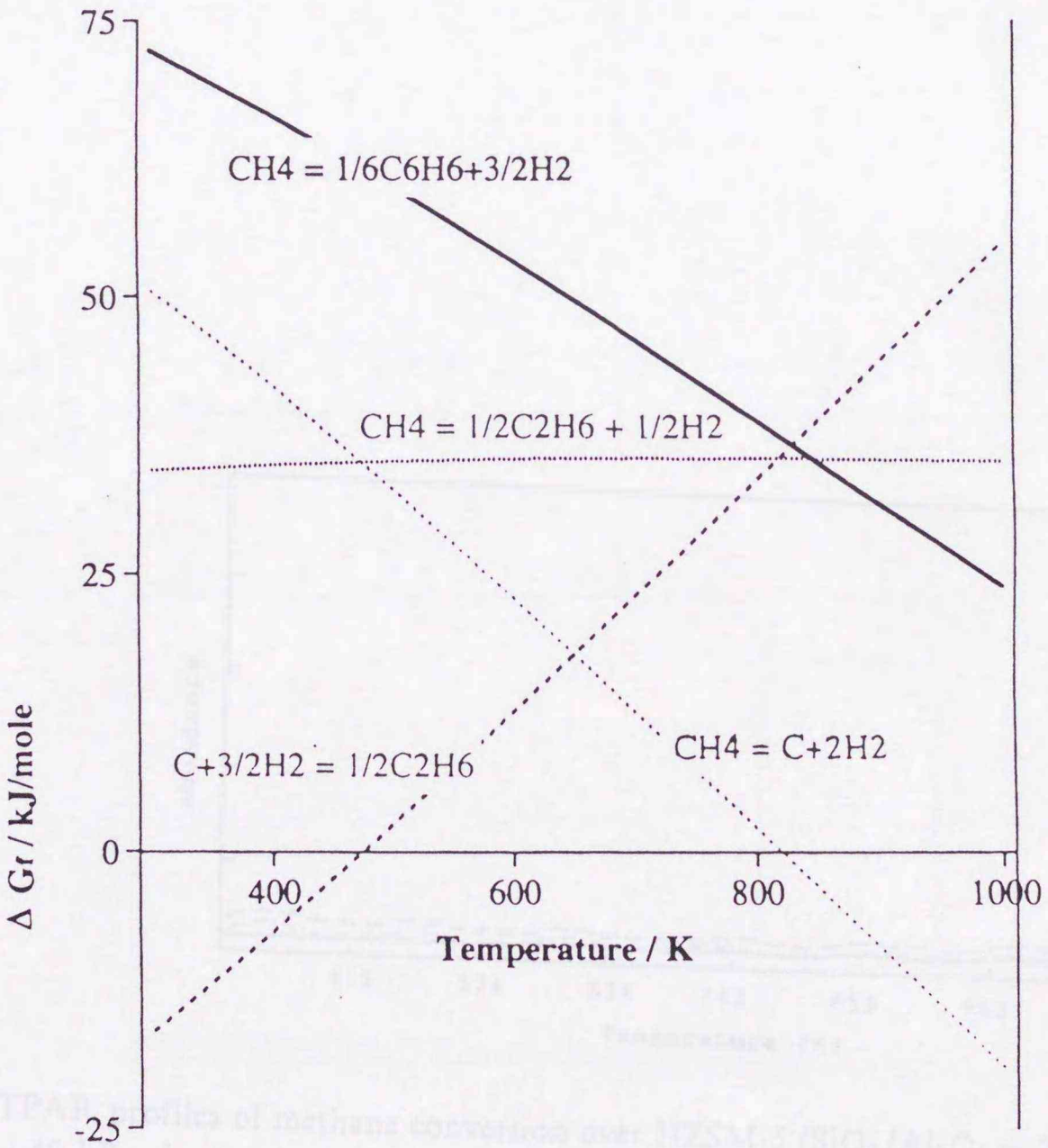
Table 2
The results obtained for CH_4 conversion with O_2

Reaction	Catalyst	Conv.(%)	Sel.(%)
$CH_4 + 1/2O_2 \rightarrow 1/2C_2H_4 + H_2O$	Sm_2O_3	5.8	93
	Li/ Sm_2O_3	41.2	54
$CH_4 + O_2 \rightarrow CH_3OH$	Mo/SiO_2	1.0	86
		8.2	46

The data were taken from references 1 and 2.
1. K. Aoki et. al, Catal. Today, 45 (1998) 29.
2. H. D. Gesser et al., Catal. Today, 42 (1998) 183.



R. van Santen et al., J. Catal, JACS (1992)
M. Ichikawa et al., Stud. Surf. Sci. Catal., J. Mol. Catal. (1996)



Thermodynamics for some non-oxidative reactions of methane

Fig. 1.

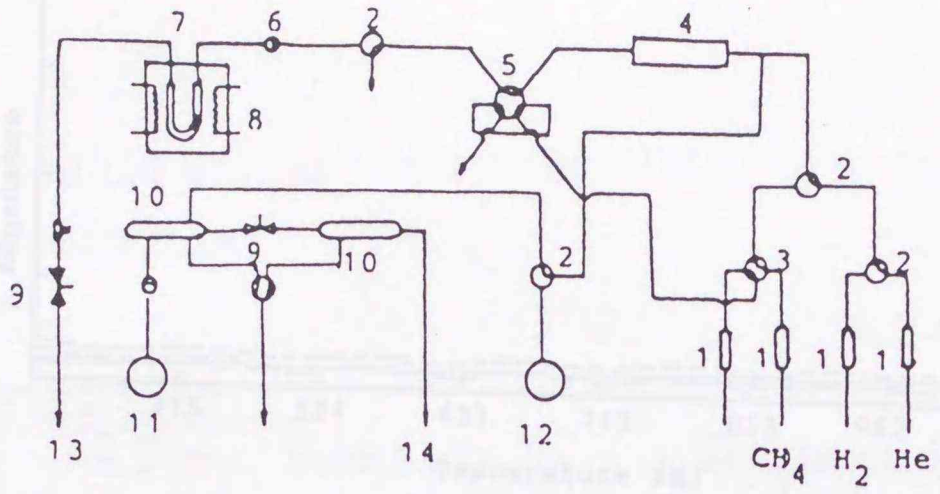


Fig. 2. Schematic diagram of the setup for TPAR experiments. 1, purifier; 2, three-way valve; 3, four-way valve; 4, mass flow controller; 5, six-way valve; 6, injection hole; 7, reactor; 8, heater; 9, valve; 10, buffer; 11, vacuum gauge; 12, gauge; 13, mass spectrometer; 14, mechanical pump.

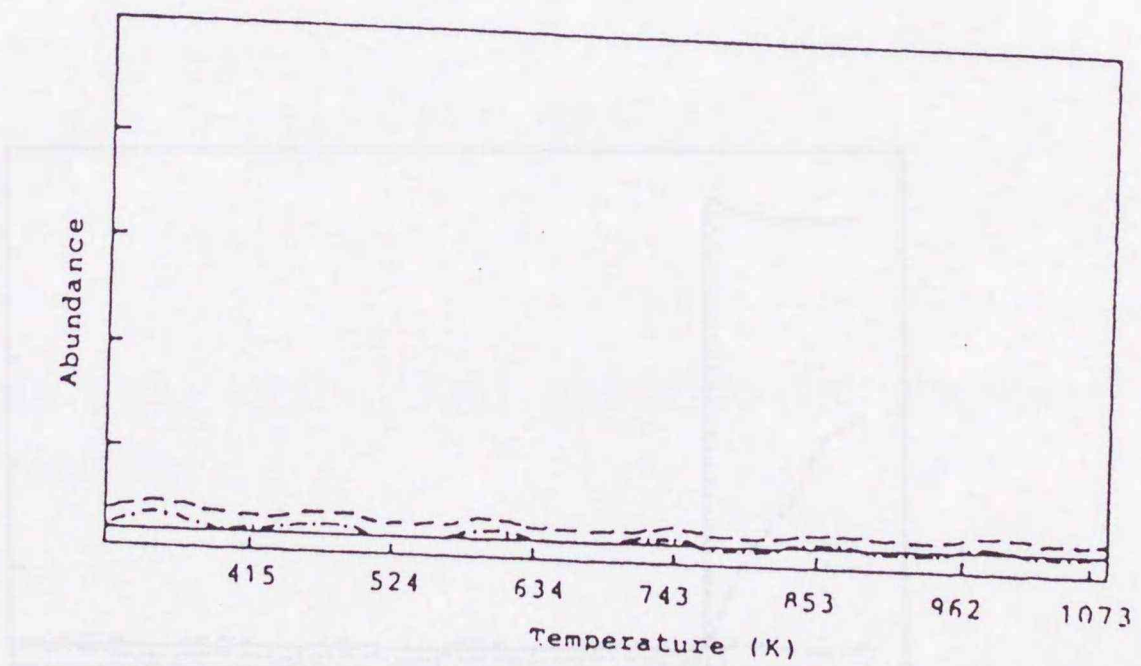


Fig. 3. TPAR profiles of methane conversion over HZSM-5 ($SiO_2/Al_2O_3 = 25$). $F/W = 9000$ ml/g h, $P = 40$ kPa. (· · ·) $m/e = 78$ (C_6H_6); (———) $m/e = 2$ (H_2); (– – –) $m/e = 26$ (C_2H_4); (– · –) $m/e = 30$ (C_2H_6).

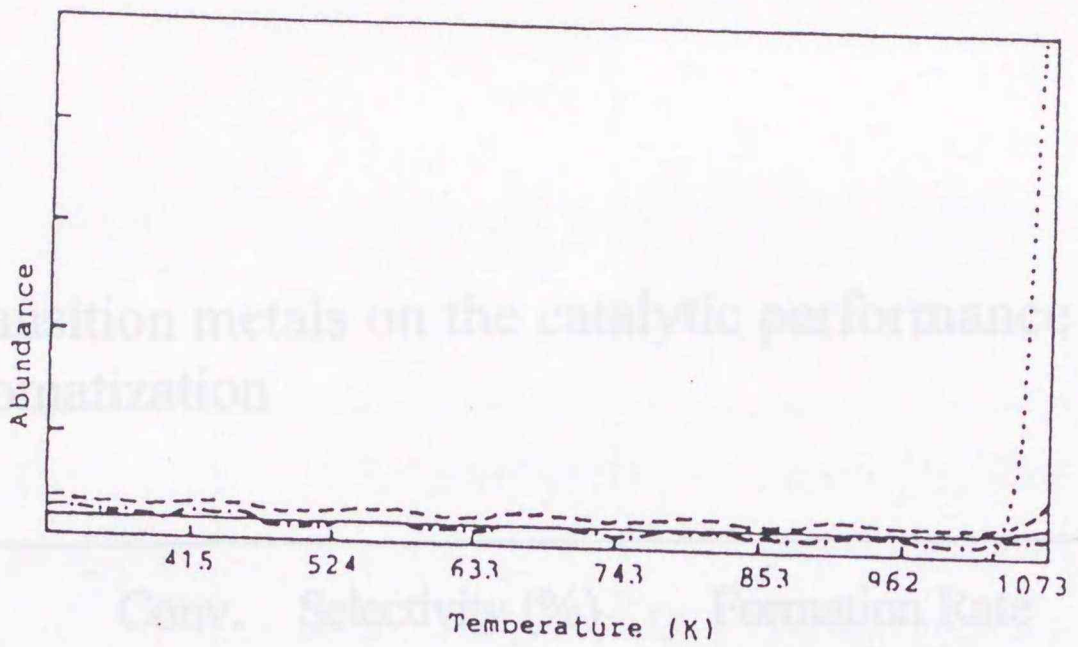


Fig. 4. TPAR profiles of methane conversion over ZnHZSM-5 ($SiO_2/Al_2O_3 = 25$). $F/W = 9000$ ml/g h, $P = 40$ kPa. (···) $m/e = 78$ (C_6H_6); (———) $m/e = 2$ (H_2); (– – –) $m/e = 26$ (C_2H_4); (–·–) $m/e = 30$ (C_2H_6).

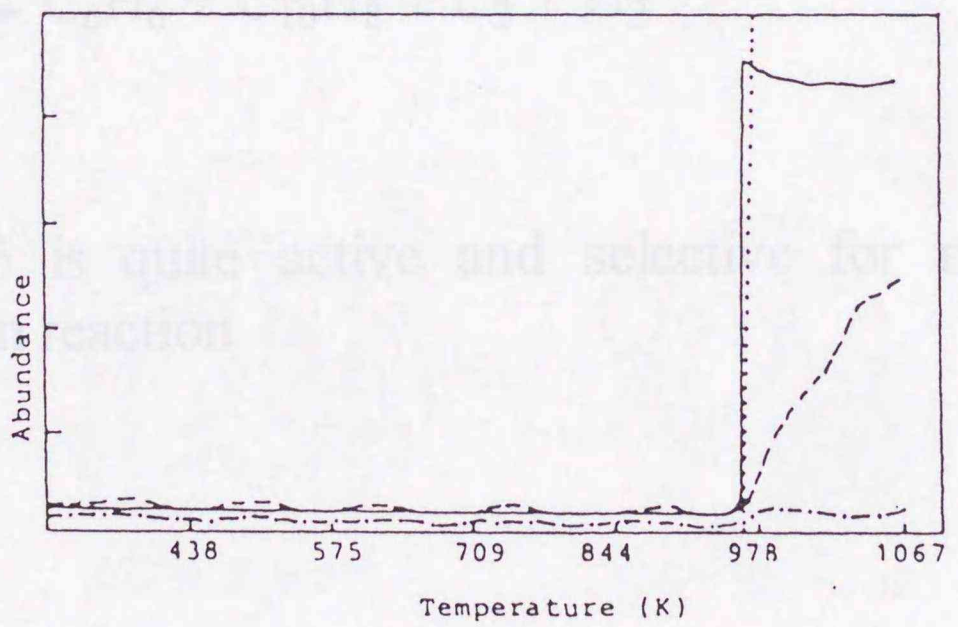


Fig. 5. TPAR profiles of methane conversion over MoHZSM-5 ($SiO_2/Al_2O_3 = 25$). $F/W = 9000$ ml/g h, $P = 40$ kPa. (···) $m/e = 78$ (C_6H_6); (———) $m/e = 2$ (H_2); (– – –) $m/e = 26$ (C_2H_4); (–·–) $m/e = 30$ (C_2H_6).

Table 3
Effect of transition metals on the catalytic performance for methane aromatization

Catalyst	Conv. (%)	Selectivity (%)			Formation Rate (nmole/s/g-cat)		
		HC	Coke	CO	C_6H_6	$C_{10}H_8$	C_2
3%Mo/HZSM-5	9.0	53	38	8	97	14	47
10%Nb/HZSM-5	0.8	16	74	10	2	0	5
HZSM-5	0.7	12	81	7	0.5	0	7

The data were taken after about 60 min on stream at 973K and 3atm and SV= 1440 ml/h/g-cat

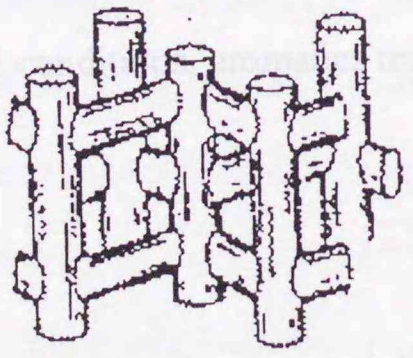
$$CH_4 \longrightarrow C_6H_6 + C_{10}H_8 + C_2 + H_2$$

Mo/HZSM-5 is quite active and selective for methane aromatization reaction

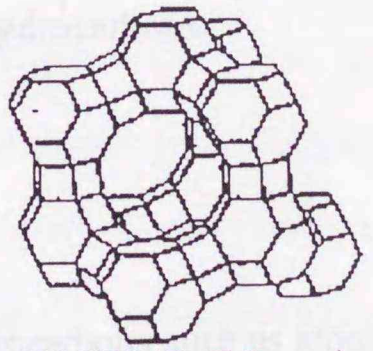
Table 4
Effect of supporting materials on catalytic performance for methane aromatization

Catalyst	Conv.(%)	Selectivity(%)			Formation Rate (nmole/s/g-cat)		
		HC	Coke	CO	C_6H_6	$C_{10}H_8$	C_2
Mo/HZSM-5	9.4	63	36	1	119	29	25
Mo/USY	6.4	13	84	2	21	0	13
Mo/SiO_2	5.3	12	87	2	4	0.3	10
Mo/FSM-16	6.8	9	88	3	14	0	24
Mo/Mordenite	7.3	8	83	9	9	0	23
Mo/Al_2O_3	7.4	6	89	5	9	0	14

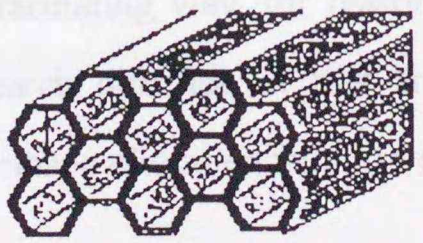
The data were taken after 40 min on stream at 973K and 1atm;
Mo loading is 3 wt.%



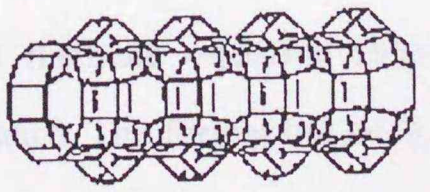
ZSM-5(0.55)



USY(0.74nm)



FSM-16(2-5nm)



Mordenite(0.7nm)

Chapter 3
Activity and stability enhancement of Mo/HZSM-5-based catalysts for methane non-oxidative transformation to aromatics and C_2 hydrocarbons: Effect of additives and pretreatment conditions

Abstract

The effect of additive and pretreatment condition on the activity and stability of Mo/HZSM-5-based catalyst for methane non-oxidative transformation to aromatics and C2 hydrocarbons is investigated. Activity and selectivity of Mo/HZSM-5-based catalysts can be modified by the addition of a second metal component, and the catalytic performance of the catalyst is very sensitive to the atmosphere of pretreatment at high temperature. High methane conversion of over 10% and quite stable activity have been obtained at a reaction temperature of 973 K over Mo/HZSM-5, Mo-W/HZSM-5 and Mo-Zr/HZSM-5 catalysts pretreated by air at a temperature of 873 K. Catalyst pretreatment under air atmosphere at a high temperature may lead to an increase in pore size of the catalysts and a decrease in methane conversion and activity maintenance. However, the catalysts can be stabilized under the atmosphere of methane. A new Mo phase is formed under the methane atmosphere, which is a perquisite of the formation of aromatics and C_2 hydrocarbons.

Keywords: Methane non-oxidative transformation, Mo/HZSM-5-based catalysts, additives, pretreatment conditions, aromatics and C2 hydrocarbons.

1. Introduction

Direct transformation of methane to more valuble hydrocarbons such as aromatics or C2 hydrocarbons is a facinating way for reasonable utilization of natural gas resources. There are two research direction in this area: i) methane oxidative coupling to C2 hydrocarbons, ii) methane oligomerization to aromatics. The former has been extensively

studied over the past for about a decade. However, the latter one is thermodynamically more difficult, especially in the absence of oxygen. The minimum temperature for the conversion of methane pyrolytically to benzene is about 1 173 K, but the temperature for obtaining 6-10 wt.% of benzene is 1480-1580 K [l]. Numerous attempts have been made to catalyze these reactions at lower and more feasible temperature. In 1966, the synthesis of aromatic hydrocarbons from methane with 4.2-7.2% aromatics yield over silica gel at 1273 K was reported [2]. In addition, methane aromatization reaction over other catalyst systems such as boron nitride (BN) [3], multifunctional multimetal oxides [1.4], high silica zeolite supported Pt-Cr catalysts [5], metal oxide and supported metal catalysts [6], high Ga-contained Pt/H-Ga-silicates [7], Mo/ HZSM-5 and Zn/HZSM-5 catalysts [8], carbonaceous materials [9] has been investigated since 1980. More recently, the effect of W additive on the catalytic activity and coking rate of Mo/HZSM-5 catalyst for methane and ethane aromatization has been reported •[10]. Methane activation and conversion over Mo modified acidic zeolite catalyst can proceed without the need of any oxidants. Compared with methane oxidative coupling (MOC) and methane partial oxidation reactions, the advantages of the methane non-oxidative transformation process is that the selectivity to higher hydrocarbon products is high and the main product, benzene, is easier to be separated from the methane feed. In addition, many problems causing from the side reaction such as methane complete oxidation can be avoided under non-oxidative reaction conditions. Recently, the study of methane non-oxidative transformation on Mo modified zeolite catalysts attracts more attention. An increasing number of papers on this research area have been published recently [11-16], in which characterization of catalytic and physical properties of the catalysts has been reported. However, the reported catalytic reaction results of methane over Mo-containing HZSM-5, especially the results on the activity and stability of catalysts are very different since they depend on the preparation and pretreatment conditions of the catalysts. Enhancement of the catalytic activity and stability of the catalysts is significantly important for obtaining a commercialized process for this reaction. In order to obtain a highly active and stable catalyst for the reaction, the

effect of pretreatment conditions and additives on the catalytic performance of Mo/HZSM-5-based catalysts are presented here.

2. Experiment

2.1. Catalyst preparation

Commercially available ZSM-5 zeolite (Si02/Al203=50) was first converted into the ammonium form (NH4ZSM-5) by repeated ion exchange (4 times) with IN NH4N03 aqueous solution at around 368 K for I h. It was then dried at about 383 K for 4 h. HZSM-5 and Mo/HZSM-5 were prepared as described previously [8]; Mo-Zr/HZSM-5 was prepared by consecutively impregnating NH4ZSM-5 with zirconium nitrate and ammonium heptamolybdate aqueous solution; Mo-W/HZSM-5 was prepared by co-impregnating NH4ZSM-5 with ammonium molybdate and ammonium tungstate aqueous solution; Mo-V/HZSM-5 was prepared by co-impregnating NH4ZSM-5 with ammonium molybdate and ammonium vanadate aqueous solution; Mo-La/HZSM-5 was prepared by consecutively impregnating NH4ZSM-5 with lanthanum nitrate and ammonium heptamolybdate aqueous solution. They were dried at 383 K for 4 h and calcined at 773 K for 4 h. The Mo loading of these samples is 2%. Finally, the catalysts were pressed, crushed and sorted into 20–40 mesh.

2.2. Catalytic tests

Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow quartz reactor. The catalysts were first pretreated under air or ,He stream in the temperature range of 773-973 K for 30 min., then the stream was switched to methane and the reactor was brought to the reaction temperature. All the catalytic tests were performed at a pressure of 200 kPa and a methane space velocity of 1440 ml g~1 h~1. The products were withdrawn periodically from the outlet of the reactor and

analyzed by an on-line Shimadzu GC-9A gas chromatography with a 2 m long Porapak Q column and a hydrogen frame ionization detector. Conversion and selectivity were calculated on the carbon number basis.

2.3. Coke deposition and BET surface area measurements

Specific surface area and pore size were determined by the BET method with Micrometrics ASAP-2000 equipment using nitrogen as analysis gas. The amount of coke deposited on the catalysts was determined by TG-DTA method.

2.4. Temperature-Programmed Surface Reactions (TPSR)

The experiment was performed with about 200 mg catalyst placed in a U-shape quartz reactor. Firstly, the catalyst zone was pretreated under a He stream at 873 K for 30 min and then brought to room temperature. At room temperature, the stream was switched to methane. Temperature-programmed methane reaction was started from room temperature to 973 K at 10 K min~ I and then held at 973 K for 30 min. The product such as CO (m/e=28), C02 (m/e=44), C2H4 (m/e=26), C2H6 (m/ e=30), C6H6 (m/e=78) was monitored with TE-150 multiple channel mass spectrometer. The reaction pressure is 34 kPa.

2.5. Material

Methane feed is over 99.99% pure.

3. Results and discussion

3.1. Effect of additive and pretreat,ment atmosphere

Tab]e I shows the effect of additives on the reactivity of methane over Mo/ HZSM-5-based catalysts. The results in Table I indicate that the activity and se]ectivity to aromatics can be improved by the addition of Zr or W to MO/HZSM-5. The addition of Zr is most effective in improving the activity of catalyst at a reaction temperature of 923 K and a Zr content of 1.0% . The addition of V Leads to a decrease in methane conversion and selectivity to aromatics, but the selectivity to C2 hydrocarbons is slightly increased. The effect of catalyst pretreatment atmosphere on the catalytic activity of Mo-Zr/HZSM-5 is summarized in Table 2. It is clear from Tab]e 2 that the catalytic activity of Mo-Zr/HZSM-5 can be enhanced when it is pretreated under flowing air at a temperature of 873 K. The effect of pretreatment conditions on specific surface area and pore size of the catalyst is also examined. The results are summarized in Table 3. The treatment of Mo-Zr/HZSM-5 under an air atmosphere and a high temperature of 973 K Leads to a decrease in BET specific surface area and an enlargement of average pore diameter of the catalyst. The BET specific surface area and pore volume of the catalyst are also decreased with time on stream at a reaction temperature of 973 K, which result from coke deposition on the catalyst. The BET surface area and pore volume can be completely recovered after the coke is removed by combustion with air at a temperature of 773 K. Therefore, the effect of air and methane atmospheres on the specific surface area and pore volume of the catalyst is very different.

3.2. Effect of pretreatrnent temperature

The effect of pretreatment temperature on the catalytic performance of Mo-Zr/ HZSM-5 cata]yst is compared in Figs. 1-3. Mo-Zr/HZSM-5 catalysts pretreated under flowing air at 973, 923 and 873 K are described as Mo-Zr/HZ-973, Mo-Zr/ HZ-923 and Mo-Zr/HZ-873, respectively. Methane conversion and activity maintenance are very sensitive to the pretreatment temperature of the catalyst. Mo-Zr/ HZ-873 exhibits quite high and stable activity and selectivity to aromatics with time on stream. The methane conversion is over 10% with selectivity of more than 93% to aromatics and about 6% to C2 hydrocarbons.

The amount of coke deposited on the catalysts is less than 0.25% of methane feed. The catalytic activity and stability of Mo-Zr/HZSM-5 for methane aromatization are evidently decreased with increasing pretreatment temperature of the catalyst as shown in Figs. 2 and 3. Therefore, the pretreatment conditions are crucial for obtaining highly active and stable cata]yst. In order to compare Mo/HZSM-5 with Mo-Zr/HZSM-5 and Mo-W/ HZSM-5, methane conversion and selectivity to aromatics and C2 hydrocarbons as a function of time on stream over Mo-W/HZSM-5 and Mo/HZSM-5 are shown in Figs. 4 and 5. Enhancement of catalytic activity maintenance by Zr or W is also clear from Figs. 4 and 5.

3. 3. Nature of the active center

The pure methane reaction process on Mo-Zr/HZSM-5 at elevated temperature is shown in Fig. 6. It is clear from Fig. 6 that methane reaction on Mo-Zr/HZSM-5 initiates with C02 and CO formation. C6H6, C2H4 and C2H6 are then formed after the disappearance of CO.* products. The formation of carbon oxides cannot be simply ascribed to the reduction of M003 by methane. A sharp peak of CO product is still appeared in the case of Mo/HZSM-5 catalyst after reduction under H2 stream at 973 K as shown in Fig. 7. It is suggested that Mo phase transformation takes place at the first step of methane reaction on the catalysts, which is a prerequisite of aromatics and C2 hydrocarbon formation. The new Mo phase most possibly is molybdenum carbide (MoC). The formation of molybdenum carbide active phase for methane non-oxidative transformation to aromatics and C2 hydrocarbons, therefore, is suggested as follows, $CH_4 \rightarrow C + 2H_2$

$MoO_3 + C \rightarrow MoC + CO_2 + CO$ $MoO_2 + 3C \rightarrow MoC + 2CO$ On the active phase, methane non-oxidative transformation to higher hydrocarbons occurred. The air pretreatment of the catalyst at a suitable temperature may induce the formation of molybdenum oxide which favors the formation of carbide active phase. The activity of the catalyst, therefore, is evidently enhanced by air pretreatment as shown in Table 2.

Mechanism for methane activation and transformation to aromatics and C2 hydrocarbons has been discussed in our previous papers [8,10,12].

4. Conclusions

The catalytic activity and stability of Mo/HZSM-5 can be enhanced by the addition of Zr or W, and it is also very sensitive to pretreatment conditions. High methane conversion of over 10% and quite stable activity can be obtained at a reaction temperature of 973 K over the catalysts pretreated by air at a temperature of 873 K. Pretreating catalysts under air atmosphere at high temperature may lead to an increase in pore size of the catalysts and a decrease in methane conversion and activity maintenance. However, the catalyst can be stabilized under the atmosphere of methane. A new Mo phase is formed under methane atmosphere, which is a prerequisite of the formation of aromatics C2 hydrocarbons.

Acknowledgements

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Table 1
Effect of additives on the reactivity of methane over Mo/HZSM-5-based catalysts

Additives	Additive content (%)	Conversion (%)	Selectivity (%)			
			C_2	Benzene	Toluene	B+T (Ar)
–	0	3.6	8.3	86.1	5.6	91.7
La	1.0	3.3	6.1	87.9	6.0	93.9
W	0.5	4.0	5.0	87.5	7.5	95.0
V	1.0	2.7	11.1	77.8	11.1	88.9
Zr	0.5	3.1	6.5	87.1	6.4	93.5
Zr	1.0	5.2	5.8	86.5	7.7	94.2
Zr	2.0	3.4	6.5	79.4	4.1	93.5

reaction temperature: 923 K

Table 2
Effect of pretreatment conditions on the catalytic performance of Mo-Zr/HZSM-5

Pretreatment conditions		Conversion (%)	Selectivity			
Temperature (K)	Atmosphere		C_2	Benzene	Toluene	B+T (Ar)
923	air	5.2	5.8	90.9	3.3	94.2
923	He	2.6	4.0	88.5	7.5	96.0
873	air	5.5	4.0	86.5	9.5	96.0
873	He	2.0	10.0	85.0	5.0	90.0
773	air	4.2	10.0	70.2	19.8	90.0
773	He	2.6	12.7	80.8	6.5	87.3

GHSV = 1440 ml g^{-1} h^{-1}; reaction pressure = 200 kPa; reaction temperature = 923 K.

Table 3
Effect of pretreatment atmosphere at high temperature on the BET surface area and pore volume of Mo-Zr/HZSM-5 catalyst

Treatment conditions		BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})		Average pore diameter (A)
			Micropore	Total	
Fresh		130	0.04227	0.0669	15
Methane atmosphere 973 K	with coke	87	0.0314	0.0461	20
	after combustion of coke	138	0.0443	0.0687	15
Air atmosphere 973 K		96	0.0313	0.0564	18

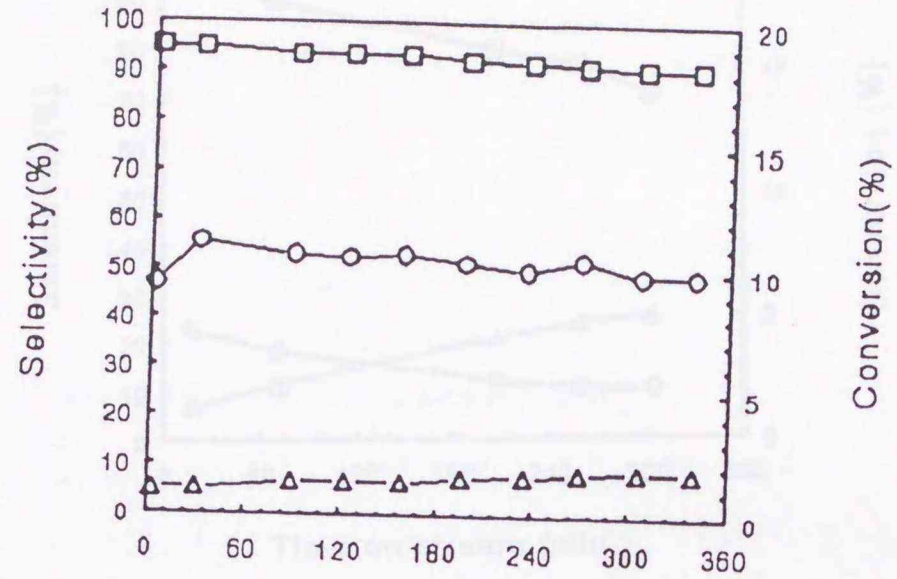


Fig. 1. Methane conversion and selectivity to aromatics and C_2 as a function of time on stream over Mo-Zr/HZ-873 catalyst at 973 K.

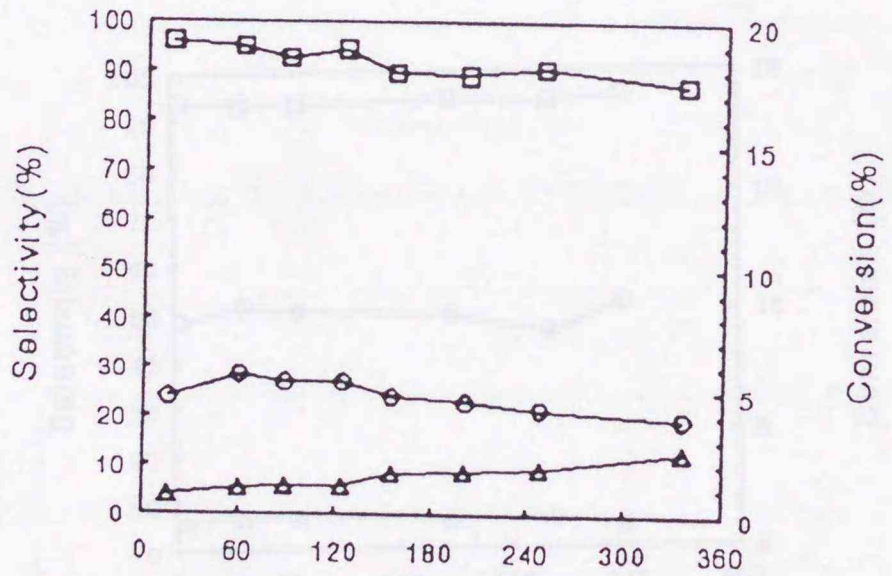


Fig. 2. Methane conversion and selectivity to aromatics and C_2 as a function of time on stream over Mo-Zr/HZ-923 catalyst at 973 K.

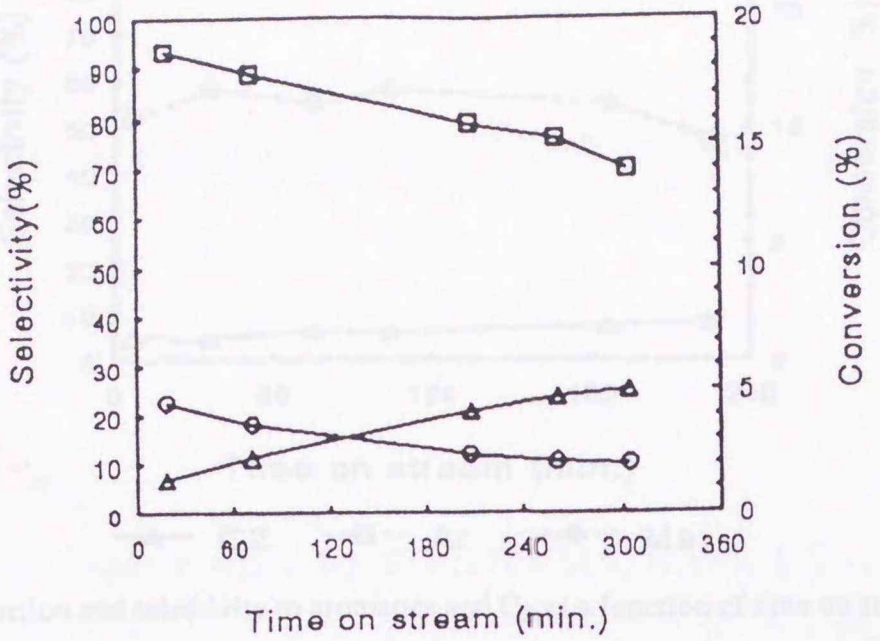


Fig. 3. Methane conversion and selectivity to aromatics and C_2 as a function of time on stream over Mo-Zr/HZ-973 catalyst at 973 K.

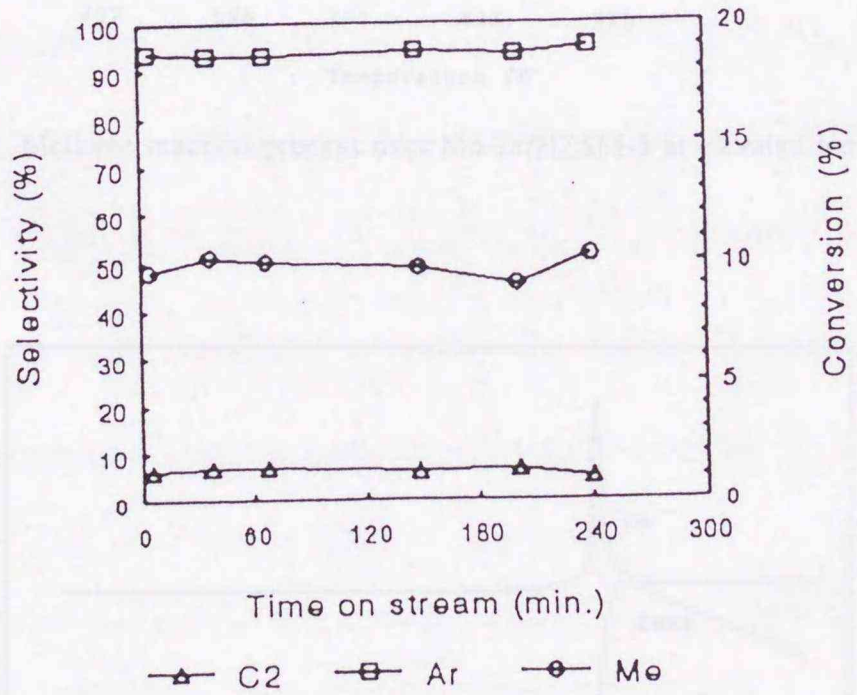


Fig. 4. Methane conversion and selectivity to aromatics and C_2 as a function of time on stream over Mo-W/HZ-873 catalyst at 973 K.

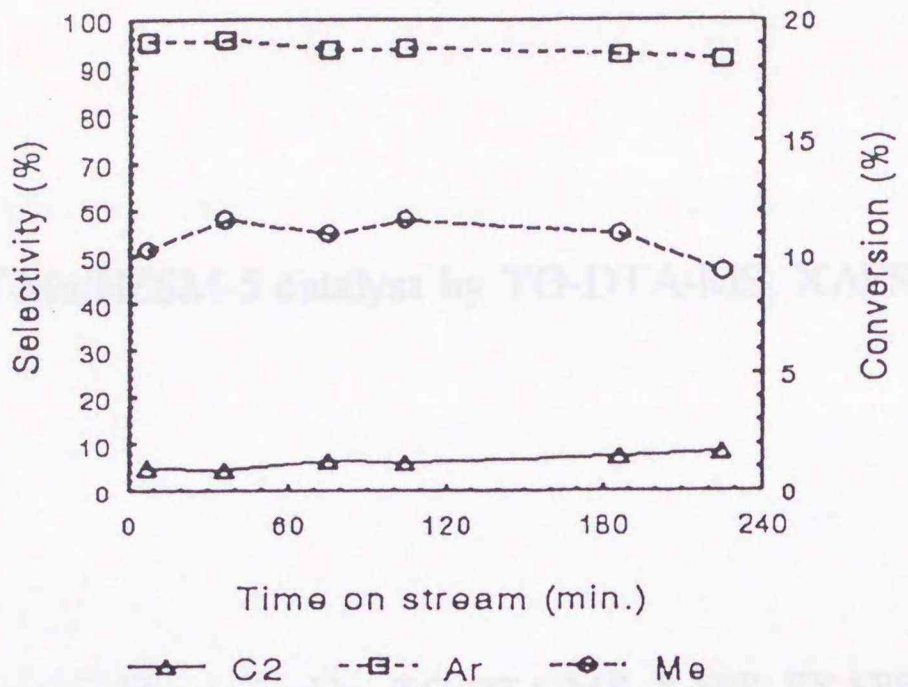


Fig. 5. Methane conversion and selectivity to aromatics and C_2 as a function of time on stream over Mo/HZ-873 catalyst at 973 K.

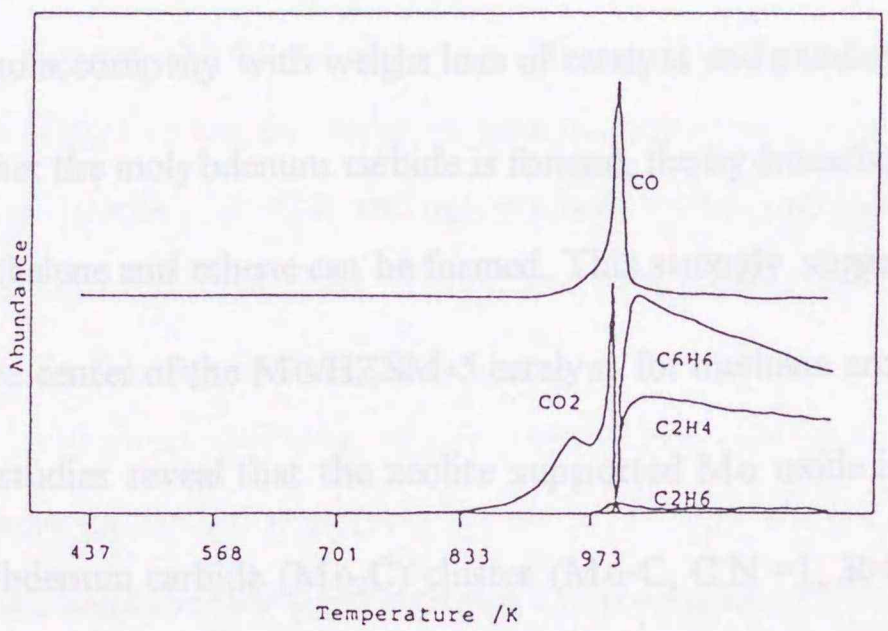


Fig. 6. Methane reaction process over Mo-Zr/HZSM-5 at elevated temperatures.

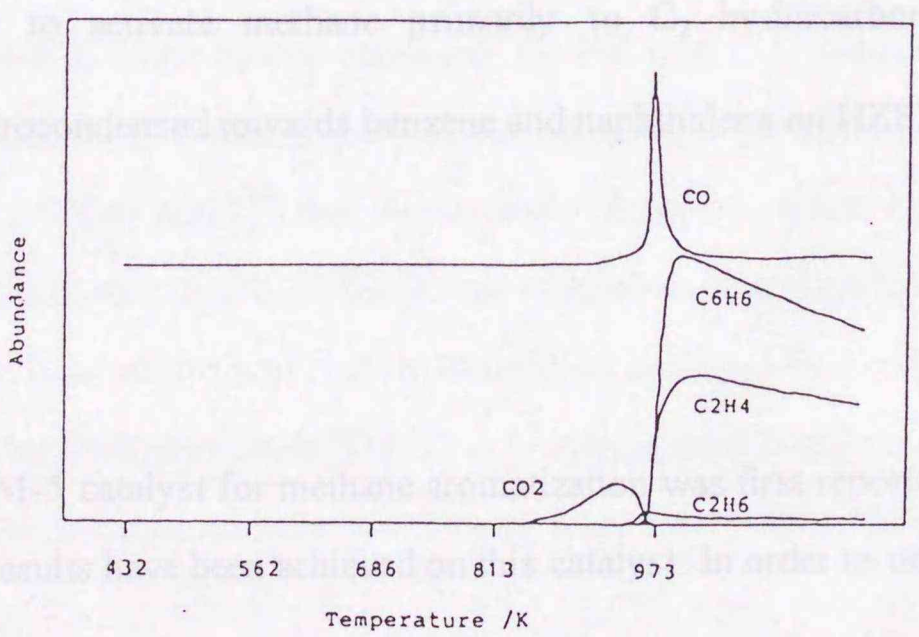


Fig. 7. Methane reaction process over hydrogen reduced Mo-Zr/HZSM-5 at elevated temperatures.

Chapter 4

Characterization of Mo/HZSM-5 catalyst by TG-DTA-MS, XAFS, EXAFS SEM and TEM

Abstract

Mo/HZSM-5 catalyst is characterized by TG-DTA-MS, XAFS, EXAFS, SEM and TEM techniques. TG-DTA-MS experiments indicate that the Mo oxide is reduced by methane to its carbide at about 962 K on HZSM-5 support, which is a strong endothermic process and accompany with weight loss of catalyst and production of CO, H_2O and H_2. Only after the molybdenum carbide is formed, the hydrocarbon products such as benzene, naphthalene and ethene can be formed. This strongly suggests that the Mo carbide is the active center of the Mo/HZSM-5 catalyst for methane aromatization. The XANES/EXAFS studies reveal that the zeolite supported Mo oxide is converted with methane to molybdenum carbide (Mo_2C) cluster (Mo-C, C.N.=1, R= 2.09; Mo-Mo, C.N.=2.3-3.5; R 2.98 A). The formed Mo carbide exists on HZSM-5 support in the uniform particles. The highly dispersed metal carbide on HZSM-5 support acts as the active center to activate methane primarily to C_2 hydrocarbons, which are secondarily dehydrocondensed towards benzene and naphthalene on HZSM-5 support

1 Introduction

Since Mo/HZSM-5 catalyst for methane aromatization was first reported in 1993 [1], many promising results have been achieved on this catalyst. In order to understand the

mechanism for methane aromatization on this catalyst and the structure of the catalyst, we have conducted TG-DTA-MS, XAFS/EXAFS, SEM/TEM experiments in this chapter.

2 Experiments

2.1. DTA-TG-MS experiments

DTA-TG-MS experiments were performed with a DTA-TG-MS combined instrument (Mas Science DTA-2020S + Thermolab). Fig. 1 briefly shows the scheme of the setup for TG-DTA-MS experiments. About 40 mg catalyst was paced in a alumina container under flowing 150 ml/min He and 15 ml/min methane with ramping the temperature of 10 K/min. The weight change of catalyst was recorded by TG, heat effect of the reaction was recorded by DTA and the products for the reaction were monitored by MS at the same time during the catalyst was heated from room temperature to 973K by a programmed temperature.

2.2. XAFS/EXAFS experiments and analysis

The powdered samples were charged under nitrogen in an in-situ XAFS cell with a Kapton film window (0.5mg) to prevent exposure of the sample to air. Mo K-edge XAFS (X-ray absorption fine structure) measurements were conducted on the sample of Mo/HZSM-5 after impregnation, calcination at 873 K, and reaction with methane at 873 K and 973 K at BL-10B at the photon factory of the National Laboratory for high Energy Physics (KEK-PF,Tsukuba, Japan). The energy and the current of the electron (or position) were 2.5 GeV and 250 mA, respectively. A Si(311) channel-cut monochromator was used. The XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) was analyzed by a computer program supplied by Technose Co. LTD [2]. k^3 -weighted EXAFS function was Fourier transformed into R-space using the k-range from 3.5-18 $Å^{-1}$. The Hanning

function used was δ=0.5 $Å^{-1}$. The phase shift was not corrected for the preliminary Fourier transformation. The inverse Fourier transform was calculated to obtain a filtered EXAFS function. The R range of an inverse Fourier transformation was taken from 1.09 to 3.31 Å. The Hanning function of Δ=0.05 Å was used as a window function. The fitting EXAFS parameters of the sample were determined for coordination number (C. N.) and interatomic distance R, to minimize σ and correction of threshold energy (ΔEo). The backscattering amplitudes and phase shift functions of Mo-Mo, Mo-C, and Mo-O bondngs are corrected using those of Mo foil (Mo-Mo), Mo_2C (Mo-Mo, Mo-C), and MoO_3 (Mo-Mo), Mo-O). The EXAFS parameters for discussion were fixed around the optimum value, and the residual factor R was calculated to offer the optimum values for the other parameters. The real value was estimated using a residual factor R which is smaller than twice the optimum value.

3 Results and discussion

It is evidently indicated from TG-DTA-MS spectra in fig. 2 that the Mo oxide is firstly reduced by methane to its carbide at about 962 K on HZSM-5 support. The phase transformation process from molybdenum oxide to its carbide is a strong endothermic process as shown by DTA profile, which accompany with weight loss of catalyst as shown by TG profile, and CO, H_2O and H_2 are produced at the same time as monitored by Mass Spectra. Only after the molybdenum carbide is formed, the hydrocarbon products such as benzene, naphthalene and ethene can be formed. This strongly suggests that the Mo carbide is the active center of the Mo/HZSM-5 catalyst for methane aromatization. The reduction of Mo oxide by methane to its carbide is quite different from its reduction by hydrogen to Mo metal. The TG-DTA-MS spectra of Mo/HZSM-5 in hydrogen flow in fig. 3 indicate that there is no heat effect can be identified by DTA profile for reduction process of Mo oxide by hydrogen, although the catalyst weight loss is identified as by TG profile and H_2O product is monitored by

MS.

In order to obtain more direct evidence for the formation of molybdenum carbide, the XANES/EXAFS experiments were conducted. Figure 4 shows some XANES spectra of 6 wt% loading Mo/HZSM-5 calcined, treated in flowing methane at 973 K for 1 and 24h. The spectra of MoO_3 , Mo foil and a Mo_2C powder were observed as references. All the spectra (figs. 4c and 4d) of Mo/HZSM-5 after methane reaction at 973 K showed identical edge position, similar to Mo carbide (fig 4e) and Mo foil (fig 4f) as the first inflection point in the rapidly rising portion of the edge. This position was assigned an energy of 20003.9 eV. It is known that edge features move to lower energy as the oxidation state of Mo is reduced [3,4], as shown for Mo/HZSM-5 sample after the reaction with methane at 973 K, compared with those of the calcined sample (fig 4b) and MoO_3 (fig 4a). The only notable difference between Mo foil and Mo_2C XANES spectra was a separation of the two broad peaks at 20.04 KeV and 20.03 KeV above the absorption edge. The XANES spectrum of Mo foil showed a larger separation than the Mo_2C spectrum. The XAFS of the Mo/HZSM-5 sample reacted with methane at 973 K for 1 and 24 h (figs. 4c and 4d) look basically identical to the Mo_2C reference spectrum (fig. 6e) not to the Mo foil (fig. 4f).

The FT K-edge EXAFS spectra in fig 5 indicate that the Mo-Mo distance for Mo oxide is between 3 and 4 Å. After the catalyst exposed to methane at 973 K, it changes to between 2 and 3 Å, which is at the exactly same position as the Mo-Mo distance of Mo_2C reference sample and is at the quite different position from that of Mo foil sample. This results have further improved that molybdenum oxide is reduced by methane to its carbide and not to Mo metal on HZSM-5 support after reaction with methane. HZSM-5 supported Mo carbide is the active center for methane aromatization reaction.

By fitting the EXAFS spectra, some structure parameters have been obtained and listed in table 1. Table 1 indicates that the Mo-Mo distance of the formed Mo carbide is same as bulky molybdenum carbide, although it is supported on HZSM-5 zeolite.

However, the coordination number of supported Mo carbide is 2.1-3.5 is much lower than that of bulky Mo carbide, which is 12.

The surface morphology of the formed molybdenum carbide supported on HZSM-5 was observed by scanning electronic microscope (SEM) as shown in fig. 6. After methane reaction, the clear molybdenum carbide can be observed by SEM imagine, which exists in the uniform particle on HZSM-5 support. However, before the reaction of methane, no any particles but only zeolite crystal can be observed. This indicates that the Mo oxide is highly dispersed on the zeolite after calcination.

The cross-section of the catalyst is observed by transmission electronic microscope (TEM) as shown in fig. 7. It is indicated in fig. 7 that the particles is mainly dispersed on the surface of the zeolite crystal.

Based on the above results, we have proposed a mechanism for methane aromatization on Mo/HZSM-5, which is schemed as fig. 8. The first step for the reaction is that Mo oxide supported on HZSM-5 was reduced by methane to its carbide, and methane was oxidized to CO, H_2O and H_2. HZSM-5 supported Mo carbide is the active center for methane activation. On the formed Mo carbide, methane are first dehydrogenated to CHx species, which are dimerized to C_2Hy species such as ethene. C_2H_4 is secondarily converted to aromatics such as benzene, naphthalene even coke on HZSM-5 zeolite.

4 Conclusion

The TG/DTA/MS , XANES/EXAFS and SEM/TEM studies reveal that HZSM-5 supported Mo oxide is endothermally converted with methane around 955 K to molybdenum carbide (Mo_2C) cluster (Mo-C, C.N.=1, R= 2.09; Mo-Mo, C.N.=2.3-3.5; R 2.98 A). . The formed Mo carbide exists on HZSM-5 support in the uniform particles. The highly dispersed metal carbide on HZSM-5 support acts as the active center to

activate methane primarily to C_2 hydrocarbons, which are secondarily dehydrocondensed towards benzene and naphthalene on HZSM-5 support

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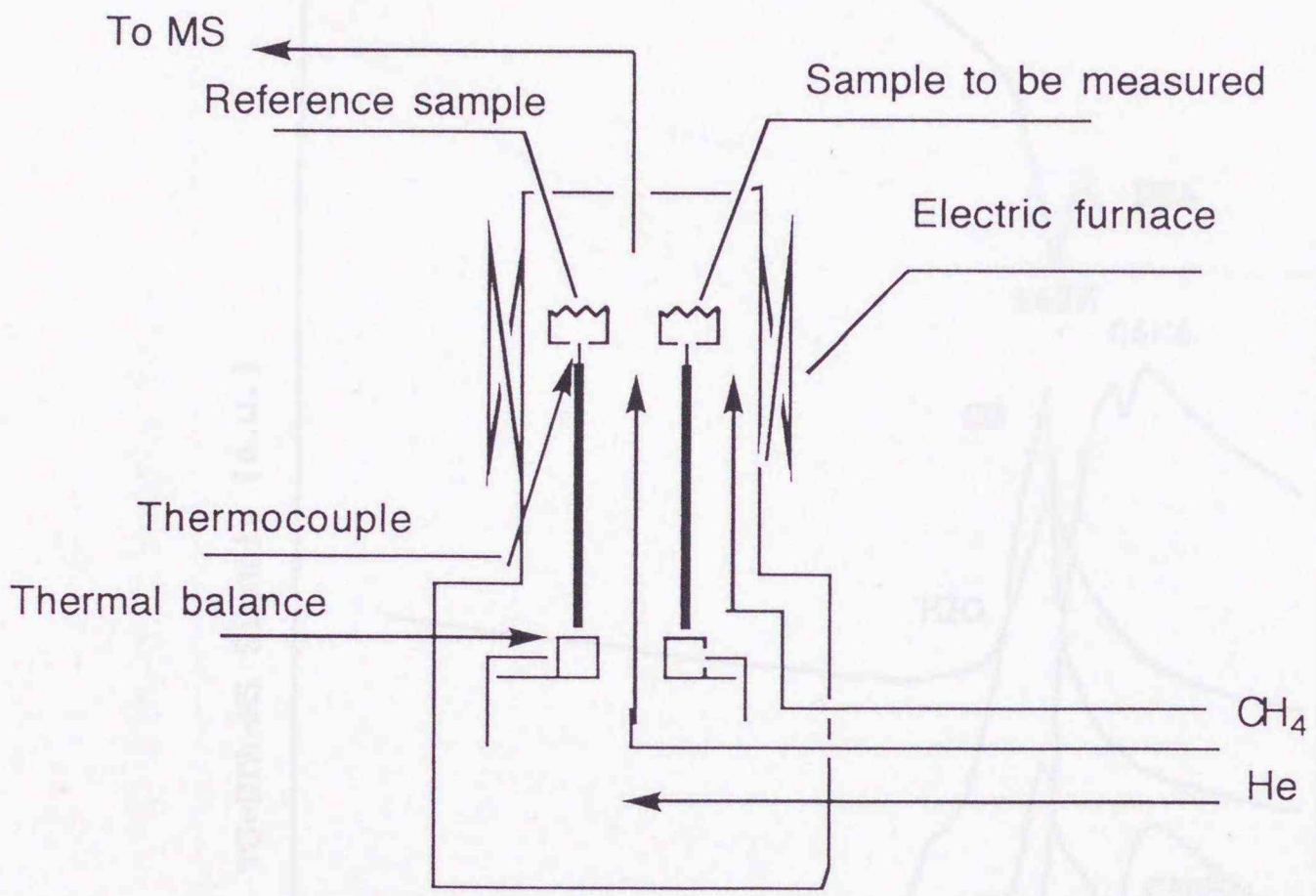
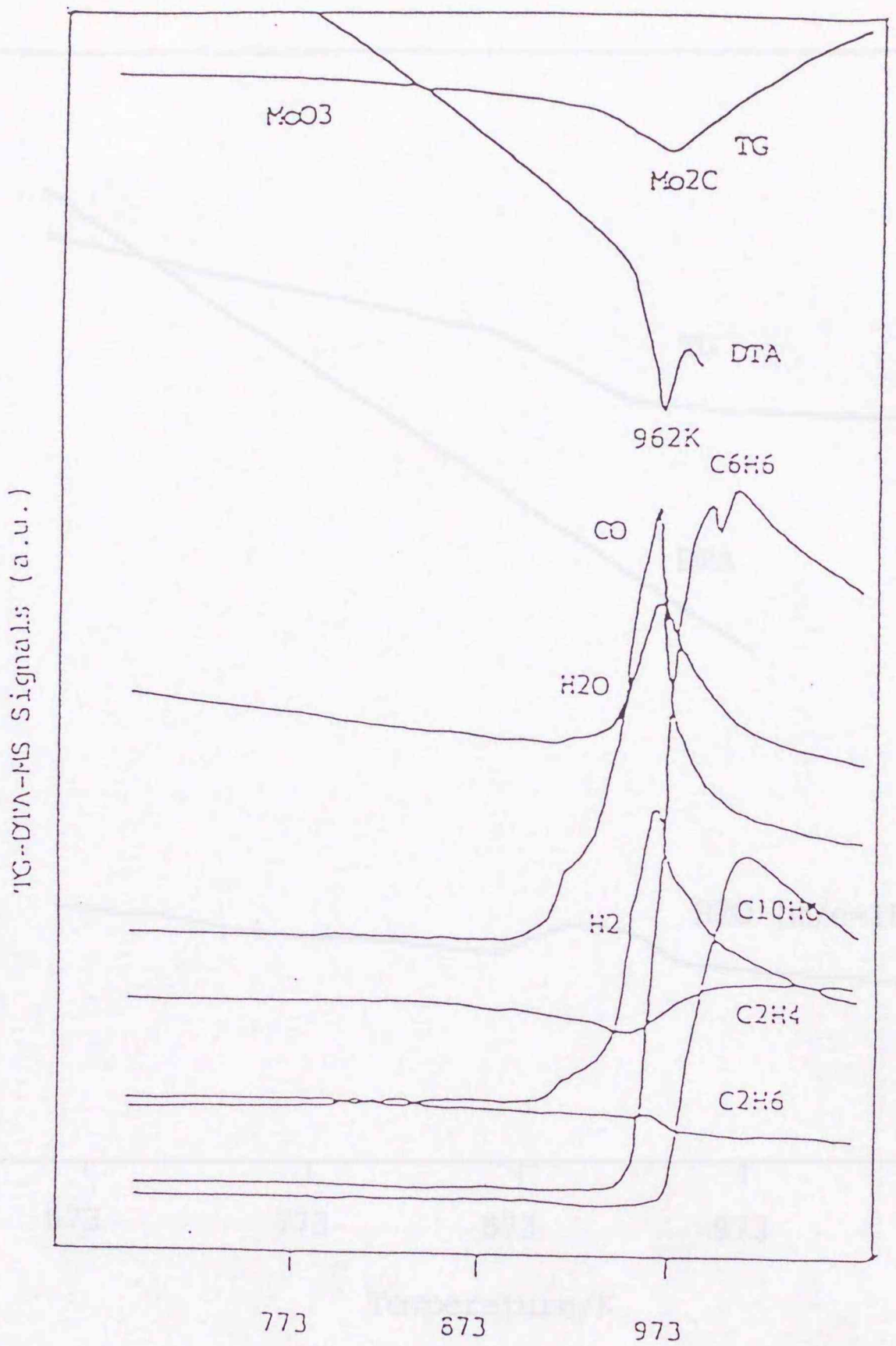


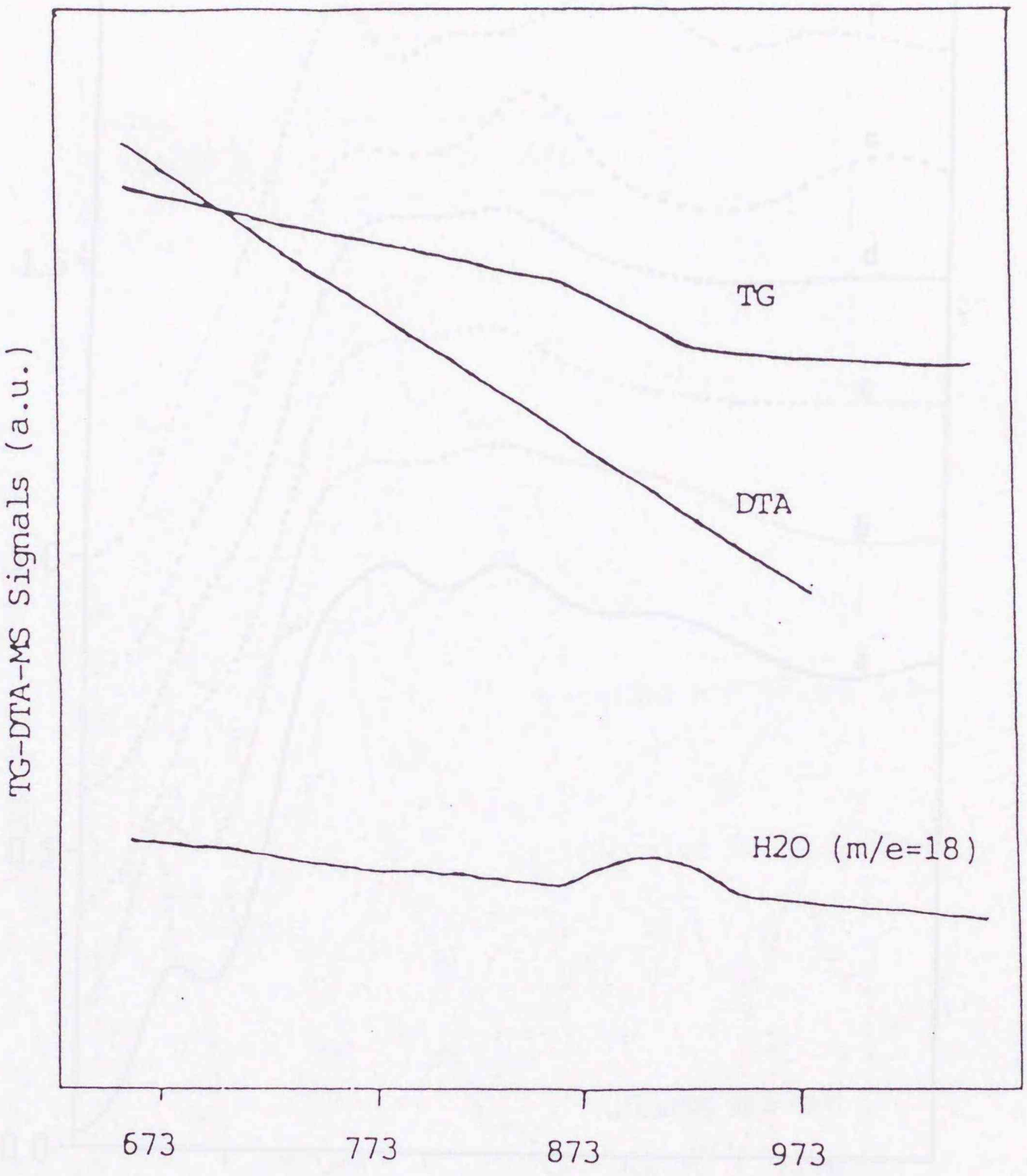
Fig. 1.
Schematic diagram of the setup for TG-DTA-MS experiment

Fig. 2. TG-DTA-MS spectra of 3wt% Mo/HZSM-5 in methane flow



Flow rate of CH_4 = 15 ml/min
CH_4/He = 10%
Heating rate = 10 K/min

Fig. 3. TG-DTA-MS spectra of 3wt% Mo/HZSM-5 in hydrogen flow



Flow rate of H_2 = 15 ml/min
H_2/He = 10%
Heating rate = 10 K/min

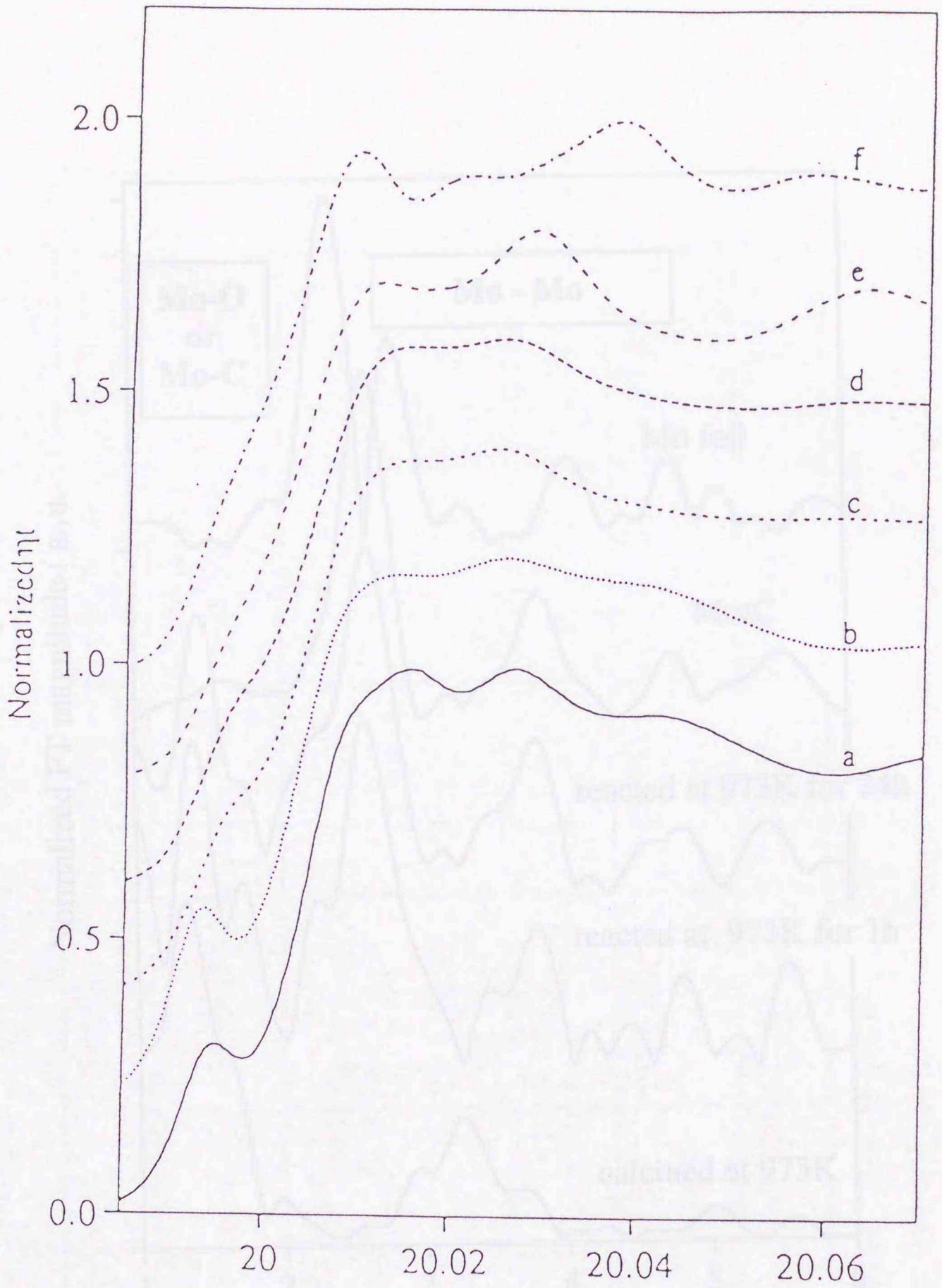
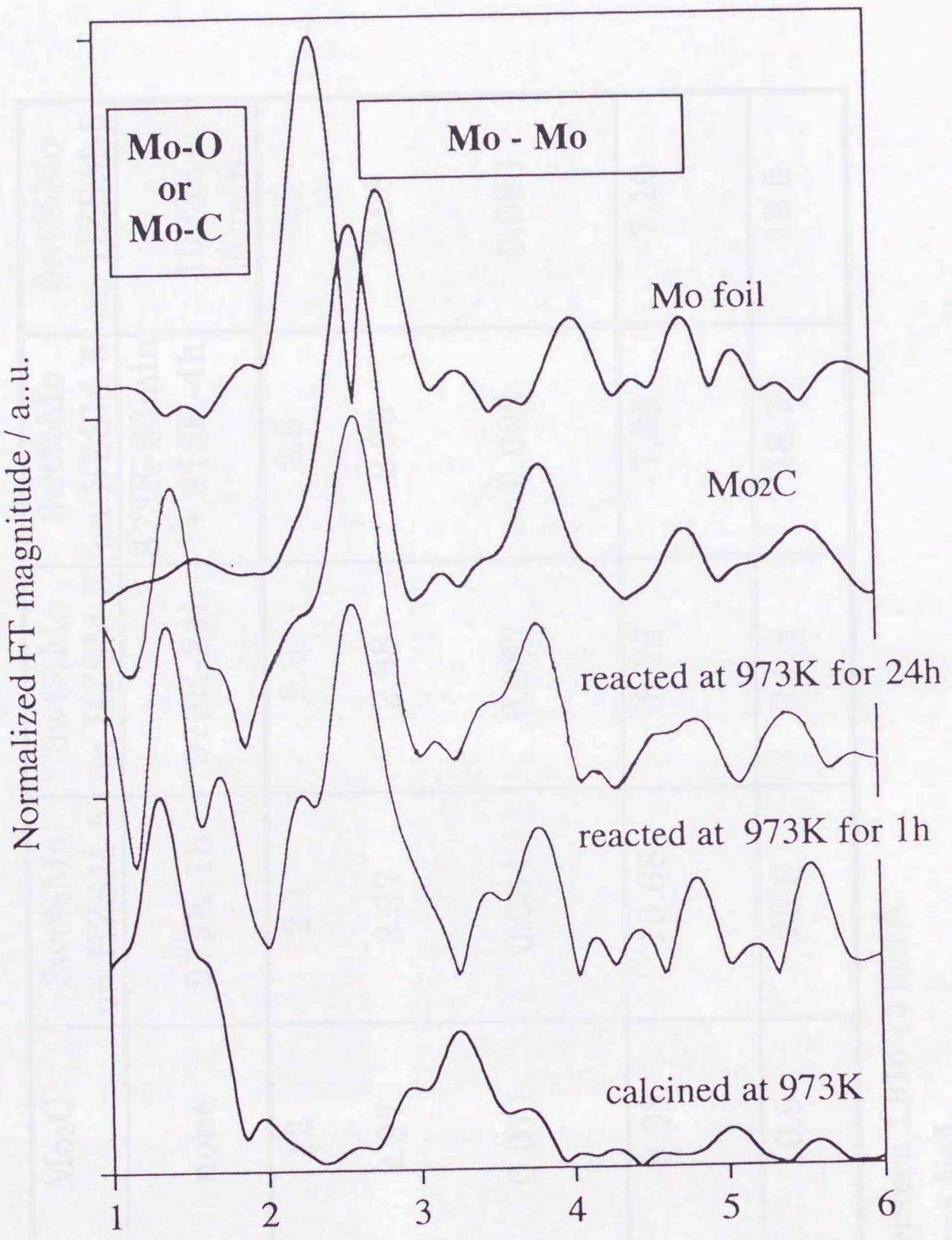


Fig. 4. Mo K edge XANES spectra of (a) MoO_3 crystal; (b) 6 wt% Mo/HZSM-5 (SiO_2/Al_2O_3 ratio of 39.5) after calcined at 873 K for 2 h; (c) after (b) treated with methane at 973 K for 1 h; (d) after (b) treated with methane at 973 K for 24 h; (e) Mo_2C powder; and (f) Mo foil as the reference.

Fig. 5
K-edge EXAFS spectra of calcined and reacted 3wt%Mo/HZSM-5



Mo-oxide was transformed to Mo_2C after CH_4 reacted at 973K

Table 1. Mo K-edge EXAFS parameter fitting*

Compounds		Mo_2C	3wt%Mo on HZSM-5	3wt%Mo on HZSM-5	6wt%Mo on HZSM-5	6wt%Mo on HZSM-5
Treatment#		none	973K-1h	973K-24h	873K-30min + 973K-4h	1023K-30min
N		12	2.1	2.3	2.5	3.5
R / Å	Mo-Mo	2.97	2.97	2.98	2.96	2.98
σ/ Å^{-1}		0.071	0.084	0.087	0.095	0.088
△E / eV		-9.38	-10.68	-8.75	-7.88	-7.10
R factor / %		10.9	23.9	14.3	18.7	13.5

*Fitted in R-space between 1.915 - 3.000 Å

treated with methane feed

Fig. 6.
SEM image of Mo/HZSM-5 before and after methane reaction

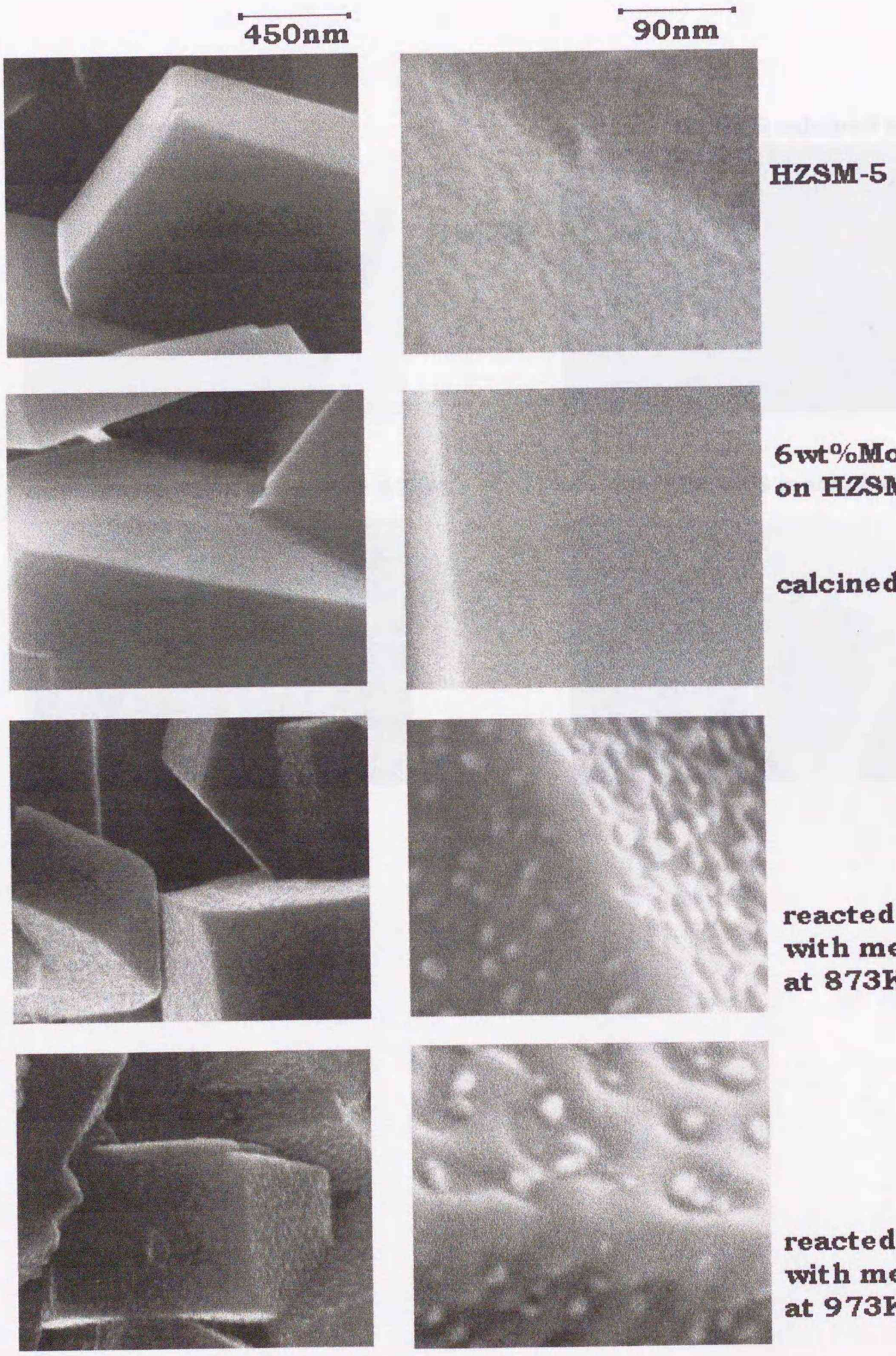


Fig. 7.
TEM image of Mo/HZSM-5 before and after methane reaction

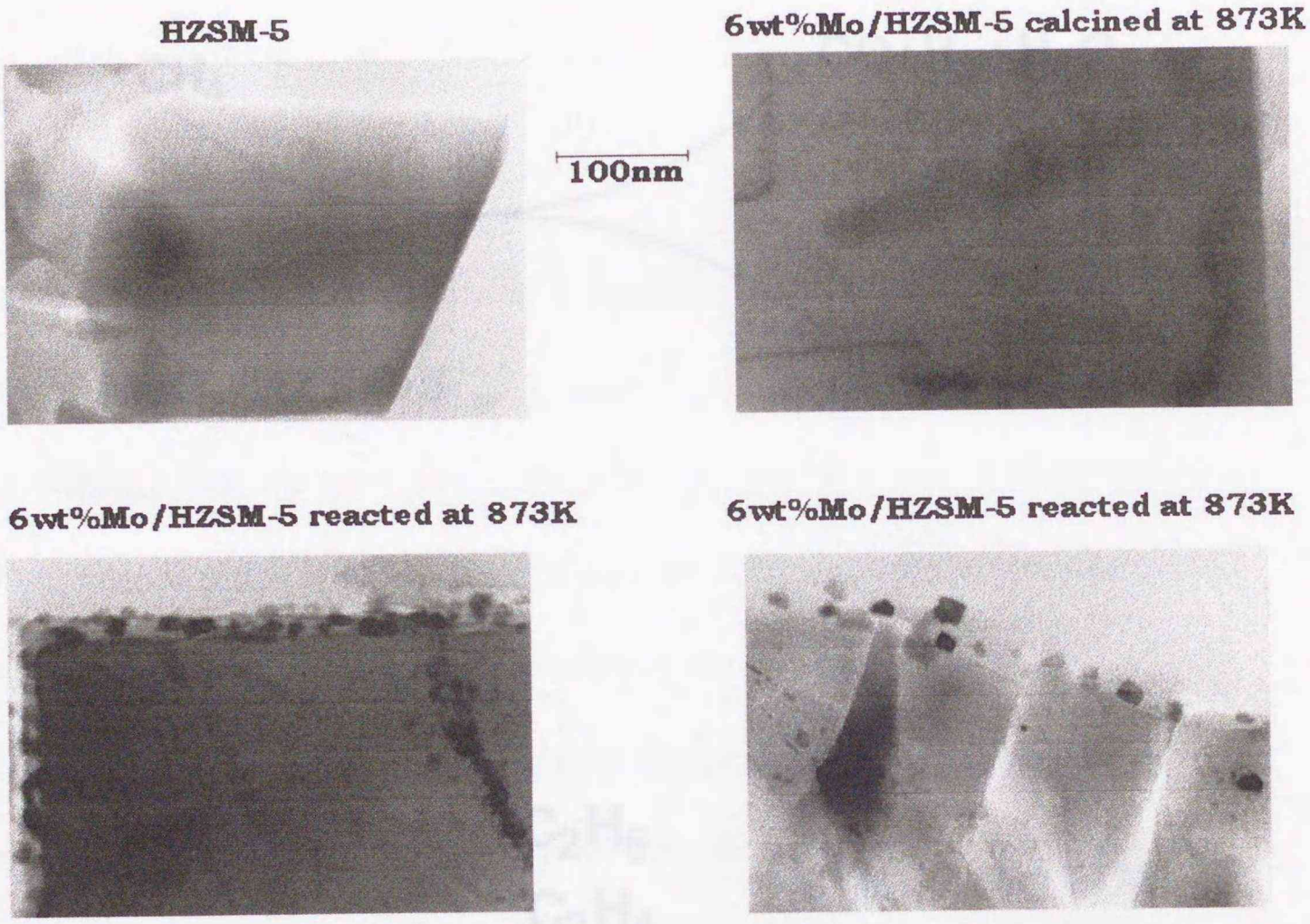
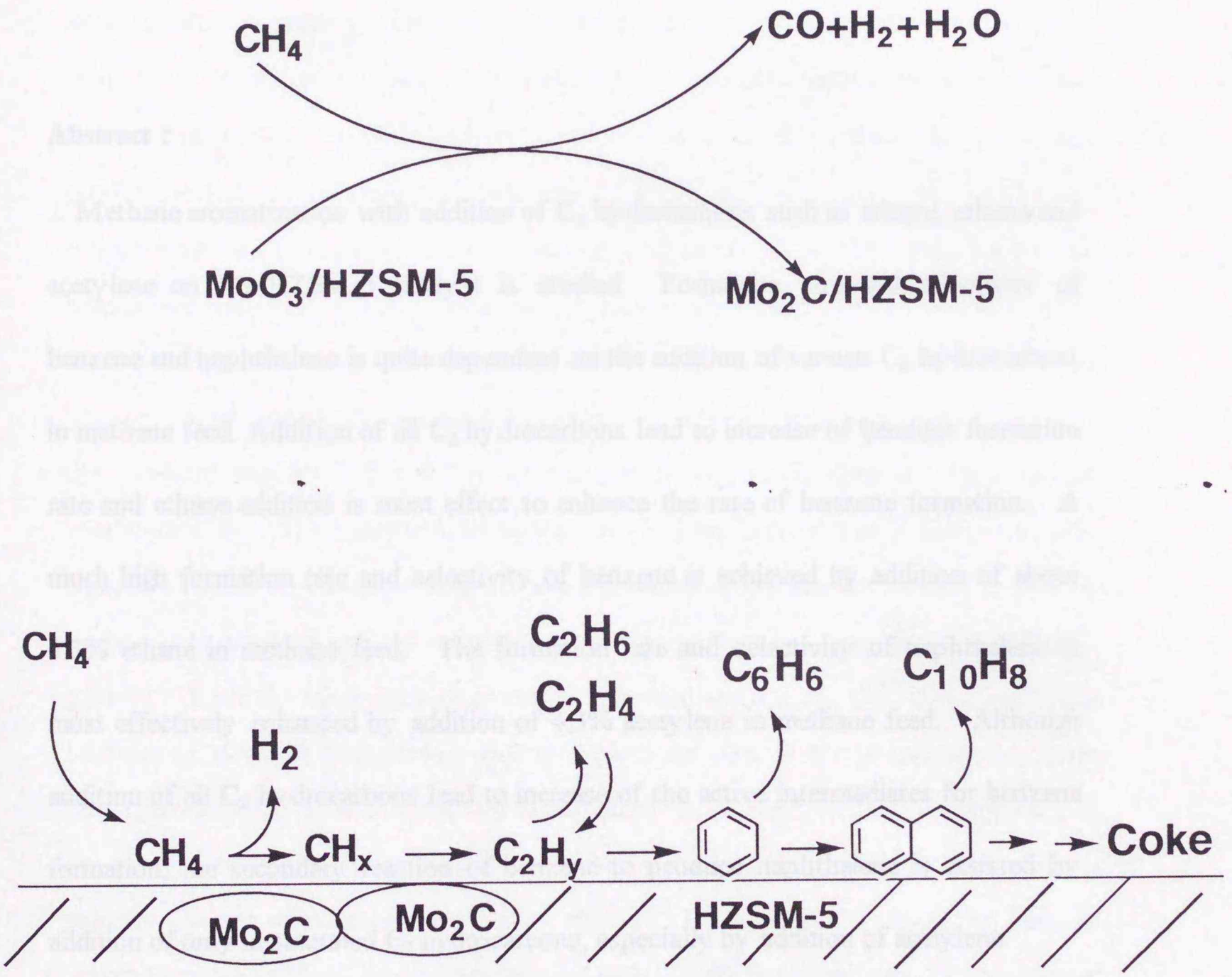


Fig. 8. Mechanism for methane aromatization on Mo/HZSM-5



Chapter 5

Methane Aromatization with Addition of C_2 hydrocarbons on Mo/HZSM-5

Abstract :

Methane aromatization with addition of C_2 hydrocarbons such as ethane, ethene and acetylene on Mo/HZSM-5 catalyst is studied. Formation rate and selectivity of benzene and naphthalene is quite dependent on the addition of various C_2 hydrocarbons in methane feed. Addition of all C_2 hydrocarbons lead to increase of benzene formation rate and ethane addition is most effect to enhance the rate of benzene formation. A much high formation rate and selectivity of benzene is achieved by addition of about 4.3% ethane in methane feed. The formation rate and selectivity of naphthalene is most effectively enhanced by addition of 4.3% acetylene in methane feed. Although addition of all C_2 hydrocarbons lead to increase of the active intermediates for benzene formation, the secondary reaction of benzene to produce naphthalene is assisted by addition of only unsaturated C_2 hydrocarbons, especially by addition of acetylene.

Keywords:

methane aromatization , Mo/HZSM-5, C_2 addition, benzene, naphthalene

1 Introduction

Mo/HZSM-5 catalyst was first employed to non-oxidative dehydrogenation and aromatization reaction of methane in 1993 [1]. The catalytic tests were performed in a continuous-flow stainless steel reactor and in a quartz tubular microflow reactor. The product was analyzed by a GC equipped with a FID detector and by a TE-150 mass spectrometer, respectively, but only benzene as aromatic product was measured in the experiment conditions. About two years later, more information on this reaction system was reported by other authors [2-4] and by us [5-6]. Recently, the unique catalytic activity of molybdenum-containing HZSM-5 catalyst for aromatics production directly from methane has attracted an increasing attention [7-20]. The characterization, preparation and modification of catalyst and reaction kinetics have been investigated by various techniques[7-15]. The catalytic activity and stability of Mo/HZSM-5 have been improved by addition of different modifiers [6,16-19]. It has also been found that the catalytic activity and stability of catalyst is very dependent on pretreatment conditions [16]. More recently, Ichikawa et al [19] and Lunsford et al. [20] gave more complete results on products analysis and evaluation of the amount of naphthalene in hydrocarbon product and coke deposited on the catalyst by using internal standard method. From the view point of potential industrial application, the natural gas is the mixtures of methane with some higher hydrocarbons such as C_2 hydrocarbons. The rate of aromatics such as benzene and naphthalene for aromatization of pure methane is not so high to obtaine a commercialized process for this reaction. It is important to enhance the rate of aromatic products by adding C_2 hydrocarbons to methane feed. In view of aromatization of C_2 hydrocarbons, mainly Zn/HZSM-5 and Ga/ HZSM-5 type catalyst has been reported. Little attention has been paid to aromatization of C_2 on Mo/HZSM-5 type catalyst. In addition, It has been accepted that C_2 species is the intermediates for benzene formation on the catalyst. Investigation of the role of C_2 species is key crucial to understand the mechanism of methane aromatization. Therefore, the study on methane aromatization with addition of C_2 hydrocarbons is of

significance not only in academy but also in industry. Here, aromatization of methane with addition of C_2 hydrocarbons is presented.

2 Experimental

Mo/HZSM-5 was prepared by impregnating NH_4ZSM-5 (SiO_2/Al_2O_3=40) with $(NH_4)_6Mo_7O_{24}4H_2O$ aqueous solution, followed by drying at 383 K for 4 h and calcination at 773 K for 4 h. The ratio of Mo/ NH_4ZSM-5 in weight is about 3%.

Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow straight type quartz reactor at a pressure of 100 kPa (1 atm) and a methane space velocity of 1440 ml/g/h. The products were withdraw periodically from the outlet of reactor and analyzed by two on-line gas chromatography of Shimadazu GC-9A and GC-8A equipped with a flame ionization detector (FID) and a thermoconductive detector (TCD) respectively. 2.2% Ar in methane was employed as internal standard. Formation rate of products, methane conversion and product selectivity were calculated by an internal standard analyzing method. Below, the method is presented briefly. Even if the total flow rate changed at outlet from inlet of reactor (F_{Total}^{intlet} ,F_{Total}^{outlet}). Flow rate of non-reactive internal standard gas (F_{st}) doses not change.

$$F_{st} = F_{Total}^{outlet} \times X_{st}^{outlet} = F_{Total}^{inlet} \times X_{st}^{inlet}$$

Here, X_{st} refer to concentration of the internal standard gas.

Formation rate of i product (F_i) can be calculated as,

$$F_i = F_{Total}^{outlet} \times X_i^{outlet} = F_{st} \times X_i^{outlet} / X_{st}^{outlet}$$

By the same way, methane conversion ($C_{methane}$) can be calculated as,

$$C_{methane} = (F_{methane}^{inlet} - F_{methane}^{outlet}) / F_{methane}^{inlet} = 1 - F_{methane}^{outlet} / F_{methane}^{inlet}$$

$$= 1 - F_{Ar} \times X_{methane}^{outlet} / X_{Ar}^{outlet} \times F_{methane}^{inlet}$$

C_2 conversion (C_{C2}) is calculated as, $C_{C2} = (F_{C2}^{inlet} - F_{C2}^{outlet}) / F_{C2}^{inlet}$

Coke selectivity = 1- (produced HC+produced CO)/(converted methane+converted C_2).

The raw materials of methane and C_2 hydrocarbons are over 99.99% pure.

3 Results and discussion

3.1 Effect of various C_2 hydrocarbon addition on formation rate of benzene and naphthalene

Formation rate of benzene and naphalene for methane aromatization with and without addition of about 2.4% C_2 (in mole) such as ethane, ethene and acetylene on 3% Mo/HZSM-5 was compared. The results are shown in figs 1 and 2. Fig 1 indicates that the rate of benzene formation is increased by addition of various C_2 hydrocarbons to methane feed. Ethane addition is most effective to enhance rate of benzene formation. Fig 2 indicates that the rate of naphthalene formation is increased by addition of ethene and acetylene. Acetylene addition is most effective to enhance the rate of naphthalene formation.

3.2 Effect of C_2 concentration in methane feed

Formation rate of benzene as a function of C_2 concentration in methane feed are shown in fig 3 . It is shown in fig 3 that the rate of benzene formation is maximized at the ethane concentration of 4.3% or at the acetylene/ethene concentration of about 2.4% in methane feed. The rate of benzene formation is doubled by addition of 4.3% ethane and it is increased by 50% by addition of 2.4% ethene or acetylene in methane feed. The Rate of benzene formation contributed from methane aromatization with or without addition of ethane and the rate of benzene formation contributed from ethane aromatization are compared in fig 4. Fig 4 indicates that more methane and ethane converted to benzene when about 4.3% ethane is added to methane feed. It is also shown in fig 4 that the rate of benzene formation is very high and quite stable with time on stream for methane aromatization with addition of 4.3% ethane.

Formation rate of naphthalene as a function of C_2 concentration in methane feed are shown in fig 5 . It is shown in fig 5 that the rate of naphthalene formation increases sharply with increase of acetylene concentration in methane feed. The rate of

naphthalene formation increases by about 4 times by addition of 4.3% acetylene and it increases only a little by addition of ethane or ethene in methane feed. The Rate of naphthalene formation contributed from methane aromatization with or without addition of 4.3% acetylene and the rate of naphthalene formation contributed from acetylene aromatization are compared in fig 6. Fig 6 indicates that much more methane and acetylene converted to naphthalene when about 4.3% acetylene is added to methane feed. It is also shown in fig 6 that the rate of naphthalene formation is very high and quite stable with time on stream for methane aromatization with addition of 4.3% acetylene. Naphthalene formation rate for aromatization of methane with addition of about 4.3% acetylene over Mo/HZSM-5 at 973 K is up to 80 nmole/s/g, which is much higher than the sum of naphthalene formation rates contributed from pure methane and from 4.3% acetylene balanced in Ar gas at the same reaction temperature.

Effect of C_2 addition in methane feed on selectivity of benzene and naphthalene products is compared in table 1. It is indicated in table 1 that enhancement of the selectivity for production of benzene and naphthalene is dependent on the nature of C_2 additives. The order of C_2 additives for enhancing the selectivity of benzene is as below,

ethane > ethene > acetylene.

The order of C_2 additives for enhancing the selectivity of naphthalene is as below,

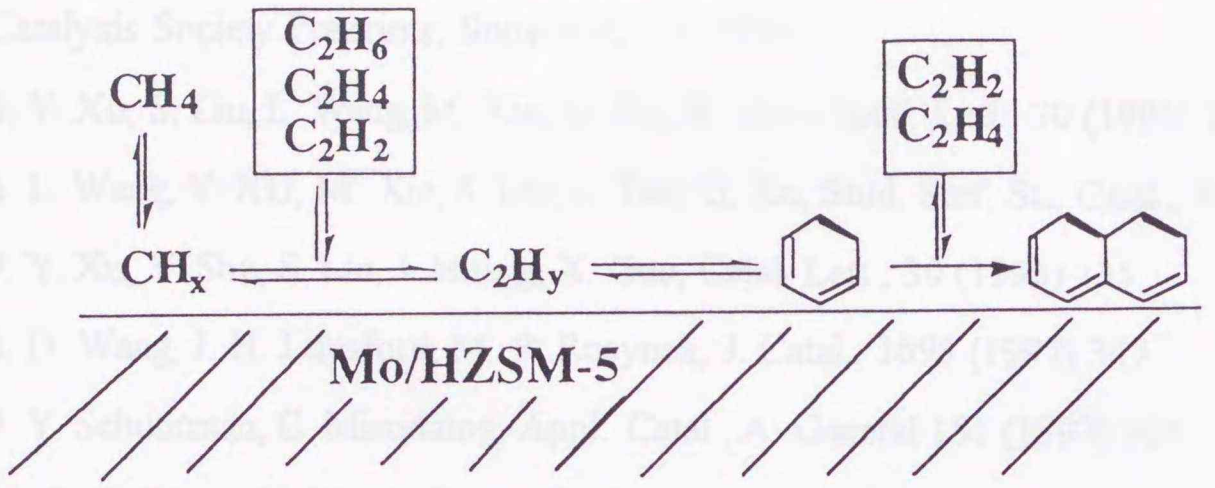
acetylene > ethene > ethane

3.3 Mechanism for the role of C_2 in enhancing production of benzene and naphthalene

The mechanism for promoting effect of C_2 hydrocarbons on aromatization of methane is schemed as follows,

According to the scheme, the concentration of intermediates such as $[CH_x]$, $C_2H_y]$ for producing benzene is increased by addition of C_2 hydrocarbons in methane feed, which is responsible for increase of benzene formation rate. The unique role of acetylene for enhancing rate and selectivity of naphthalene is contributed to its reaction with benzene

to produce naphthalene.



Scheme for the role of C_2 addition to methane in enhancing production of benzene and naphthalene

4 Conclusion

Methane aromatization with addition of C_2 hydrocarbons such as ethane and ethene and acetylene on Mo/HZSM-5 catalyst is studied. Formation rate and selectivity of benzene and naphthalene is quite dependent on addition of various C_2 hydrocarbons in methane feed. Addition of all C_2 hydrocarbons lead to increase of benzene formation rate and ethane addition is most effect to enhance the rate of benzene formation. A much high formation rate and selectivity of benzene is achieved by addition of about 4.3% ethane in methane feed. The formation rate and selectivity of naphthalene is most effectively enhanced by addition of 4.3% acetylene. Although addition of all C_2 hydrocarbons lead to increase of the active intermediates for benzene formation, the secondary reaction of benzene to produce naphthalene is assisted by addition of only unsaturated C_2 hydrocarbons, especially addition of acetylene.

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Captions of figures and table:

Fig 1. Effect of addition of 2.4% C_2 hydrocarbons to methan on benzene production

Fig 2. Effect of addition of 2.4% C_2 hydrocarbons to methan on naphthalene production

Fig 3. Effect of C_2 concentration in methan on rate of benzene formation

Fig4. Comparation of benzene formation rate with time on stream for methane aromatization with and without addition of ethane

Fig 5. Effect of C_2 concentration in methan on rate of naphthalene formation

Fig 6. Comparation of naphthalene formation rate with time on stream for methane aromatization with and without addition of acetylene

Table 1. Effect of C_2 addition in methan on selectivity of benzene and naphthalene

Fig 1. Effect of addition of 2.4% C_2 hydrocarbons to methane on benzene production productionon Mo/HZSM-5 at 973 K

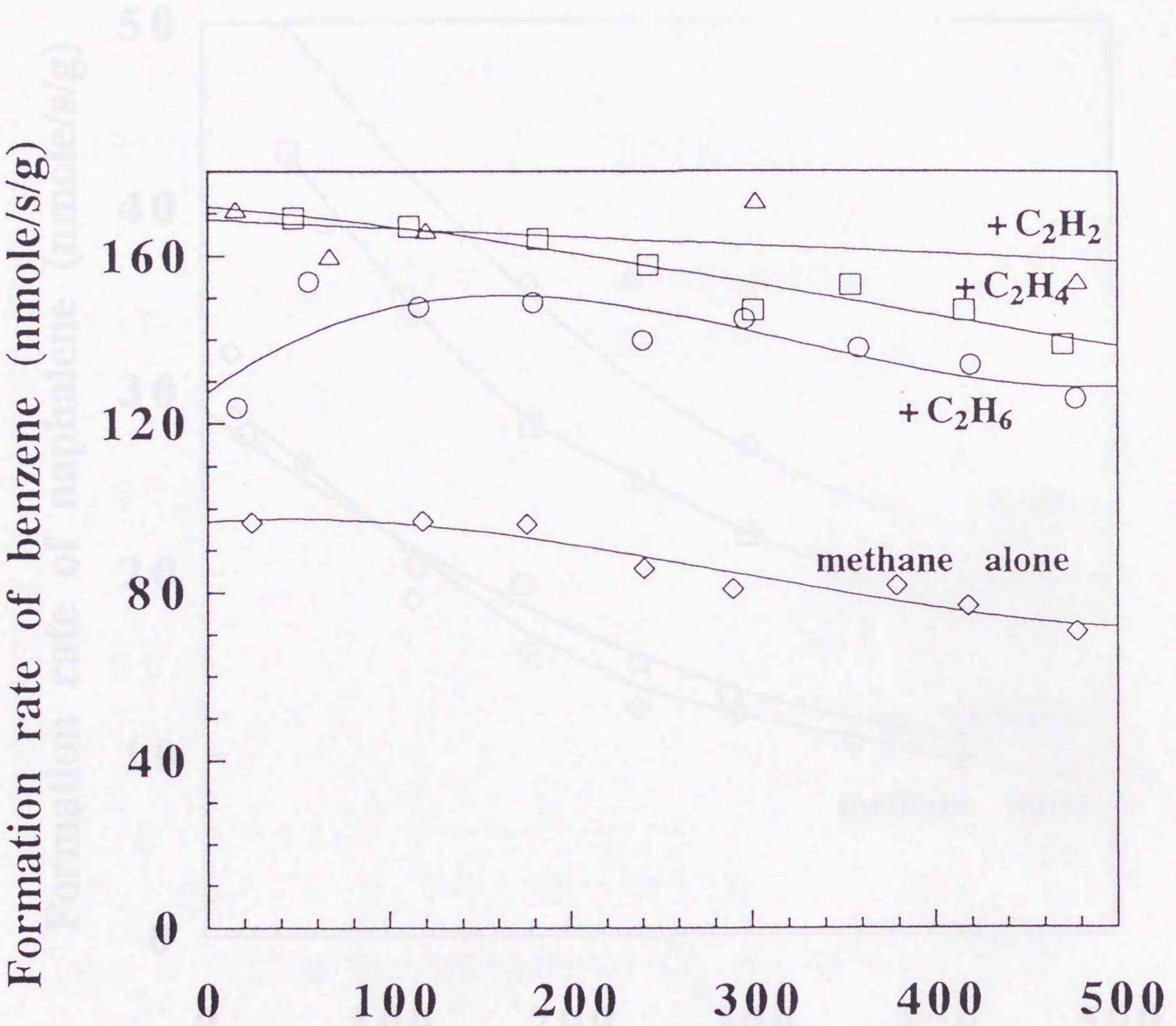


Fig 2. Effect of addition of 2.4% C_2 hydrocarbons to methane on naphthalene production over Mo/HZSM-5 at 973 K

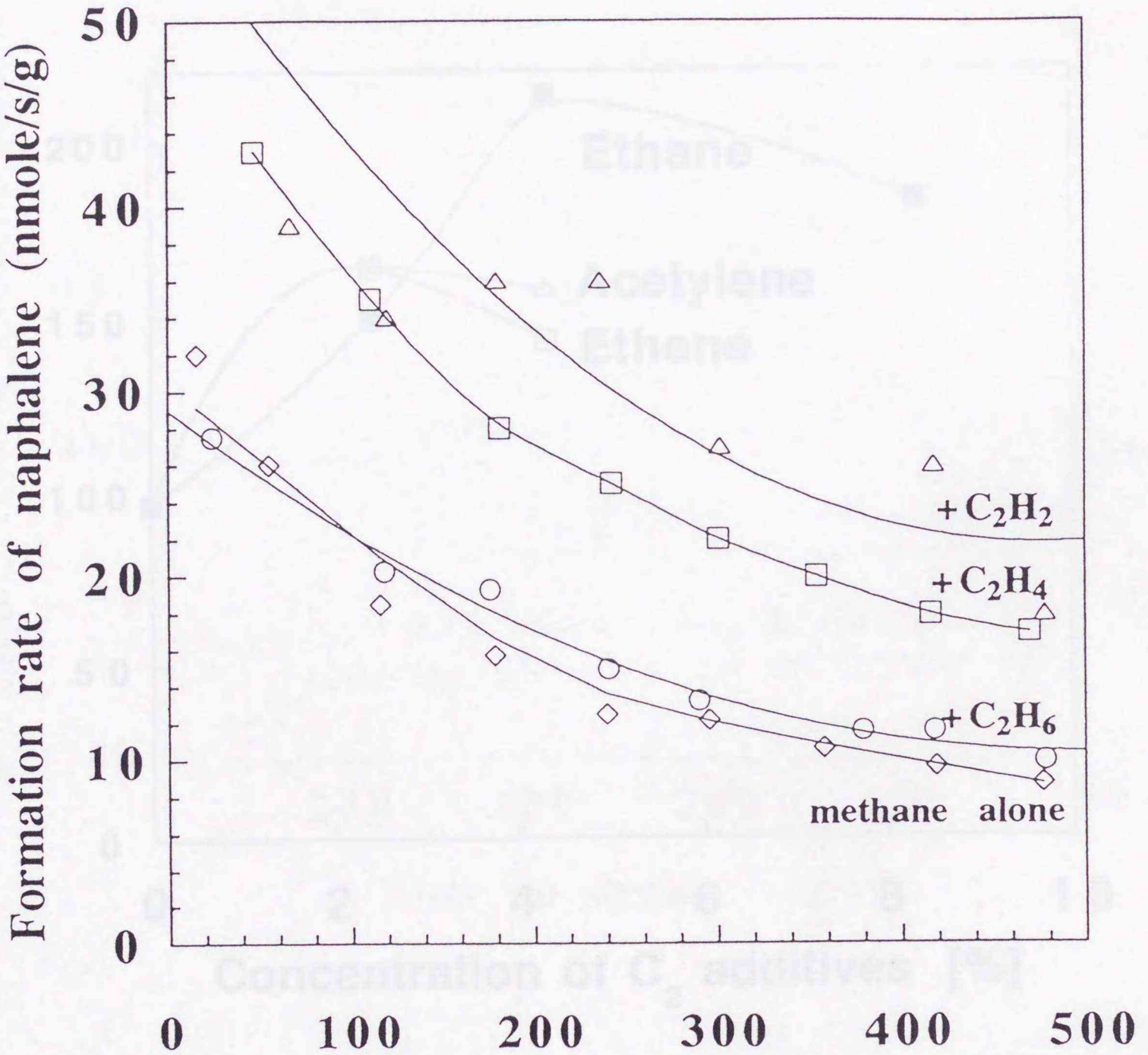
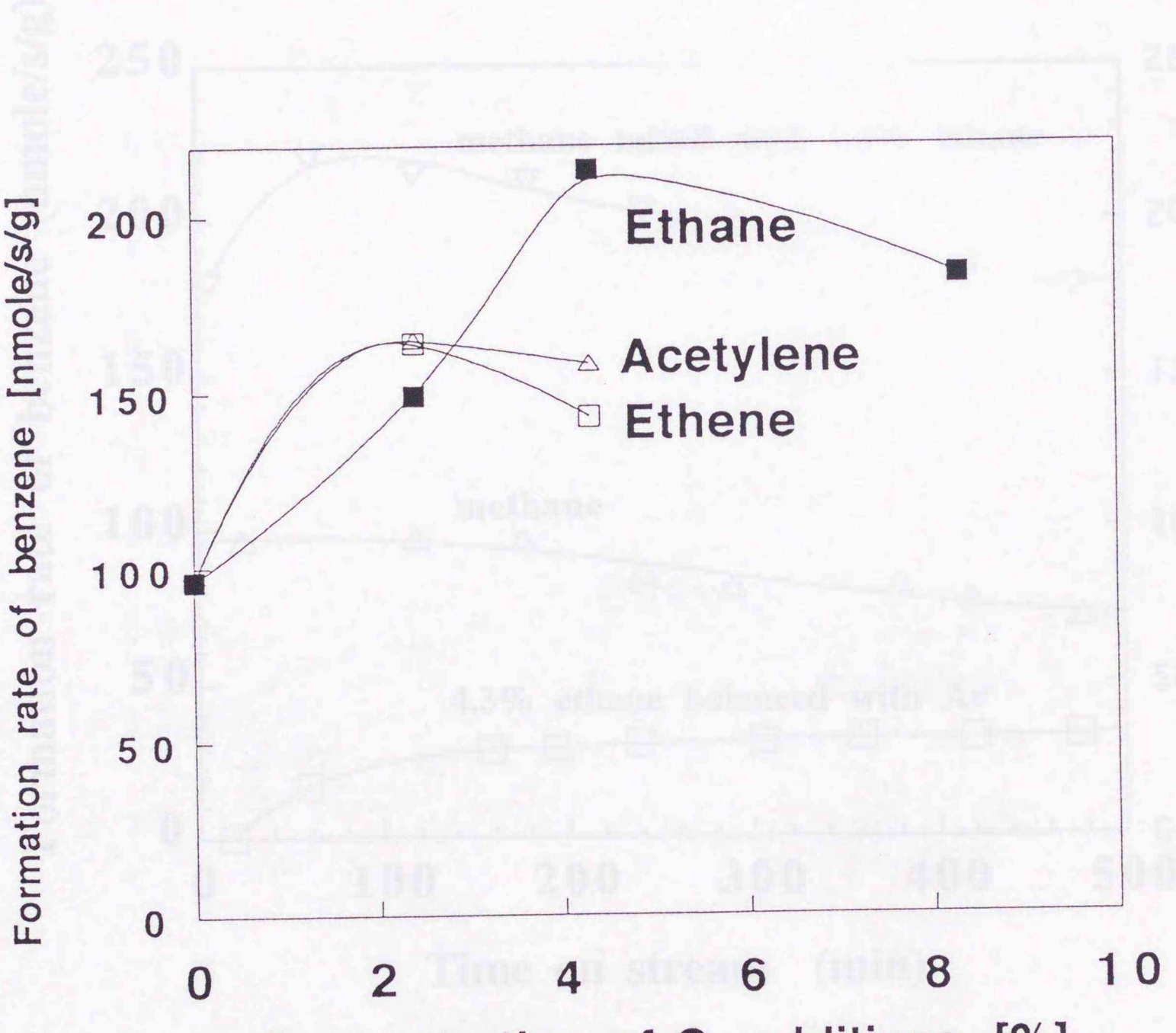
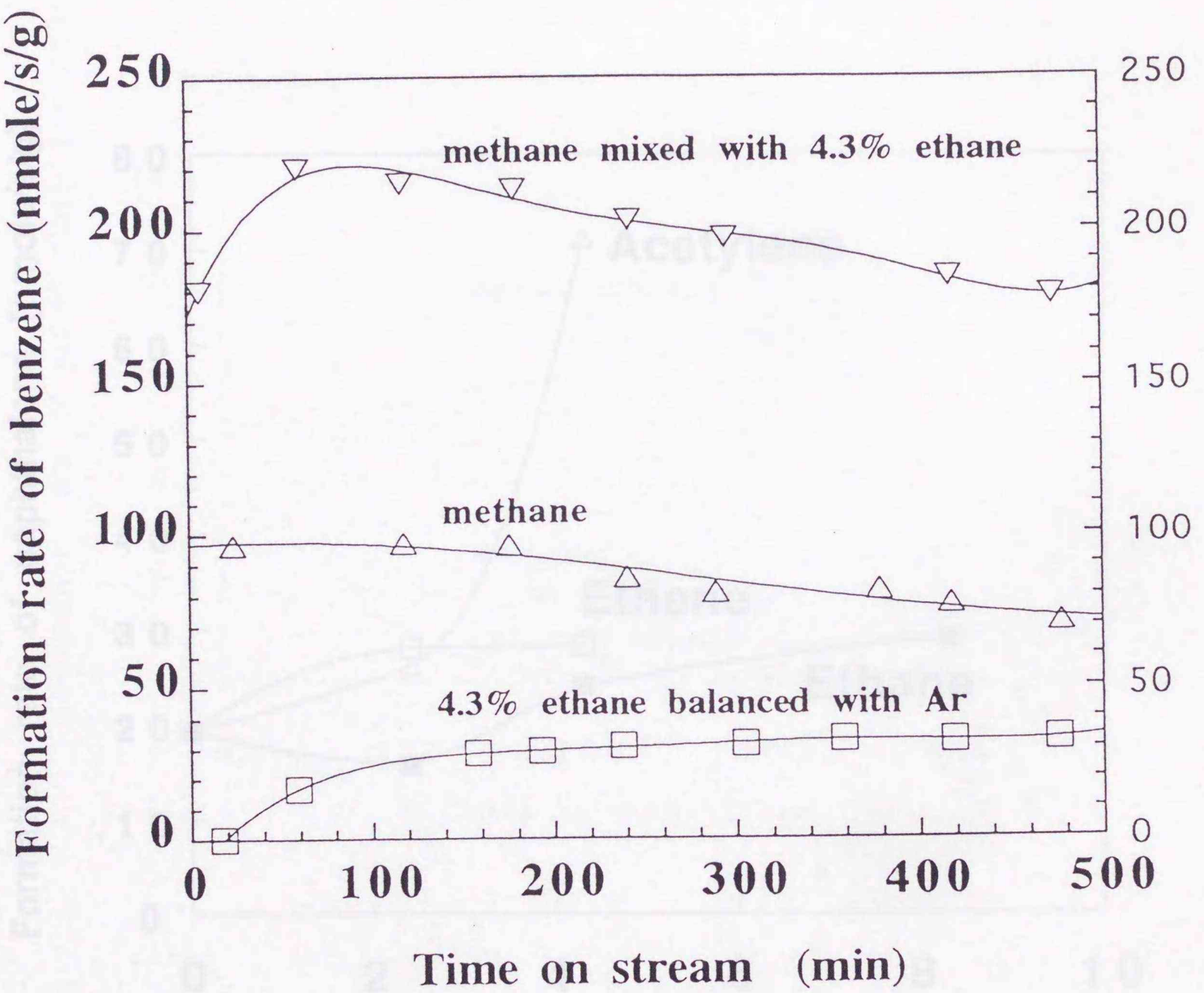


Fig 3. Effect of C_2 concentration in methane feed on benzene formation rate



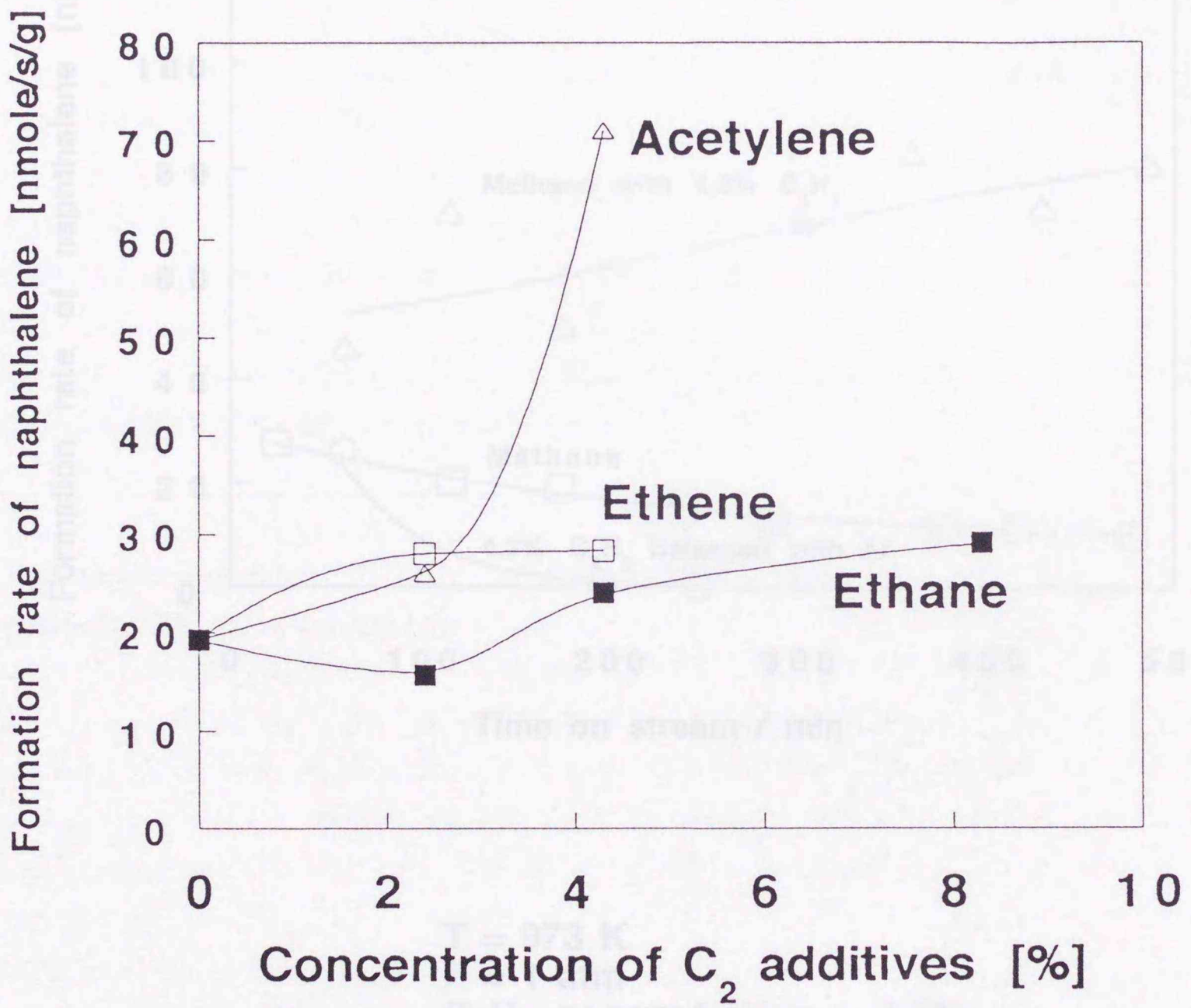
Reaction temperature = 973 K
Methane SV = 1440 ml/h/g-cat
Pressure = 1 atm

Fig 4. **Comparation of benzene formation rate with time on stream for methane aromatization on Mo/HZSM-5 with and without addition of ethane**



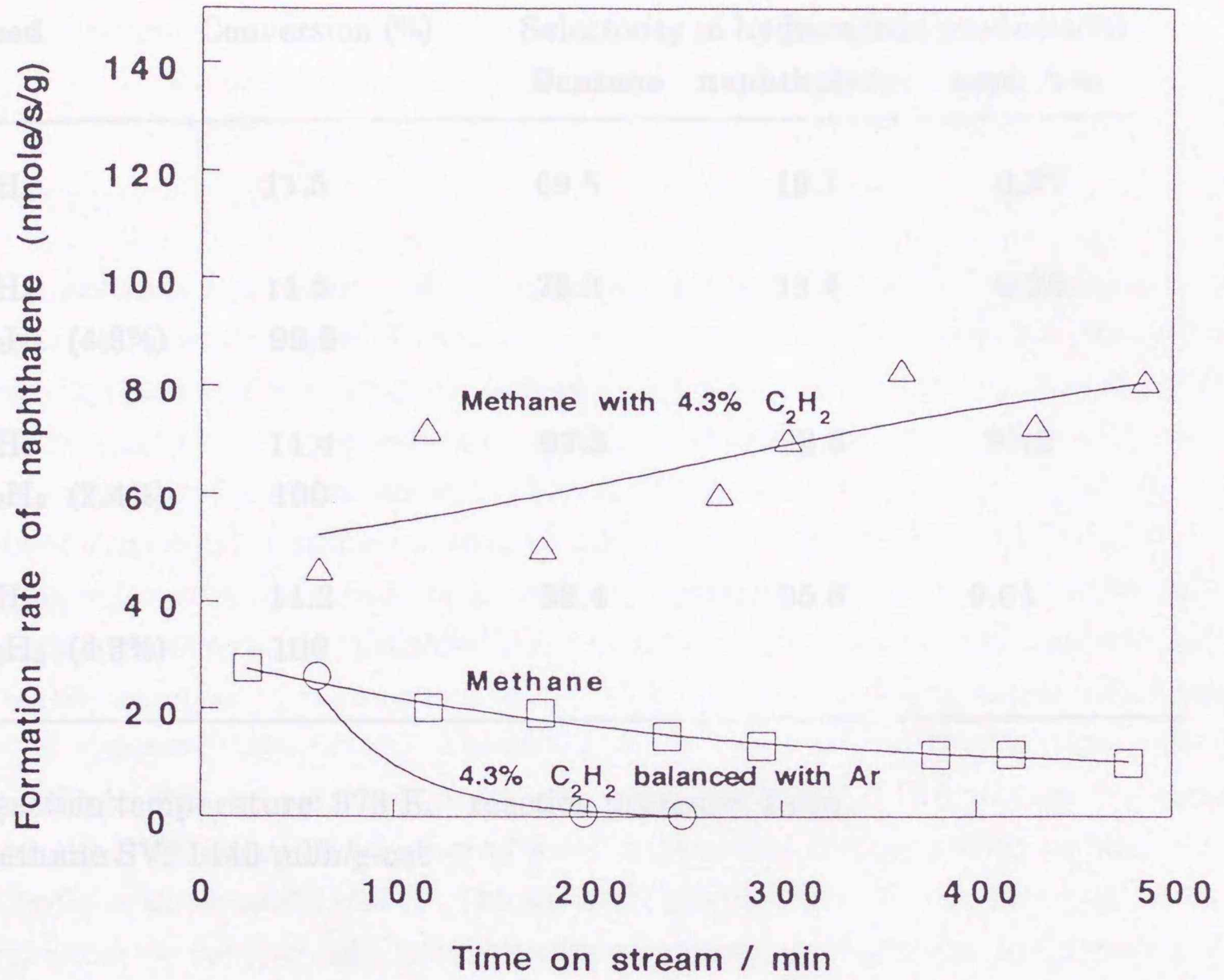
T = 973 K
P = 1atm
SV = 1440 ml/h/g-cat
ethane concentration = 4.3%

Fig 5. Effect of C_2 concentration in methane feed on naphthalene formation rate



Reaction temperature = 973 K
Merhane SV = 1440ml/h/g-cat
Pressure = 1atm

Fig 6. Comparation of naphthalene formation rate with time on stream for methane aromatization of with or without addition of acetylene



T = 973 K
P = 1 atm
C_2H_2 concentration = 4.3%

Table 1. Effect of C_2 addition on selectivity of benzene and naphthalene for methane aromatization on 3% Mo/HZSM-5

Feed	Conversion (%)	Selectivity in hydrocarbon products(%)		
		Benzene	naphthalene	naph./ben.
CH_4	11.5	69.5	19.1	0.27
CH_4	11.8	75.3	19.4	0.26
C_2H_6 (4.3%)	99.9			
CH_4	11.4	67.5	28.6	0.42
C_2H_4 (2.4%)	100			
CH_4	11.2	58.4	35.6	0.61
C_2H_2 (4.3%)	100			

Reaction temperature: 973 K, reaction pressure: 1atm,
methane SV: 1440 ml/h/g-cat

Chapter 6

Catalytic Dehydroaromatization of Methane with CO/CO_2 towards Benzene and Naphthalene on Bimetallic Mo/Zeolite Catalysts: Bifunctional Catalysis and Dynamic Mechanism

1. INTRODUCTION

In recent years a great challenge and intriguing problem in heterogeneous catalysis is the catalytic dehydrocondensation of natural gas into useful peterochemical feedstocks such as ethylene by the oxidative coupling of methane over Li/MgO and Sm_2O_3 catalysts[1] and the lower hydrocarbons by the two-step conversion of methane on Co and Ru catalysts[2], while they have not been feasible yet due to the lower yields and selectivities. Since 1993, the non-oxidative conversion of methane to benzene has been reported[3-8] on Mo/HZSM-5 catalysts in conjunction with their reactivities, reaction mechanism and catalyst characterization. Recently, we have preliminarly reported that the Fe/Co modified Mo/HZSM-5 catalysts exhibit the higher conversion of methane to aromatics such as benzene and naphthalene with a large yield of hydrogen[9],and the CO/CO_2 addition to methane effectively improve their catalyst stability[10]. This paper will present the the promotion role of CO/CO_2 addition to methane feed to effectively reduce the coke formation and improve their catalyst stability on Mo/HSM-5 and Fe/Co modified Mo/HZSM-5. The remarkably higher rates and selectivities of benzene formation in the catalytic dehydrocondensation of methane were obtained by increasing the pressure (1-5 atm) and flow rates of methane at 973K on Mo/HZSM-5 catalysts. In addition, we will discuss on the bifunctional catalysis of Mo carbide and HZSM-5 support, which have been characterized by XAFS, TG/DTA/Mass and IR spectroscopy.

2.1 Materials and catalysts preparation

3-6wt%Mo loading Mo/HZSM-5 and Fe/Co modified Mo/HZSM-5 catalysts were prepared by impregnation(incipient wetness) of NH_4ZSM-5(SiO_2/Al_2O_3=20~1900; surface area,780-925 m^2/g; Toso Co. and CRI Zeolyst, Inc.) with $(NH_4)_6Mo_7O_{24}4H_2O$, $Co(NO_3)_2$ or $Fe(NO_3)_3$ aqueous solutions. The resulting materials are dried at 393K and calcined at 773K for 6 h, similarly as reported in the previous literature[9,10]. Powdered Mo carbide(Mo_2C; 100-500 mm size) was purchased from Japan New Metal Co. and used as it. The hybrid catalysts of 3wt% Mo/SiO_2+HZSM-5 and Mo_2C+HZSM-5 were prepared by mechanically grinding both components and by the coimpregnation from the slurry solution.

2.2. Catalytic measurement and kinetic analysis

The catalytic tests were carried out under 1-5 atmospheric pressure of methane in a continuous flow system with a quartz reactor of 8mm i.d. which is charged with 0.15-0.30 g of catalyst pellets of 20-42 mesh. The feed gas mixture of 98%CH_4(99.9% purity) and 2%Ar as internal standard for analysis was introduced into the reactor at 7.5-20 ml/min[space velocity= 1000-20000 ml(g-cat.h)$^{-1}$] through a mass flow controller(Brooks 5850E) after flashing with He at 973K for 40min. Hydrocarbon products including C_2-C_4 alkanes(and/or alkenes) and condensable C_6-C_{12} aromatics such as benzene, toluene, xylene and naphthalene derivatives were analyzed by the on-line FID gas chromatography using a six-way sampling valve heating at 533K on a Porapak-P column and the one-line TCD gc for H_2, Ar, CO, CH_4 and CO_2 on an activated carbon column. The condensable materials such as benzene, toluene, xylene, naphthalene, methylnaphthalene and anthracene which were identified by using the on-line GC-MS(Perkin-Elmer, Auto System GC with 910 Q-Mass). Using an internal standard analyzing method, methane conversion, selectivities of hydrocarbon products and coke formation formed on the catalysts were evaluated according to the mass balance for carbon and hydrogen[9,10].

3. RESULT AND DISCUSSION

3.1 Methane aromatization on Mo/HZSM-5 and Fe/Co modified Mo/HZSM-5

The non-oxidative conversion of methane was conducted by flowing methane(1-5 atm) on the catalysts in the fixed bed at 973K. Using 2%Ar as the internal standard for the reaction analysis, the yields and selectivities of benzene and coke formation were carefully evaluated according to the previous work[9,10]. C_2-hydrocarbons and aromatic products such as benzene and naphthalene were continuously obtained with a considerable evolution of hydrogen (H_2/ benzene=9-18 mol/mol) on the Mo/HZSM-5, Fe/Co modified Mo/HZSM-5 catalysts. The conversion of methane(ca. 12 %) usually decreases rapidly at the initial stage and moderately at the later stage of the reaction down to 4% in 30 h possibly due to the coke formation. The major hydrocarbons produced on Mo/HZSM-5 consist of benzene(50-68%), naphthalene(45-12%) and toluene (2-5 %) as the aromatics, and C_2 products(4-12%) such as ethylene and ethane. The other carbon-containing products such as CO, propene, butene, and methylnaphthalene, phenanthrene, anthracene and tetracene as poly-condenced aromatics were produced in a small amount (totally less than several % selectivity). Further bulky substituted aromatic compounds are minorly obtained on the catalysts at 973K because of the higher activity for hydrogenolysis and molecular shape selectivity due to the limited size of micropores of HZSM-5(5-6Å) accessible only to benzene and toluene. Our obtained results on the Mo/HZSM-5 catalyst

show that the benzene selectivities based on the consumed methane did not exceed 42% at the maximum value owing to the formation of coke(32-42% sel) and polycondensed by-products.

From Fig.1a and 1b it is clear that the addition of Fe as for Co, to Mo/HZSM-5 catalysts yields a considerable enhancement of aromatic products such as benzene and naphthalene in the reaction at 973K. A maximum rates(120-150 nmol/h/g-cat) and selectivity(52-54% sel) of benzene formation and minimizing coke formation(less than 20%) was attained by the optimum addition of Co(and/or Fe) to Mo/HZSM-5. Further addition of Fe or Co to Mo/HZSM-5 results in a decrease of the aromatic products owing to substantial increase of coke formation in the methane conversion. The characterization by XRD, TG/DTA/Mass and EXAFS suggest that the binary FeMo and CoMo carbides are highly dispersed in the micro-channels of HZSM-5 zeolite in the methane conversion at 973K, implying that Fe and Co act as anchoring elements to promote the dispersion of Mo carbide as the active species for the reaction.

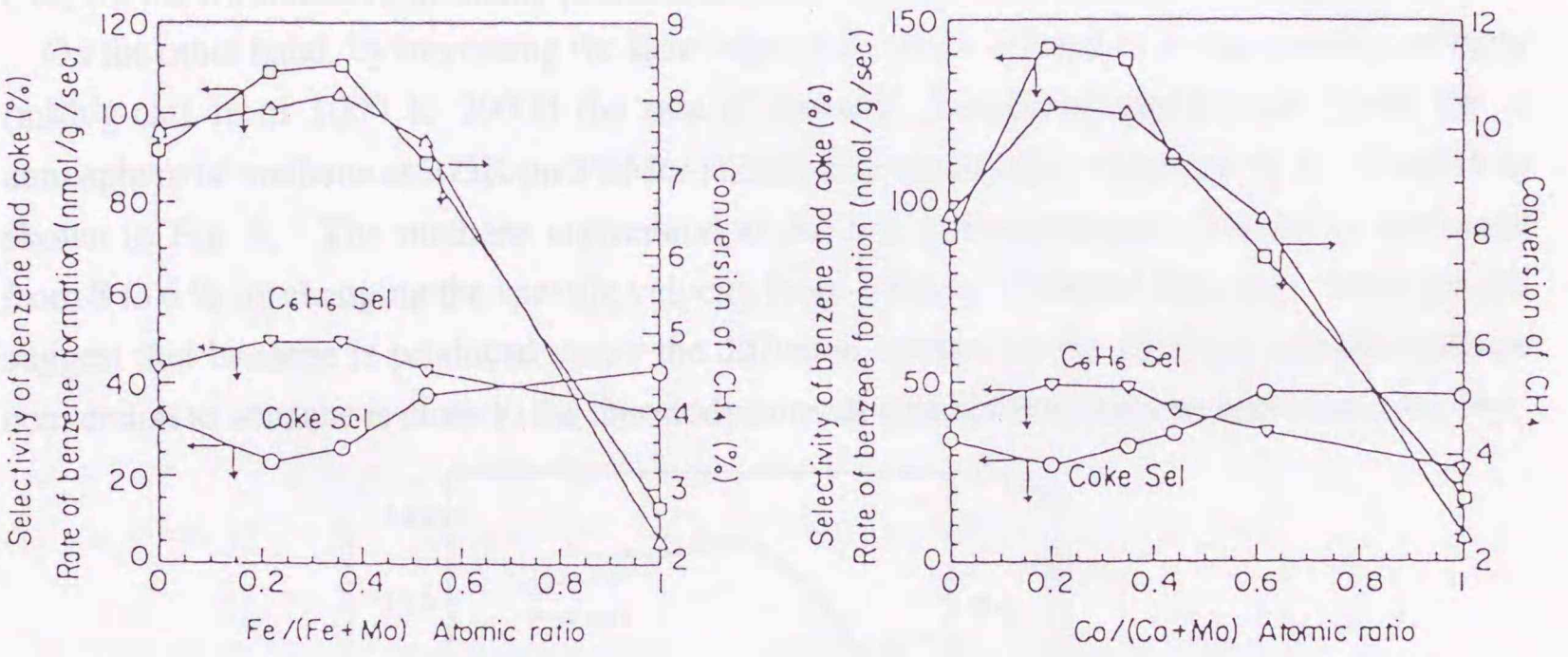


Fig.1. Catalytic performances of (a) Co-Mo//HZSM-5 and (b) Fe-Mo/HZSM-5 for methane dehydroaromatization at 973K and 1 atm as the function of the Co/Mo and Fe/Mo composition.

yields a considerable enhancement of aromatic products such as benzene and naphthalene in the reaction at 973K. A maximum rates(120-150 nmol/h/g-cat) and selectivity(52-54% sel) of benzene formation and minimizing coke formation(less than 20%) was attained by the optimum addition of Co(and/or Fe) to Mo/HZSM-5. Further addition of Fe or Co to Mo/HZSM-5 results in a decrease of the aromatic products owing to substantial increase of coke formation in the methane conversion. The characterization by XRD, TG/DTA/Mass and EXAFS suggest that the binary FeMo and CoMo carbides are highly dispersed in the micro-channels of HZSM-5 zeolite in the methane conversion at 973K, implying that Fe and Co act as anchoring elements

to promote the dispersion of Mo carbide as the active species for the reaction.

3.2. Effects of pressure and flow rate

Fig.2 shows the dependency of rates of products and coke formation in the methane reaction on 3%Mo/HZSM-5 at 973K by varing the methane pressure of 1-5 atm, respectively. It is intersting to find that the formation rates of benzene and C_2 hydrocarbons increase moderately by increasing the methane pressure. The maximum yields and selectivity (65% sel) of benzene were attained at 3-4 atm of methane by the constant flow rate of 2500 (ml/h/g-cat) at 973K, although the methane conversion is thermodynamically unfavorable for the pressurized condition($6CH_4 = C_6H_6 + 9H_2$). Moreover, it is of worthy to note that the coke formation is substantially suppressed and the catalyst stability was relatively improved by increasing the methane pressure above 3 atm on the catalyst, as shown Fig.2. This may be related with the sufficient supply of hydrogen from methane and the concentration of the surface carbon species CH_x for the formation of aromatic products such as benzene and naphthalene on the catalysts.

On the other hand, by increasing the flow rates of methane refered to as the specific velocity (ml/h/g-cat) from 1000 to 20000 the rate of benzene formation(nmol/s/g-cat) under the 3 atmosphere of methane at 973K on 3%Mo/ HZSM-5 is remarkably enhanced by ca. 10 times as shown in Fig. 3. The methane conversion at the 5 h time-on stream moderately decreased from 8 to 6 % by changing the specific velocity from 1000 to 20000(ml/h/g-cat). These results suggest that benzene is produced under the diffusion control on the catalysts and the methane conversion to benzene is close to the thermodynamical equilibrium(benzene conversion for H_2/

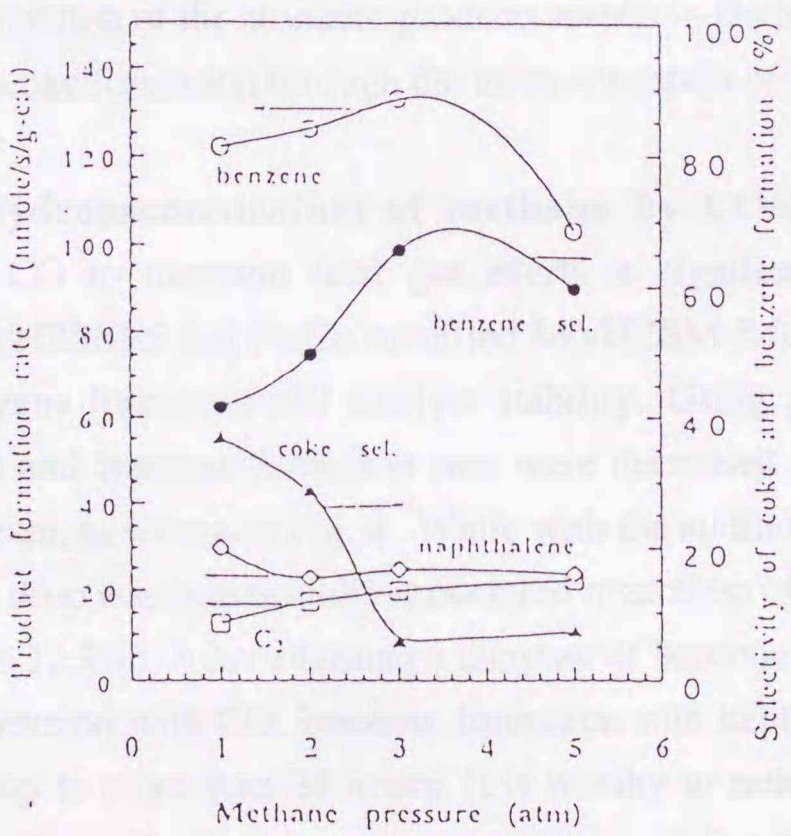
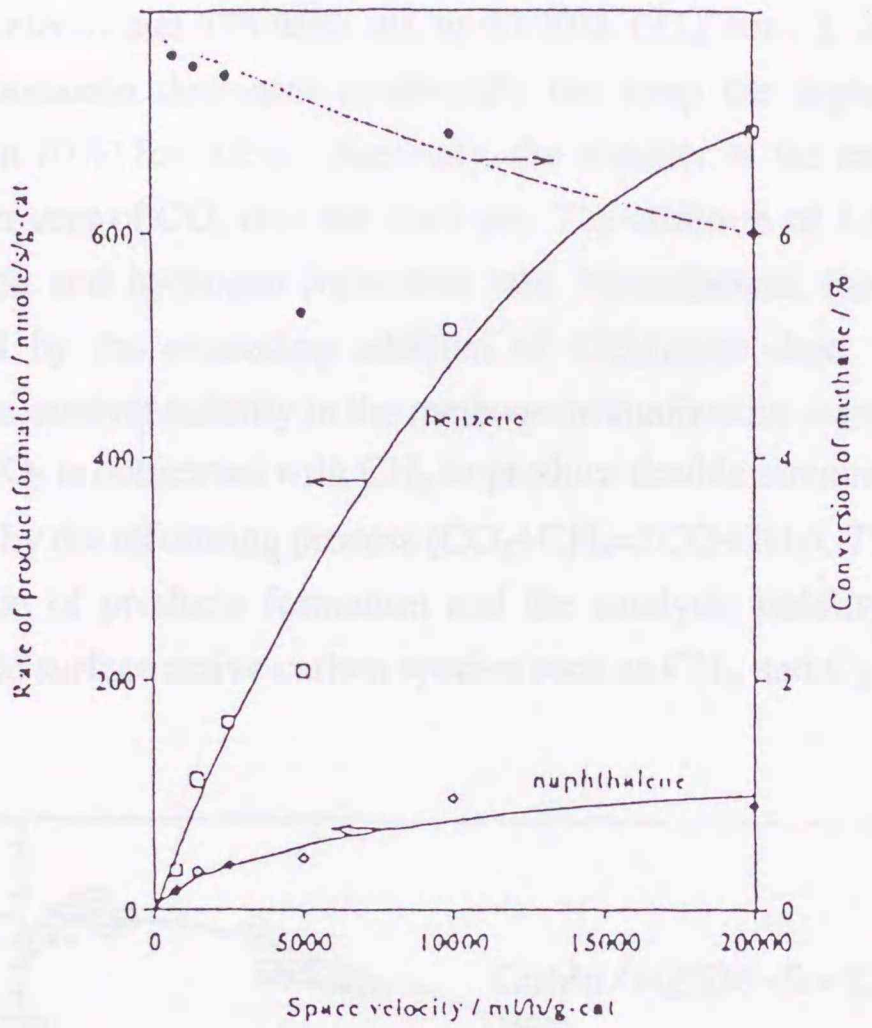


Fig. 2 Catalytic performances of 3%wt Mo/HZSM-5 for methane dehydroaromatization varing the methane pressure from 1 to 5 atm at 973K and SV=1440 ml/h/g-cat.

Fig.3. Product formation rates and methane conversion on 3%wtMo/HZSM-5 by varying specific velocity of methane(ml/h/g-cat) at 3 atm and 973K



C_6H_6=12 at 973K is calculated as 8.2% and 1 atm of methane) under the reaction conditions. The effective transportation of the aromatic products results in the higher conversion of methane and suppressing the coke formation through the micro-channels of HZSM-5.

3.3. Selective dehydroaromatization of methane by CO/CO_2 addition

The addition of CO to methane feed gas exerts a significant effect on the catalytic performances of Mo/HZSM-5 and Fe/Co modified Mo/HZSM-5 for the aromatization reaction to promote the benzene formation and catalyst stability. Using pure CH_4 as the feed gas, methane conversion and benzene formation rate were decreased greatly during 24 hours of reaction time on stream, as shown in Fig. 4. While with the addition of CO in the feed gas, the methane conversion drop was substantially moderated regardless of varying the partial pressure of CO (from 1.7% to 12.3%). After attaining a increase of benzene formation in the early stage of the methane conversion with CO, benzene formation rate kept almost constant during the prolonged reaction up to more than 24 hours. It is worthy to note that in the steady reaction stage, the amount of CO is almost kept constant before and after the reaction in all the case of CO addition. The results imply that CO is regenerated possibly due to the reaction of the surface

carbon with the active oxygen species derived from CO dissociation as shown in Scheme 1.

By addition of CO to a 1 atm methane flow at 973K the Co and Fe modified Mo/HZSM-5 catalysts at 973K and 1 atm of methane exhibit remarkable catalytic activities for the benzene formation in high selectivities (75-85% sel. at 10-13% CH_4 conv.), as shown in Fig. 4. The rate of benzene formation decreases moderately but keep the higher rates and lower coke selectivity(less than 10%) for 100 h. Similarly, the stability of the catalyst was also improved by adding a few per cent of CO_2 into the feed gas. The addition of 1.6% CO_2 yielded a higher methane conversion and hydrogen formation rate. Nevertheless, the benzene formation was greatly suppressed by the exceeding addition of CO_2(more than 12%), but it yields the improvement of the catalyst stability in the methane aromatization during the prolonged time. It is suggested that CO_2 is converted with CH_4 to produce double amount of CO and H_2 under the reaction condition by the reforming process ($CO_2+CH_4=2CO+2H_2$). The formed CO may exert a similar promotion of products formation and the catalytic stability. The excess CO_2 may greatly consume the surface active carbon species such as CH_x and C_2 species for the reaction.

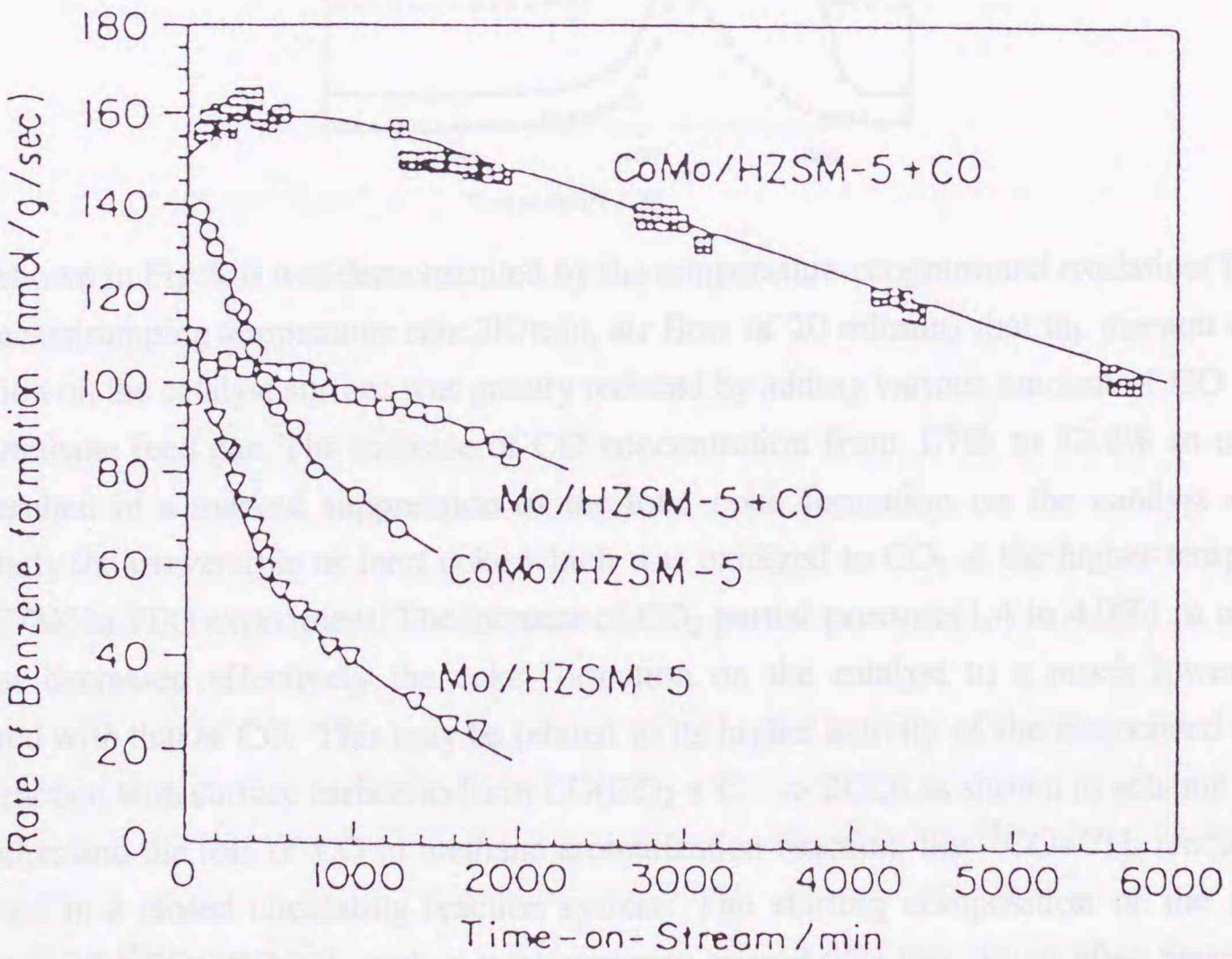
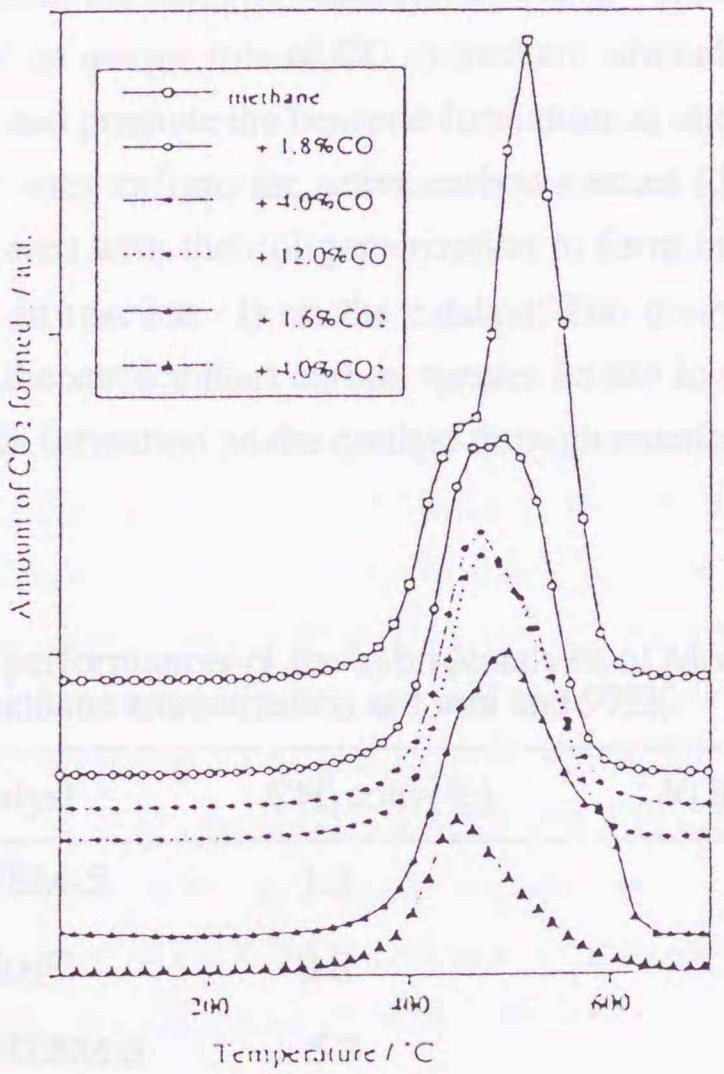


Fig. 4. Rates of benzene formation in methane aromatization with and without addition of CO (1 atm, 3.5%CO, 973K) on Mo/HZSM-5 and Co-Mo/HZSM-5 catalysts.

Fig.5. TPO pattterns as CO_2 formation by flowing air on the Mo/HZSM-5 catalysts after the reaction with CH_4, CH_4+CO and CH_4+CO_2 at 1 atm, 973K and SV=1500



As shown in Fig.5, it was demonstrated by the temperature-programmed oxidation(TPO) experiments(ramping temperature rate:2K/min, air flow of 20 ml/min) that the amount of coke deposition on the catalyst surface was greatly reduced by adding various amount of CO or CO_2 to the methane feed gas. The increase of CO concentration from 1.7% to 12.0% in methane flow resulted in a marked suppression of the total coke formation on the catalyst surface, particularly the irreversible or inert coke which was oxidized to CO_2 at the higher temperature above 773K in TPO experiment. The increase of CO_2 partial pressure(1.4 to 4.0%) in methane feed gas decreased effectively the coke formation on the catalyst to a much lower level, compared with that of CO. This may be related to its higher activity of the dissociated oxygen in the reaction with surface carbon to form CO(CO_2 + C ---> 2CO) as shown in scheme 1.

To understand the role of CO in methane aromatization reaction, the ^{13}CO+CH_4 reaction was conducted in a closed circulating reaction system. The starting composition of the mixture reactant is 8%^{13}CO+92%CH_4 with a total pressure around 220 torr. Even after 5min of the closed circulating reaction at 973K, ^{13}C atoms involved in methane ($^{13}CH_4$) reached the value of 8%. The isotopic abundance of ^{13}C incorporated in benzene molecule were detected by GC-Mass analysis as the random distribution ($^{13}CC_5H_6$-47.6%, $^{13}C_2C_4H_6$-36.7%, $^{13}C_3C_3H_6$-13.0%, $^{13}C_4C_2H_6$-2.4%, $^{13}C_5CH_6$-0.3%) regardless of the reaction time of methane on

Mo/HZSM-5. These results suggest that the carbon derived from CO dissociation is efficiently incorporated into the benzene formation and the isotopic scrambling reaction between ^{13}CO and $^{12}CH_4$ proceeds rapidly under the reaction condition at 973K. Based on the above results we suggest the mechanism of an unique role of CO in methane aromatization reaction to stabilize the catalyst performances and promote the benzene formation as shown in scheme 1. Firstly, CO dissociates on the Mo sites to form the active carbon species CH_x and C_2 species through reaction (2) and (3); followed with their oligomerization to form higher hydrocarbons such as benzene and naphthalene in reaction (1) on the catalyst; The dissociated oxygen species [O] from CO may react with the surface inert carbon species (coke) to regenerate CO, resulting in the suppression of the coke formation on the catalyst through reaction (4).

Table 1. Catalytic performances of the hybridcatalysts of MoC_2(or MoO_3/SiO_2)+ HZSM-5 in the methane aromatization at 1 atm and 973K

catalyst	CH_4 conv(%)	V(Benzene)[a]
HZSM-5	1.2	0.6
Mo_2C	0.8	3
MoC_2+HZSM-5	5.7	150
MoO_3/SiO_2	5.3	412
MoO_3/SiO_2+HZSM-5	6.2	2019
3%Mo/HZSM-5	8.5	3162

a: Specific rates of benzene formation(nmol/Mo/sec)

3.4. Bifunctional catalysis by Mo carbide and ZSM-5 zeolite support

EXAFS(Mo K-edge) and TG/DTA/Mass studies have been performed in methane conversion(1 atm, 300-973K) on 6wt% Mo/HZSM-5 using the SOR facility(KEP-10 line) and Mac Science system(TG-DTA2020S), respectively. It was demonstrated that Mo oxide on HZSM-5 is converted with methane at 923K by the evolution of H_2 and CO to Mo carbide cluster(Mo_2C; Mo-Mo; C.N.= 2.1-3.5, R-2.98Å), where the methane aromatization reaction initiats to form C_6H_6, $C_{10}H_8$ and C_2H_4 in evolving hydrogen above 923K. The results imply that Mo carbide on HZSM-5 support is an active species for the catalytic methane aromatization similarly as it has been proposed peviously by Solymosi and Lunsford[5,6,8].

To understand the bifunctional role of Mo carbide and HZSM-5 support the following

experiments were conducted. As indicated in Table 1, it was of interest to find that the specific rates of benzene formation(C_6H_6/Mo/sec) on a hybrid catalysts of MoC_2(or MoO_3/SiO_2) +HZSM-5 at 973K were greatly enhanced(50-100 times) by the mechanical mixture of each component, which shows neglegible or low activity. These imply the bifunctional catalysis for methane aromatization at the interface of Mo carbide and ZSM-5 support. The results by in-situ FTIR and EXAFS studies suggest that methane is activated on Mo carbide sites to form CH_x and C_2-species(e.g.CH_3-C;2967, 2878,1468 and 1382 cm^{-1}) which may migrate at the interface of ZSM-5 acidic support, followed by the dehydroaromatization of C_2-intermediates to benzene and naphthalene. As it is discussed in the session 3.3., the common carbon species CH_x by the dissociation of CO and methane on MoC_2 are converted to C_2-hydrocarbons, benzene and naphthalene on the acidic sites of the ZSM-5 support. The influence of SiO_2/Al_2O_3 ratio(20-1900) of the HZSM-5 zeolite on benzene production and coke formation were also investigated. It was found that there exists a sharp optimum SiO_2/Al_2O_3 ratio of 40 yielding highest rates of benzene formation and lowest coke formation. The HZSM-5 supports having too smaller or larger Si/Al ratios beyond 40 produce the Mo/HZSM-5 catalysts of poor activity for methane aromatization. The proper Bronsted acidity of HZSM-5 promotes the conversion of C_2-intermediates to benzene and naphthalene and suppress the coke formation. This bifuncti-onal catalysis of Mo_2C/HZSM-5 for methane aromatization reaction is discussed by analogy with the synergetic promotion on Pt/Al_2O_3 catalyst for the dehydroaromatization of alkanes.

4. Conclusion

(1) Catalytic dehydroaromatization of methane with CO and/or CO_2 proceeds at 973K under the higher pressure of methane(1-5 atm) on Mo/HZSM-5 and Fe/Co modified Mo/HZSM-5 towards aromatic products such as benzene and naphthalene with higher yields and stable selectivities (above 85 %) and minimizing the coke formation in the prolonged time of 100 h.

(2) The catalyst stability by adding CO and/or CO_2 to the methane feed is associated with effectively suppressing the coke formation due to CO dissociation on Mo/HZSM-5 catalysts.

(3) A remarkable synergetic promotion for benzene formation is obtained on the hybrid catalysts consisting of Mo/SiO_2+HZSM-5 and Mo_2C+HZSM-5, whereas each component shows a marginal activity in the reaction.

(4) Bifunctional catalysis of Mo/HZSM-5 is discussed by the mechanism that methane is activated on Mo sites to form CH_x and C_2-species, which may migrate at interface of ZSM-5 having the optimum acidity for the dehydrocyclization to benzene and naphthalene.

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Chapter 7
Inhibitation of coke deposition and activity enhancement for methane aromatization by varying reaction conditions on Mo/HZSM-5

Abstract:

Dependence of activity and selectivity for methane aromatization on Mo/HZSM-5 on the reaction conditions such as pressure and specific velocity of methane, CO_2 addition at high SV and reaction temperature is investigated. A high and stable benzene formation rate of about 1700 nmole/s/g-cat is achieved for methane aromatization on Mo/HZSM-5 by increasing methane pressure from 1 to 3 atm, methane specific velocity from 1440 to 10000 ml/h/g-cat and reaction temperature from 973 to 1073 K, and by adding about 2.1% CO_2 to methane feed. The rate of benzene formation with time on stream is remarkably stabilized by varying methane pressure and addition of 2.1% CO_2 in methane feed and greatly enhanced by increasing methane specific velocity from 1440 to 10000 ml/h/g-cat and reaction temperature from 973 to 1073 K. The selectivity of benzene and naphthalene and coke is also controlled by varying reaction conditions. High methane specific velocity lead to high benzene selectivity and low naphthalene selectivity. Coke selectivity is minimized at 3 atm methane.

1 Introduction

In recent years, a great challenge and intriguing problem in heterogeneous catalysis is the catalytic dehydropolymerization of natural gas into useful petrochemical feedstocks and liquid fuel. Methane aromatization on Mo/HZSM-5-based catalysts has been attracted a increasing attention. The conventional reaction conditions employed for methane aromatization on Mo/HZSM-5 are at methane pressure of about 1-2 atm, methane specific velocity of 1440 ml/s/g-cat and temperature of 973 K [1-20]. In the present study, the role of reaction conditions such as pressure and specific velocity of methane, CO_2 addition in methane feed, reaction temperature and Mo-loading on HZSM-5 support in controlling the activity and selectivity for methane aromatization is discussed.

2 Experimental

Mo/HZSM-5 was prepared by impregnating NH_4ZSM-5 (SiO_2/AI_2O_3=40, Toso Co.) with $(NH_4)_6Mo_7O_{24}4H_2O$ (Kanto Chem. Co.) aqueous solution, followed by drying at 383 K for 4 h and calcination at 773 K for 4 h. The sample was finally pressed, crussed and sorted into 20-40 mesh. Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow straight type quartz reactor. After catalyst was pretreated by air stream at 873 K for 30 min and then by He stream at 873 K for 30 min, the stream was switched to feed gas and catalyst bed was brought to reaction temperature. The products were withdraw periodically from the outlet of reactor and analyzed by two on-line gas chromatography of Shimadazu GC-9A and GC-8A equipped with a flame ionization detector (FID) and a thermoconductive detector (TCD) respectively. Hydrocarbon products were separated by a 4mm ×2m Porapak P column and Ar , CH_4, CO, CO_2, H_2 were analyzed by a 4mm×1m active carbon column. 2.2% Ar in methane was employed as internal standard. Formation rate of products, methane conversion and product selectivity were calculated by an internal standard analyzing method [19]. Formation rate of products, methane conversion and product

selectivity were calculated by an internal standard analyzing method. Below, the method is presented briefly. Even if the total flow rate changed at outlet from inlet of reactor (F_{Total}^{intlet} ,F_{Total}^{outlet}). Flow rate of non-reactive internal standard gas (F_{st}) doses not change.

$$F_{st} = F_{Total}^{outlet} \times X_{st}^{outlet} = F_{Total}^{inlet} \times X_{st}^{inlet}$$

Here, X_{st} refer to concentration of the internal standard gas.

Formation rate of i product (F_i) can be calculated as,

$$F_i = F_{Total}^{outlet} \times X_i^{outlet} = F_{st} \times X_i^{outlet} / X_{st}^{outlet}$$

By the same way, methane conversion ($C_{methane}$) can be calculated as,

$$C_{methane} = (F_{methane}^{inlet} - F_{methane}^{outlet}) / F_{methane}^{inlet} = 1 - F_{methane}^{outlet} / F_{methane}^{inlet}$$

$$= 1 - F_{Ar} \times X_{methane}^{outlet} / X_{Ar}^{outlet} \times F_{methane}^{inlet}$$

Coke selectivity = 1- (produced HC+produced CO)/converted methane. The raw materials of methane and ethane is over 99.99% pure.

3 Results and discussion

3.1 Effect of methane pressure

The reaction for benzene aromatization was conducted by varying pressure of methane. Benzene formation rate with time on stream at different methane pressure is shown in fig 1. At the lower methane pressure less than 1 atm (including 1atm), benzene formation rate decline with time on stream although it is higher at the initial stage. At the higher pressure of 2-3 atm, benzene formation rate increase with time on stream at the initial stage and then become stable. However, at so high methane pressure as 5 atm, the formation rate is somehow suppressed although a stable rate of benzene formation is still available. Therefore, a stable rate of benzene formation is achieved by conduct the reaction at the higher methane pressure higher than 2 atm. The effect of methane pressure on the selectivity of coke and formation rate of hydrocarbon products is shown in fig 2. The selectivity of coke is minimized and the selectivity and formation rate of benzene is maximized increasing methane pressure from 0.28 atm to 3

atm (fig 2). Coke selectivity at 3 atm methane is about 10 times less than that at 0.28 atm methane. High methane pressure lead to low coke selectivity, which is responsible for high stability for benzene formation. Formation rates of ethene and ethane is also quite dependent on the pressure of methane as shown in fig 3. Ethene formation rate decreases and ethane formation rate increases with increasing methane partial pressure. Higher partial pressure of methane is favorable for transformation of ethene to ethane through hydrogen transfer reaction. The coke species deposited on the catalyst at different methane partial pressure is characterized by TPO spectra. Two distinct coke species respond to different oxidation temperature can be identified by TPO spectra as shown in fig 4. The two TPO peaks are ascribed to the coke species (C_m) deposited on metal sites formed by deep dehydrogenation of hydrocarbon species and coke species (C_s) deposited on acid sites of support. It seems that high methane pressure is unfavorable to formation of the coke species (C_s) deposited on support. However, the coke species (C_m) on metal, which is contributed to formation of carbide, is independent of methane pressure.

3.2 Effect of methane specific velocity and reaction temperature

Formation rate of benzene with time on stream at 3 atm methane and different methane specific velocity is shown in fig 5. At a methane specific velocity of 1440 ml/h/g-cat, formation rate of benzene is about 130 nmole/s/g-cat and quite stable with time on stream. Benzene formation rate increases remarkably with increasing methane specific velocity. However, benzene formation rate with time on stream decline at high methane specific velocity. The coke species deposited on the catalyst at different methane specific velocity is characterized by TPO spectra as shown in fig 6. It indicates in fig 6 that high methane specific velocity mainly lead to increase of the coke species of Cs. In addition, product selectivity is also dependent on methane specific velocity as shown in fig 7. Benzene selectivity remarkably increases and naphthalene selectivity decreases with increasing methane specific velocity from 720 to 2500 ml/h/g,

and C_2 selectivity is also increases with increase of methane specific velocity. This reflect some mechanistic features of methane aromatization. Benzene is primary aromatic products and naphthalene is produced by the secondary reaction of benzene. Therefore, benzene selectivity is enhanced and naphthalene selectivity is suppressed at a higher specific velocity of methane since high SV is unfavorable for the secondary reaction. On the other side, high naphthalene selectivity is available at low methane specific velocity. Naphthalene selectivity at a lower methane specific velocity of about 720 ml/h/g is about 40%.

3.3. Effect of reaction temperature and Mo-loadings

Benzene formation rate also increases quite dramatically with increase of reaction temperature as shown in fig 8. Rate of benzene formation is almost doubled by 50 K increase from 973 K to 1023 K. Therefore, a very high benzene formation rate is achieved at high specific velocity and high reaction temperature. At the severe reaction conditions of higher SV and higher reaction temperature, benzene formation rate and coke selectivity is also dependent on the Mo-loading of Mo/HZSM-5 catalyst. The coke selectivity is minimized and benzene formation rate is maximized at the Mo-loading of about wt.6-21% as shown in figure 9.

3.4 Effect of CO_2 addition in methane feed

Although rate of benzene formation is increased remarkably by increasing methane specific velocity and reaction temperature, benzene formation rate decline sharply with time on stream because of the serious coke deposition on the catalyst at high methane specific velocity. To stabilize the catalyst at high methane specific velocity, about 2.1% CO_2 is added to the methane feed. Fortunately, The rate of benzene formation is stabilized with time on stream at high methane specific velocity by addition of 2.1% CO_2 to methane feed as shown in fig 10. It is shown in fig 10 that a high and stable benzene formation rate of about 1000 nmole/s/g-cat is achieved for methane

aromatization with about 2.1% CO_2 on 15%Mo/HZSM-5 at 1023K and methane specific velocity of 10000 ml/h/g-cat. In addition, the rate of benzene formation for methane aromatization with CO_2 is greatly increased further by increasing reaction temperature from 1023 K to 1073 K. A very high benzene formation rate of about 1700 nmole/s/g-cat is attained for methane aromatization with 2.1% CO_2 on 15% Mo/HZSM-5 at methane specific velocity of 10000 ml/h/g-cat and 1073 K as shown in fig 10. Therefore, it seems that CO_2 addition is the solution to solve the problem of the serious coke deposition on the catalyst for methane aromatization at high methane specific velocity and high temperature.

4 Conclusion

High and stable rate of benzene formation has been achieved for methane aromatization on Mo/HZSM-5 by optimizing reaction conditions including:
1) increasing methane pressure from 1 to 3 atm, 2) increasing methane specific velocity from 1440 to 10000 ml/h/g-cat and reaction temperature from 973 to 1073 K, and 3) adding about 2.1% CO_2 to methane feed. The role of 1) and 3) is to enhance the stability for benzene formation rate with time on stream and the role of 2) is to increase rate of benzene formation rate. The rate of benzene formation is about 1700 nmole/s/g-cat at the optimized conditions, which is about 17 times of that at the conventional conditions(SV=1440 ml/h/g-cat, T= 973 K and P = 1atm). The selectivity of benzene and naphthalene and coke is also controlled by reaction conditions. High methane specific velocity lead to high benzene selectivity and low naphthalene selectivity. Coke selectivity is minimized by varying methane pressure.

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Caption of figures:

Fig 1. Benzene formation rate with time on stream for methane aromatization on 3%Mo/HZSM-5 at various methane pressure

Fig 2. Formation rate and selectivity of product as a function of methane pressure for methane aromatization on 3%Mo/HZSM-5

Fig 3. Formation rate of ethane and ethene as a function of methane pressure

Fig 4. TPO profiles of Mo/HZSM-5 catalyst after methane aromatization at various methane pressure

Fig 5. Benzene formation rate with time on stream for methane aromatization on 3%Mo/HZSM-5 at various methane specific velocity

Fig 6. TPO profiles of Mo/HZSM-5 catalyst after methane aromatization at various methane specific velocity

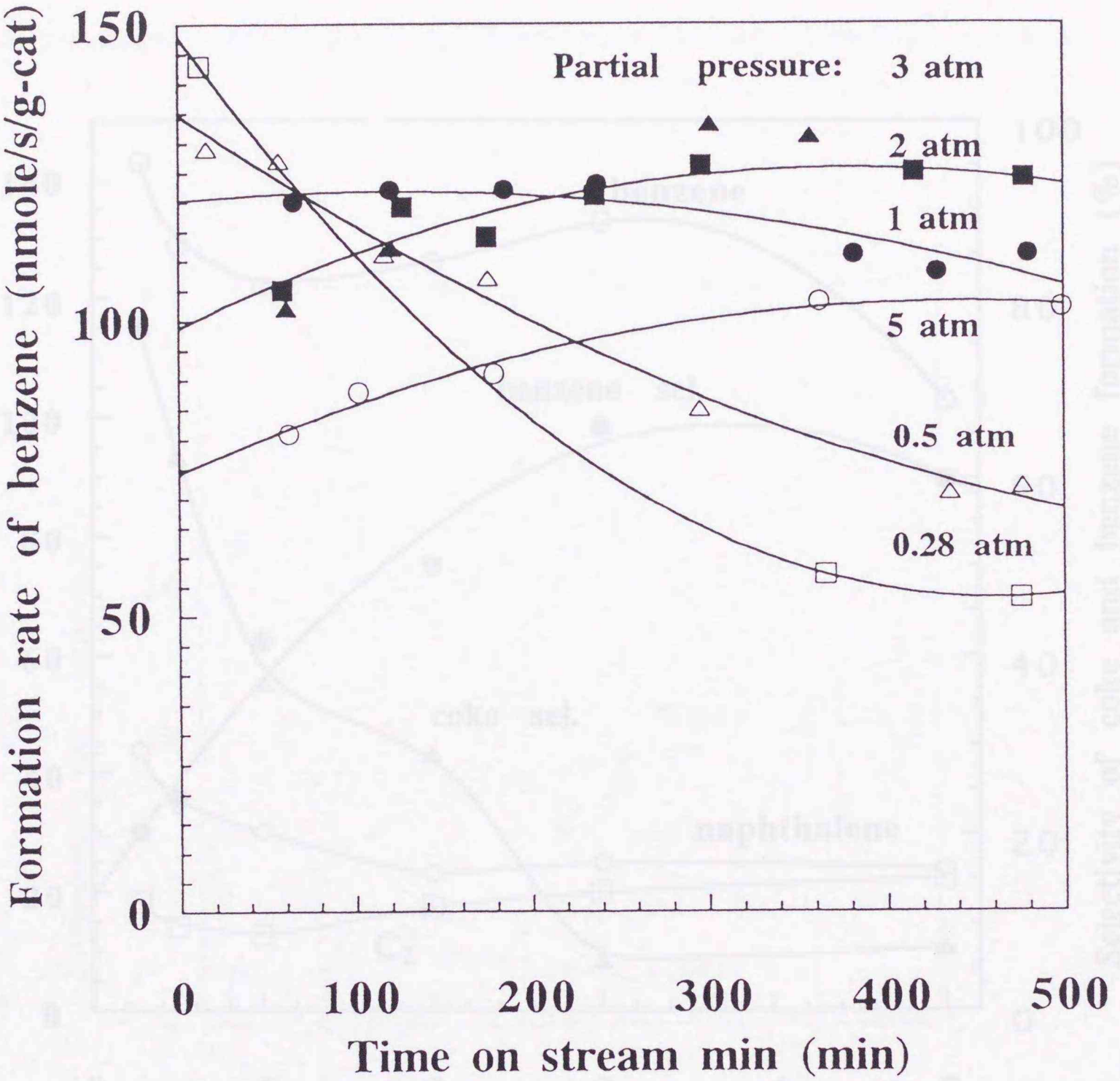
Fig 7. Formation rate and selectivity of product as a function of methane specific velocity for methane aromatization on 3%Mo/HZSM-5

Fig 8. Dependence of benzene formation rate on methane specific velocity and reaction temperature

Fig 9. Formation rate and selectivity of product as a function of Mo-loadings of Mo/HZSM-5 catalyst for methane aromatization

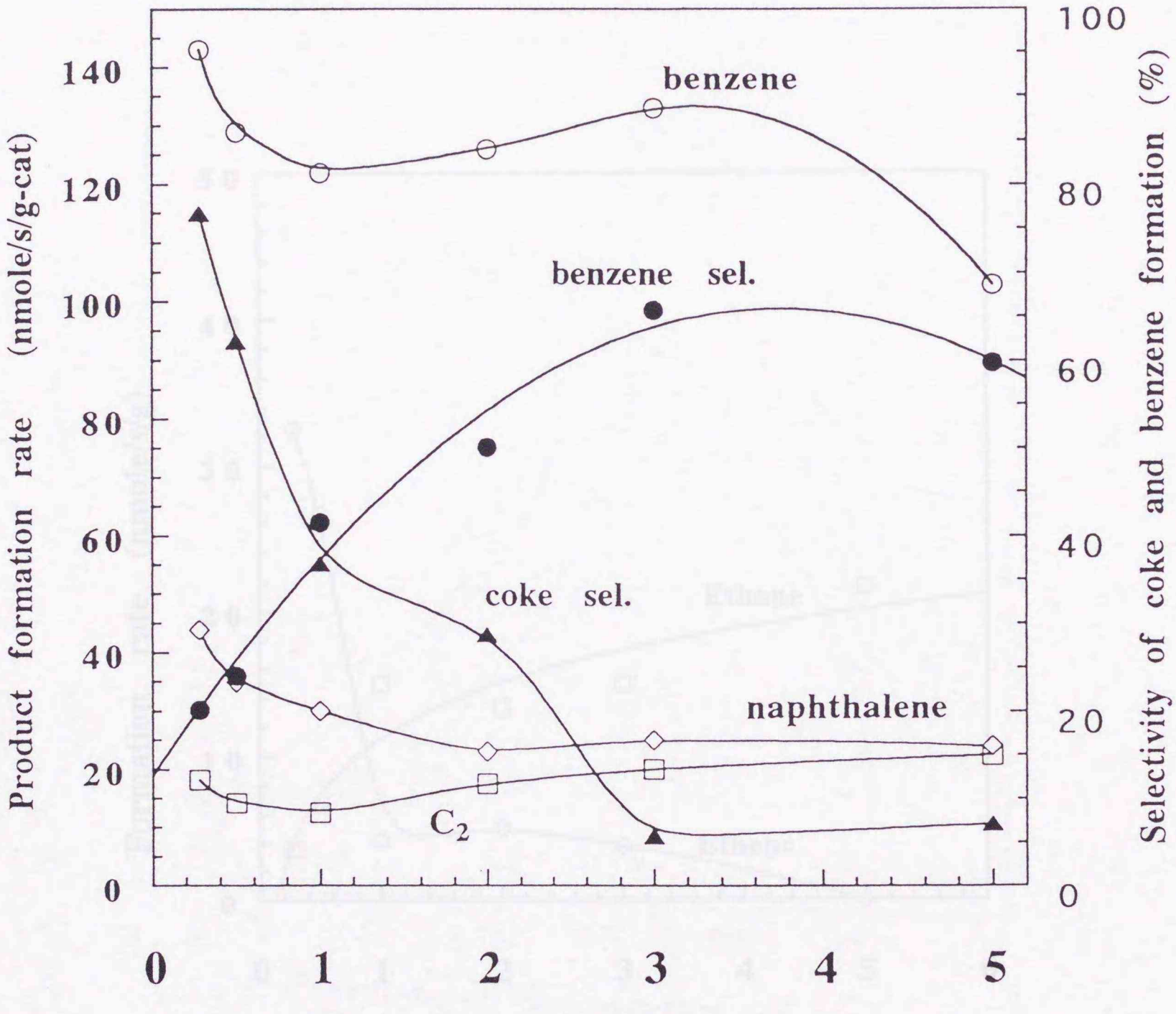
Fig 10. Effect of CO_2 addition in methane feed on the stability of benzene formation for methane aromatization on 15% Mo/HZSM-5

Fig 1. Benzene formation rate with time on stream for methane aromatization on 3% Mo/HZSM-5 at various methane pressure



Catalyst: 3% Mo/HZSM-5
SV = 1440 nmole/h/g-cat
T= 973 K

Fig 2. Formation rate and selectivity of product as a function of methane pressure for methane aromatization for methane aromatization on 3% Mo/HZSM-5



Catalyst: 3% Mo/HZSM-5
SV = 1440 ml/h/g-cat
T = 973 K

Fig 3. Formation rate of ethane and ethene as a function of methane pressure

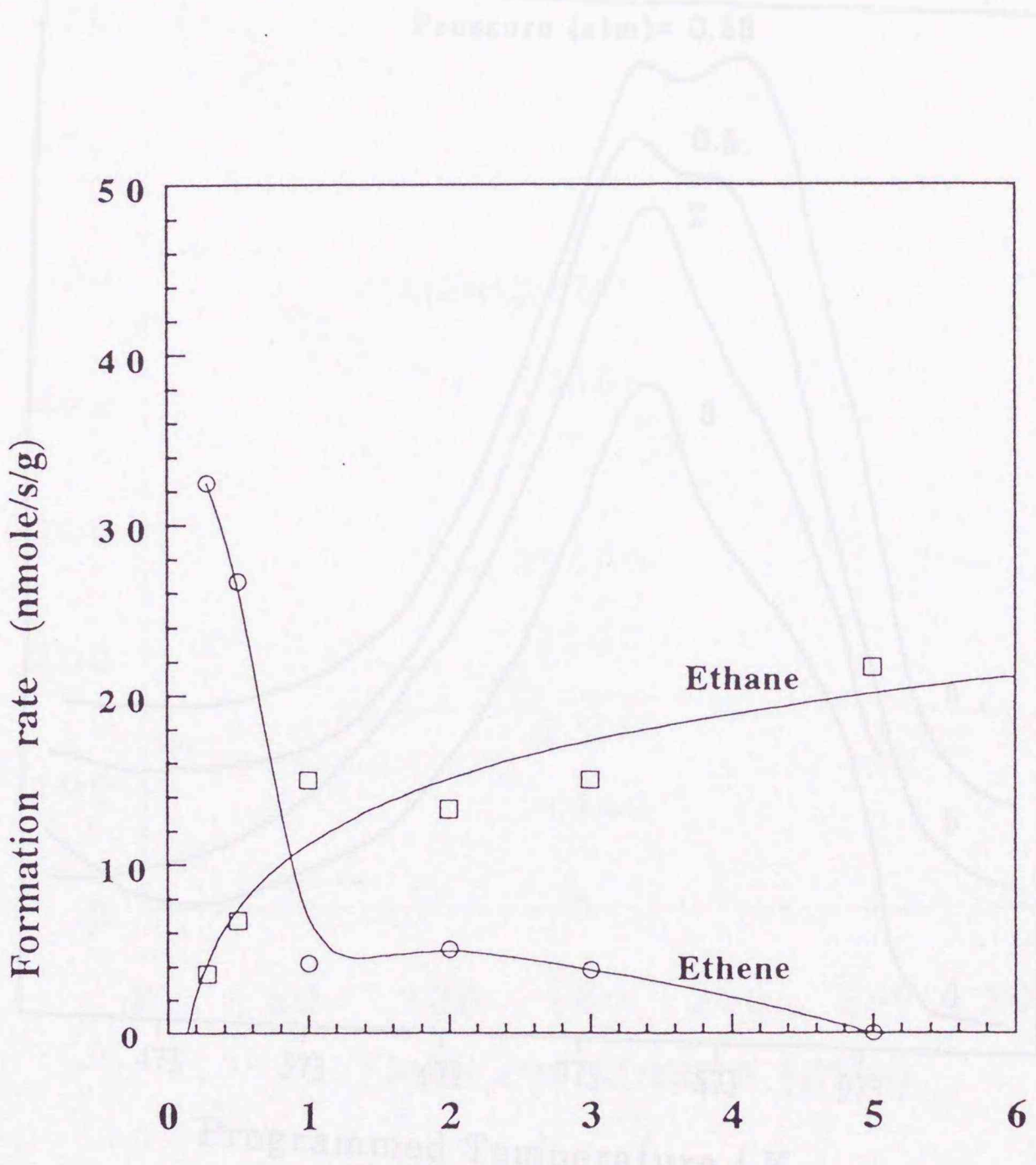


Fig 4. TPO profiles of Mo/HZSM-5 catalyst after methane aromatization at various methane pressure

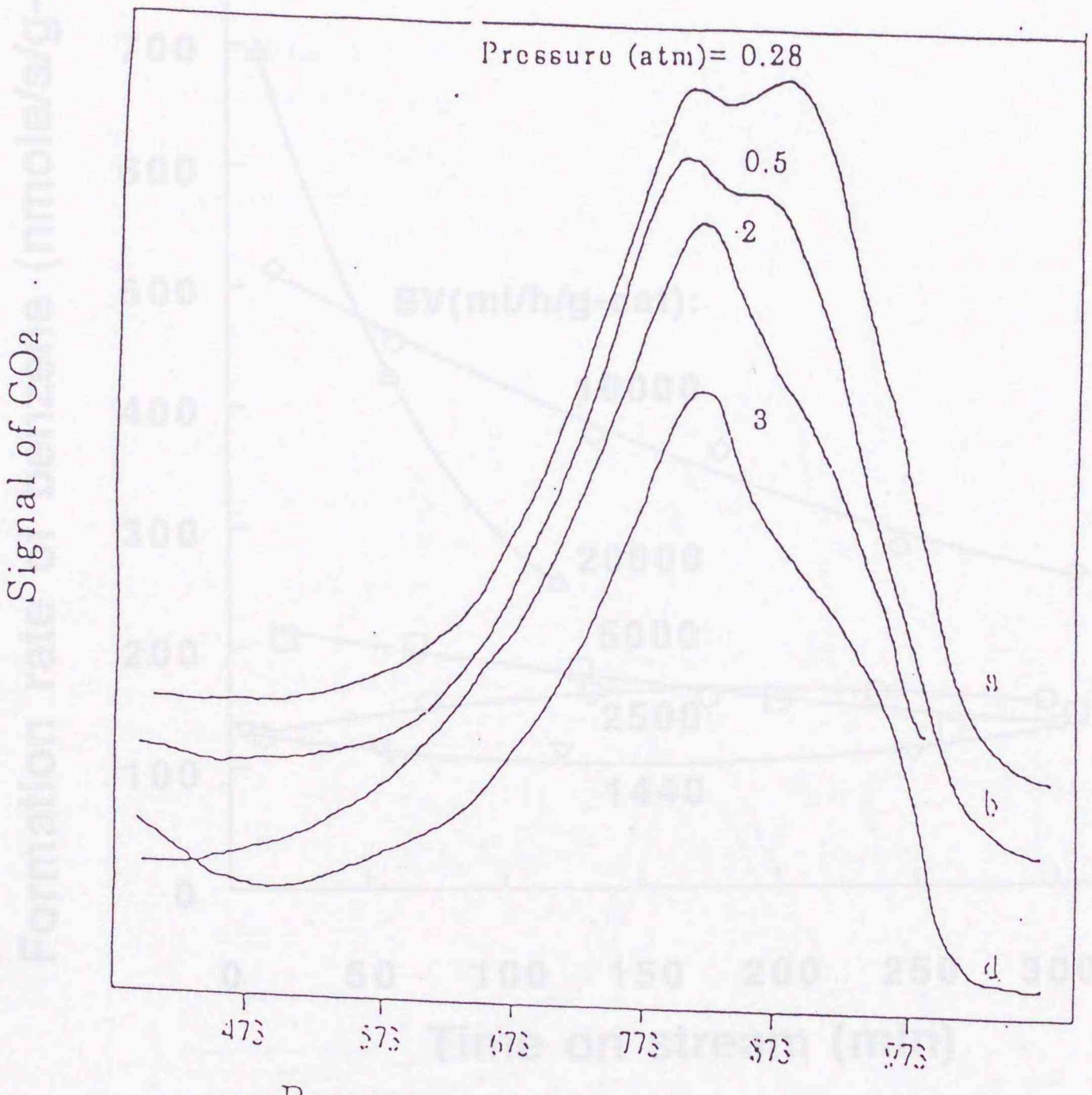
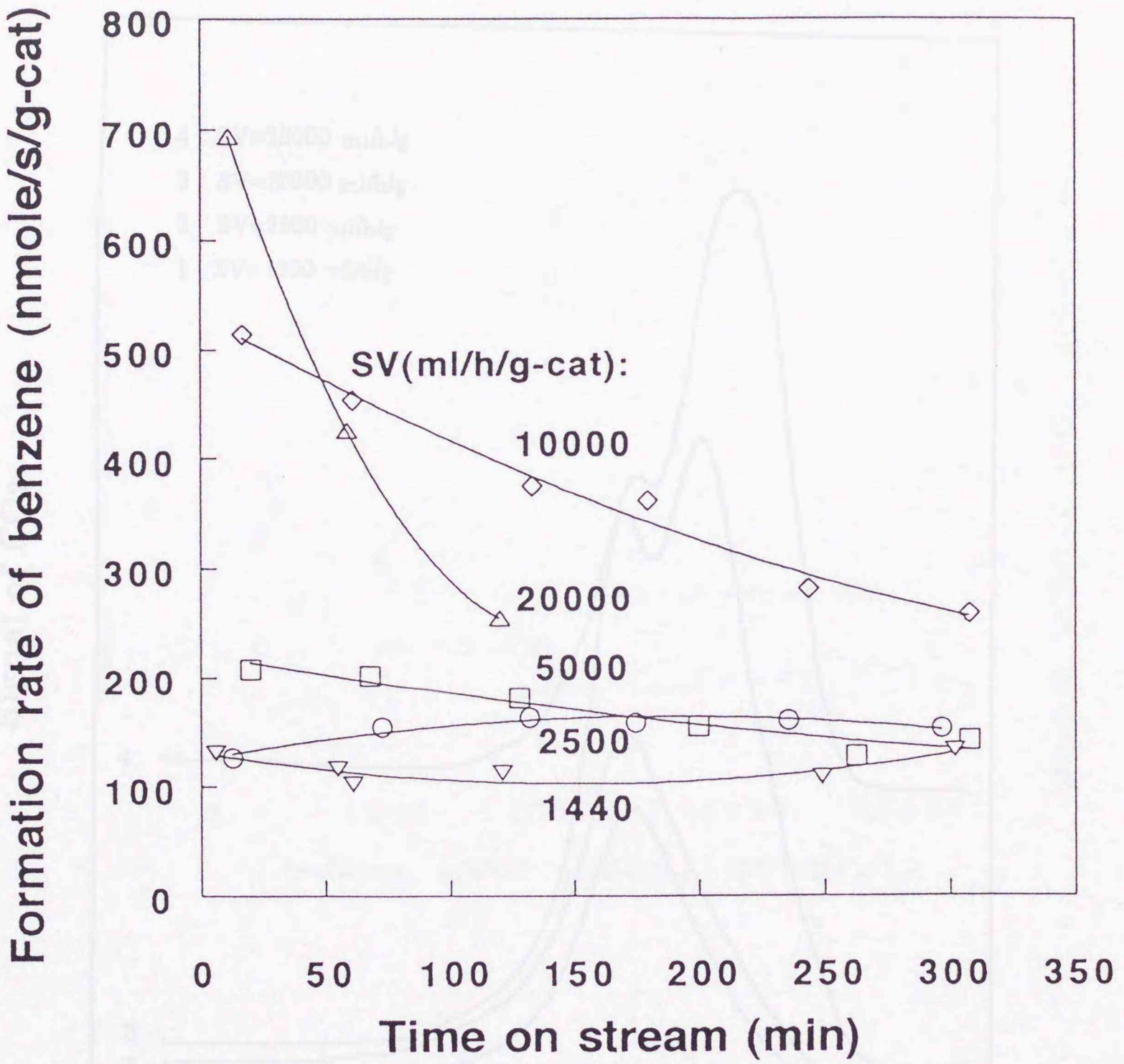


Fig 5. Benzene formation rate with time on stream for methane aromatization on 3% Mo/HZSM-5 at various methane specific velocity



Catalyst : 3% Mo/HZSM-5
Pressure : 3 atm
Temperature : 973 K

Fig 6. TPO profiles of Mo/HZSM-5 catalyst after methane aromatization at various methane specific velocity

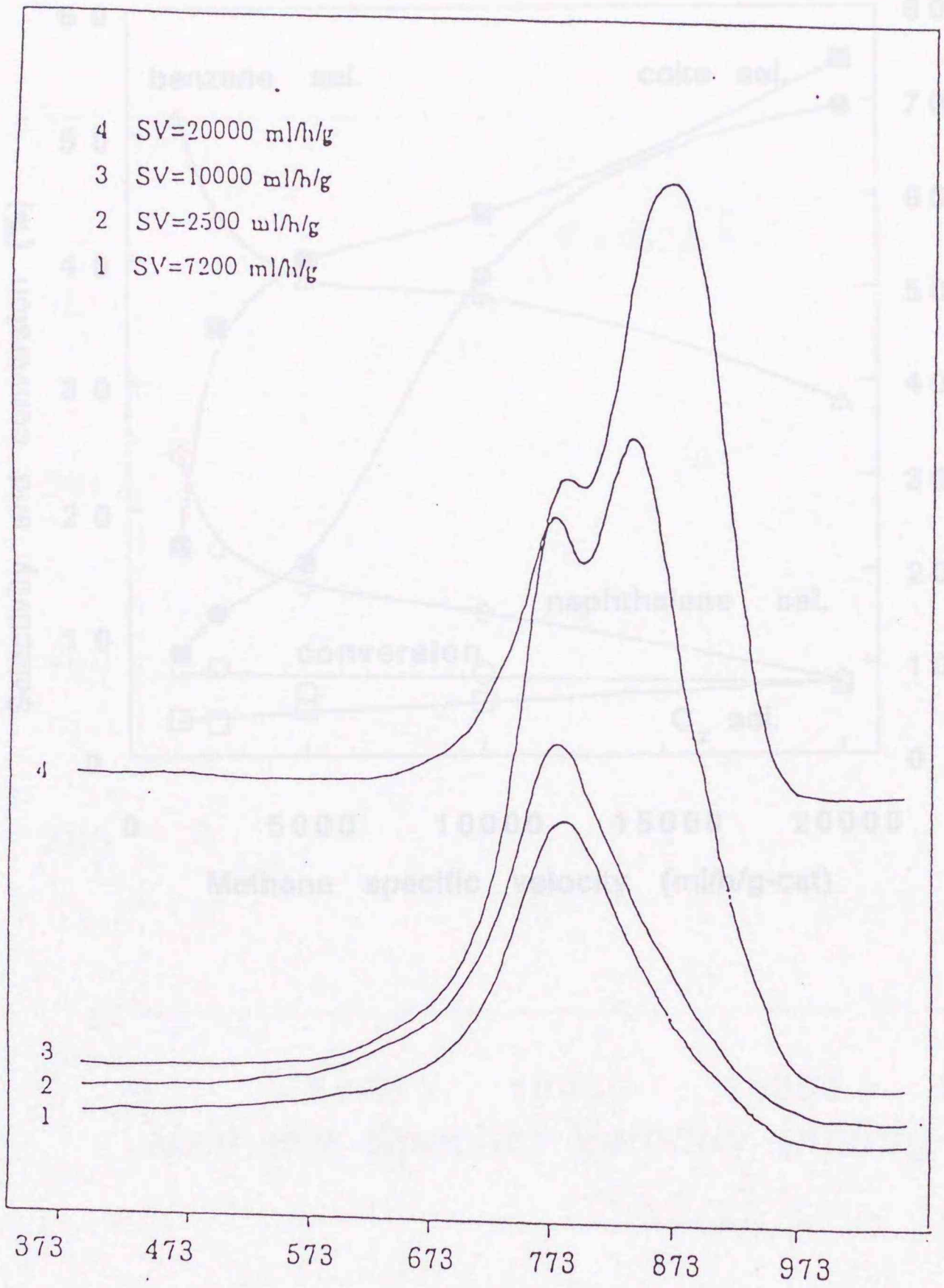


Fig 7. Dependence of benzene production on methane specific velocity on 3% Mo/HZSM-5 at 3 atm and 973 K

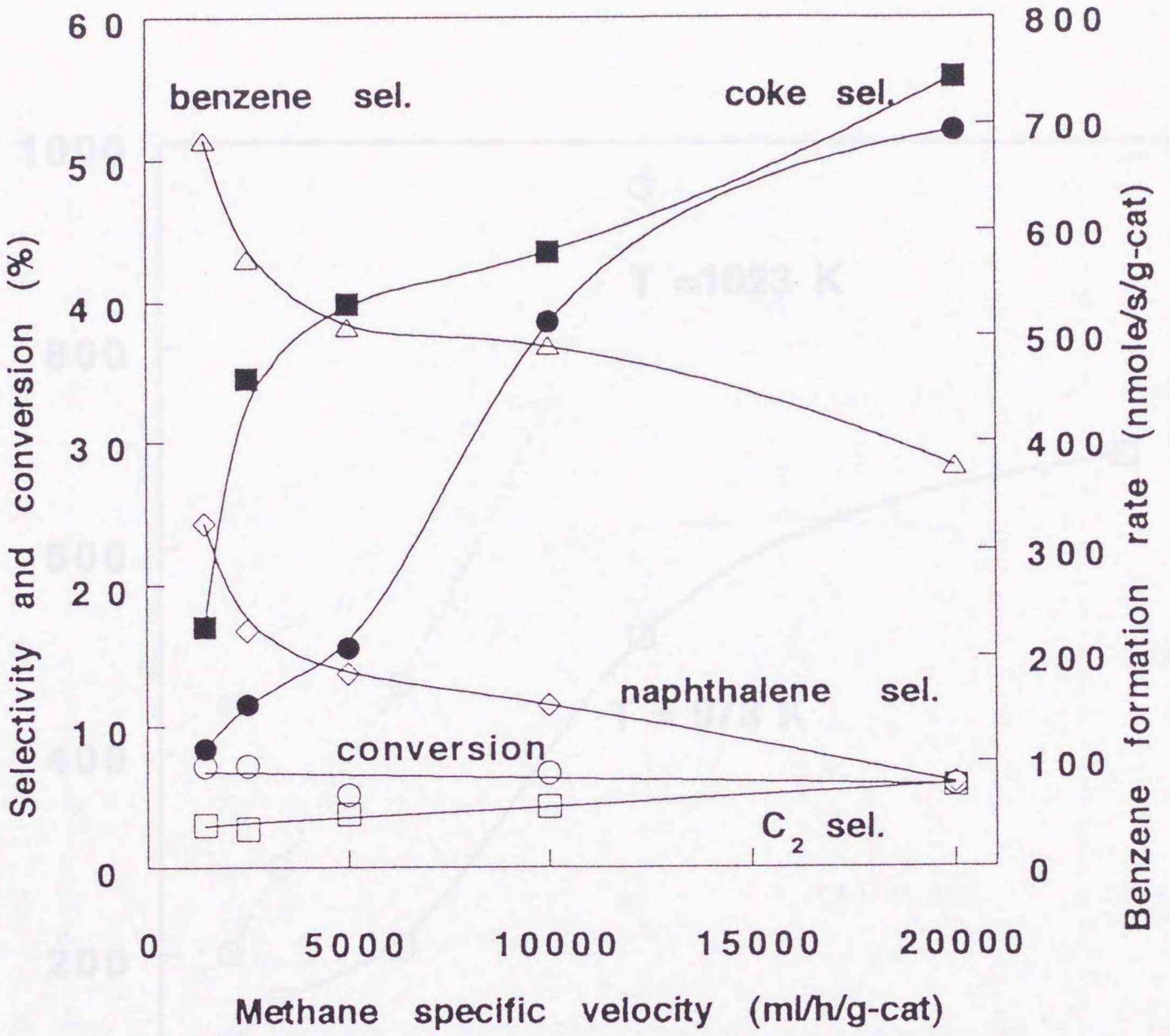
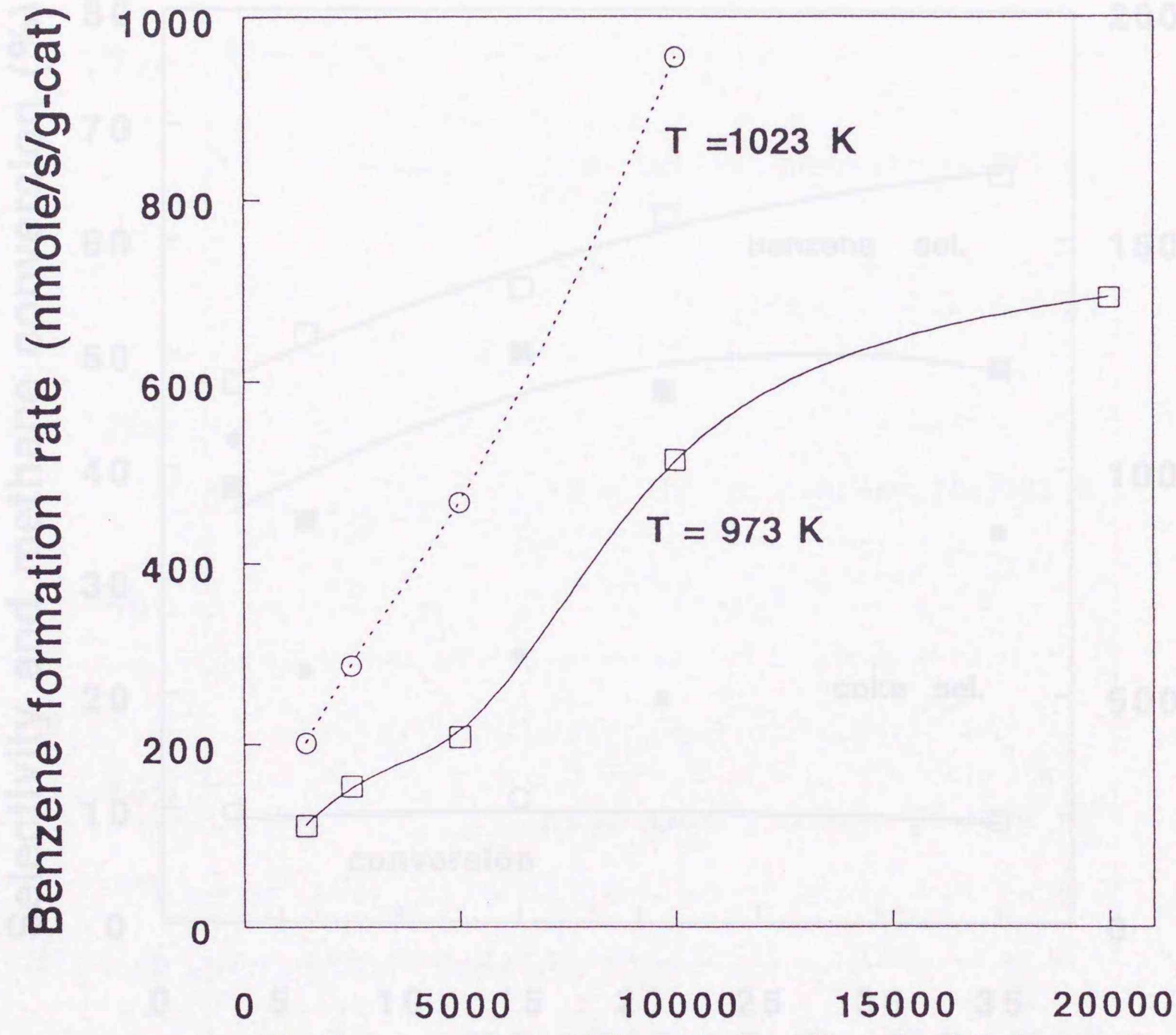
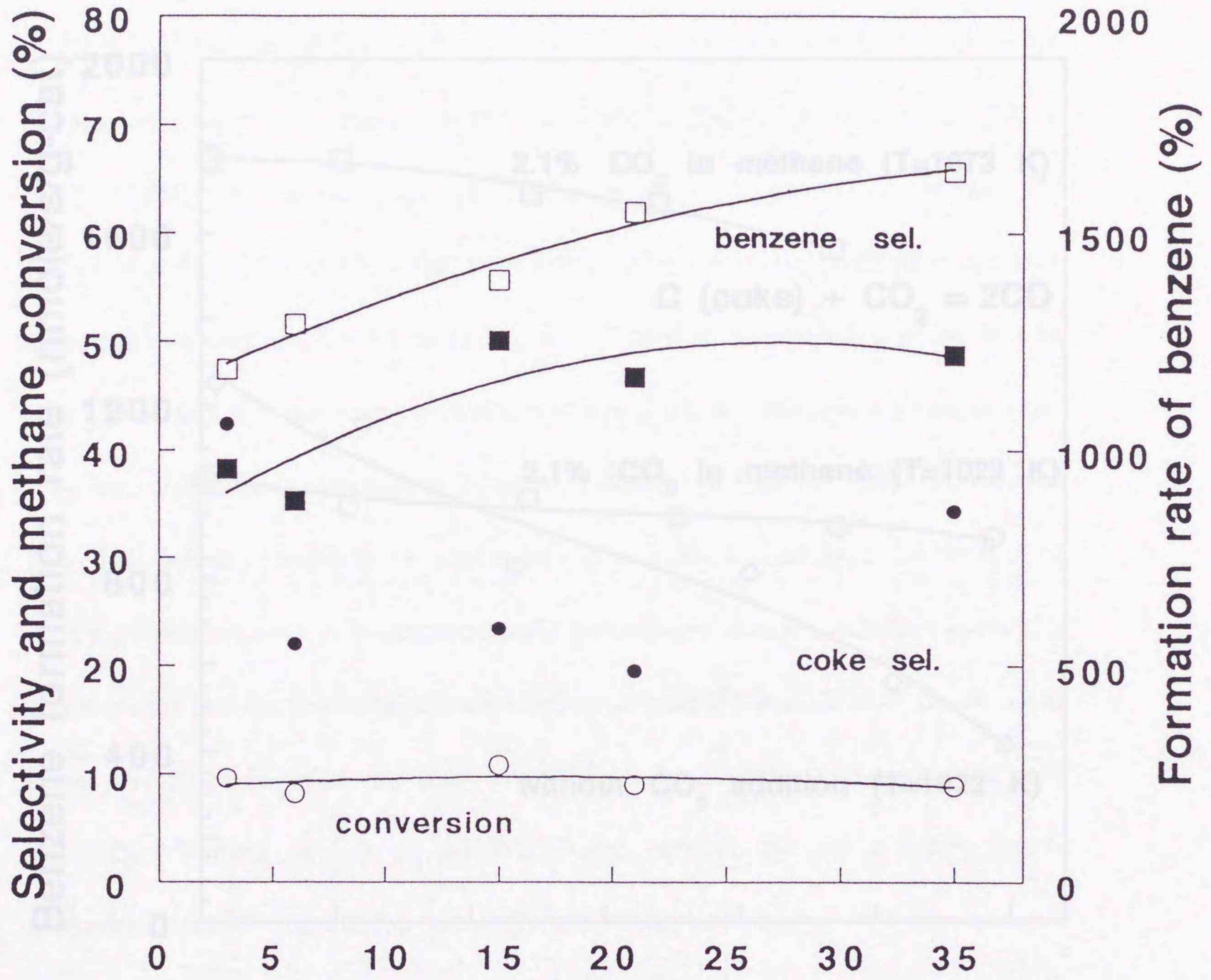


Fig 8. Dependence of benzene formation rate on methane specific velocity and reaction temperature



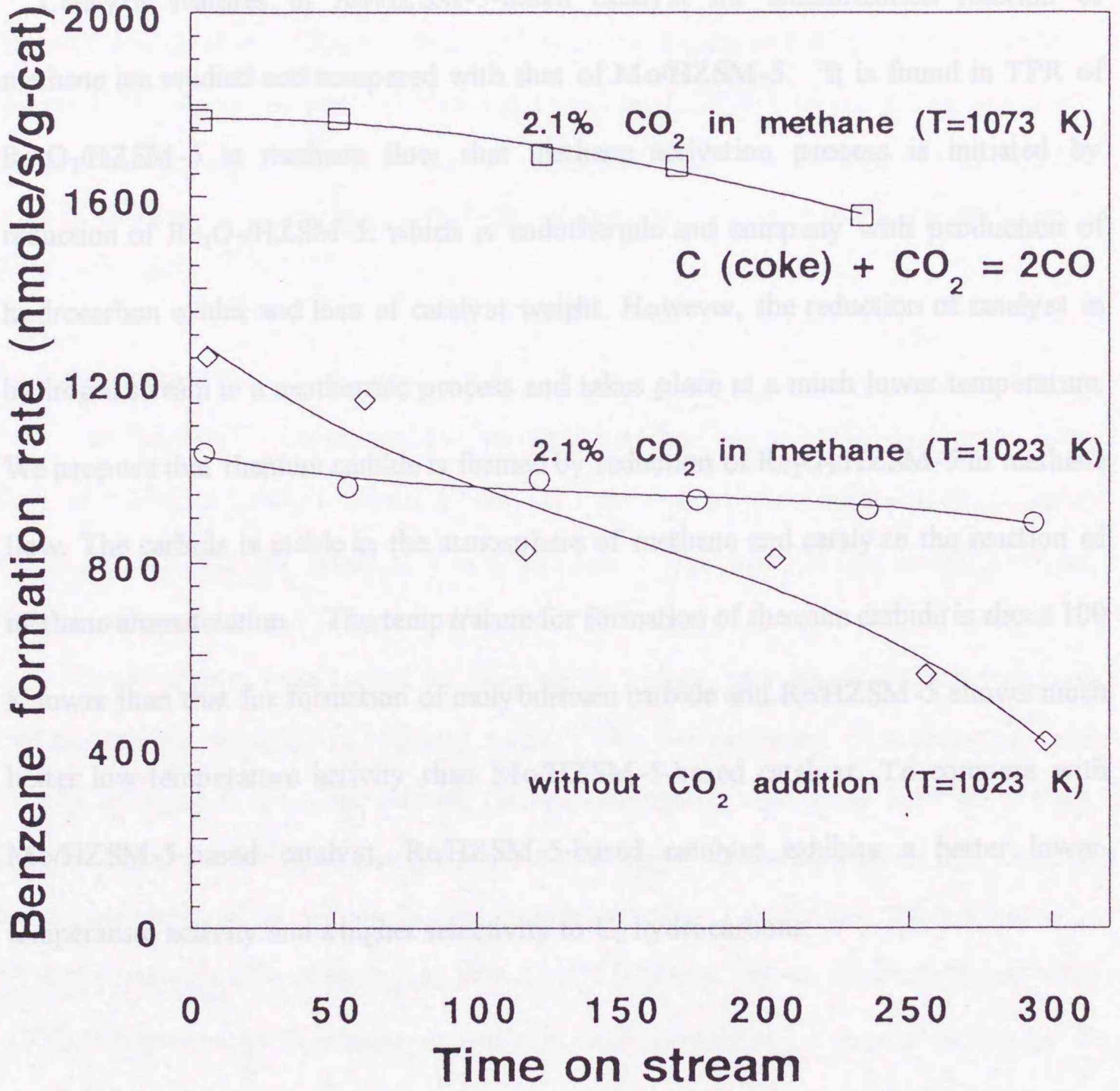
Catalyst: 3% Mo/HZSM-5
Pressure: 3 atm

Fig 9. Formation rate and selectivity of benzene as a function of Mo-loadings of Mo/HZSM-5 catalyst for methane aromatization



Catalyst: Mo/HZSM-5
Temperature: 1023 K
Pressure: 3 atm
SV=10000ml/h/g-cat

Fig 10. Effect of CO_2 addition in methane feed on the stability of benzene formation for methane aromatization on 15% Mo/HZSM-5



Catalyst: 15% Mo/HZSM-5
SV = 10000 ml/h/g-cat
P = 3 atm

Chapter 8
Catalytic performance of Re/HZSM-5 for dehydro-dimerization and dehydro-aromatization reactions of methane

Abstract

Catalytic features of Re/HZSM-5-based catalyst for aromatization reaction of methane are studied and compared with that of Mo/HZSM-5. It is found in TPR of Re_2O_7/HZSM-5 in methane flow that methane activation process is initiated by reduction of Re_2O_7/HZSM-5, which is endothermic and company with production of hydrocarbon oxides and loss of catalyst weight. However, the reduction of catalyst in hydrogen stream is a exothermic process and takes place at a much lower temperature. We propose that rhenium carbide is formed by reduction of Re_2O_7/HZSM-5 in methane flow. The carbide is stable in the atmosphere of methane and catalyze the reaction of methane aromatization. The temperature for formation of rhenium carbide is about 100 K lower than that for formation of molybdenum carbide and Re/HZSM-5 shows much better low-temperature activity than Mo/HZSM-5-based catalyst. To compare with Mo/HZSM-5-based catalyst, Re/HZSM-5-based catalyst exhibits a better lower-temperature activity and a higher selectivity to C_2 hydrocarbons.

1 Introduction

Direct transformation of methane to more valuable hydrocarbons such as aromatics or C_2 hydrocarbons is fascinating and highly desirable for more reasonable utilizing abundant natural gas resources. Recently, much attractive results for dehydrogenation and aromatization of methane over Mo/HZSM-5 catalyst have been reported and it has attracted a wide attention and interest (1-20) over the past several years. It has been suggested that molybdenum carbides supported on HZSM-5 is the active phase for methane aromatization. At the present research, the catalytic performance of Re/HZSM-5-based catalysts for dehydrogenation and aromatization of methane is presented as a alternative choice of catalyst.

2 Experimental

Re/HZSM-5 was prepared by impregnating NH_4ZSM-5 (SiO_2/AI_2O_3=40, Toso Co.) with $NH_4ReO_4 4H_2O$ (Kanto Chem. Co.) aqueous solution, followed by drying at 383 K for 4 h and calcination at 773 K for 4 h. The sample was finally pressed, crushed and sorted into 20-40 mesh.

Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow straight type quartz reactor. The raw materials of methane is over 99.99% pure. All the flow rate of gas was controlled with mass flow controllers (ASAHI Keiki Co. LTD). The products were withdraw periodically from the outlet of reactor and analyzed by two on-line gas chromatography of Shimadazu GC-9A and GC-8A equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) respectively. Hydrocarbon products were separated by a 4mm ×1m Porapak P column and Ar , CH_4, CO, CO_2, H_2 were analyzed by a 4mm×1m active carbon column. 10.7% Ar in methane was employed as internal standard. Formation rate of products, methane conversion and product selectivity were calculated by an internal standard analyzing method described elsewhere [19]. Below,the method is presented briefly.

Even if the total flow rate changed at outlet from inlet of reactor (F_{Total}^{intlet} ,F_{Total}^{outlet}).

Flow rate of non-reactive internal standard gas (F_{st}) doses not change.

$$F_{st} = F_{Total}^{outlet} \times X_{st}^{outlet} = F_{Total}^{inlet} \times X_{st}^{inlet}$$

Here, X_{st} refer to concentration of the internal standard gas.

Formation rate of i product (F_i) can be calculated as,

$$F_i = F_{Total}^{outlet} \times X_i^{outlet} = F_{st} \times X_i^{outlet} / X_{st}^{outlet}$$

By the same way, methane conversion ($C_{methane}$) can be calculated as,

$$C_{methane} = (F_{methane}^{inlet} - F_{methane}^{outlet}) / F_{methane}^{inlet} = 1 - F_{methane}^{outlet} / F_{methane}^{inlet}$$

$$= 1 - F_{Ar} \times X_{methane}^{outlet} / X_{Ar}^{outlet} \times F_{methane}^{inlet}$$

The gaseous products given off from the catalyst and heat effect, weight change of the catalyst in the carburization process were monitored with a DTA-TG-MS combined instrument (Mas Science DTA-2020S + Thermolab). The experiment was performed with about 40 mg coked catalyst paced in a alumina container under flowing 150 ml/min He and 15 ml/min methane with ramping the temperature of 5K/min.

TPSR (Temperature Programmed Surface Reaction) experiments was performed with about 200mg catalyst placed in a U-shape quartz reactor. Catalyst zone was heated in a He stream to 873 K and held at 873 K for 30 min then cooled to room temperature. At room temperature the stream was switched to methane feed. Temperature-programmed methane reaction was started from room temperature to 973 K at 10 K/min and then held at 973 K for 30 min. The products such as H_2 (m/e=2), CO(m/e=28), CO_2(m/e=44), C_2H_4 (m/e=26), C_2H_6 (m/e=30), C_6H_6 (m/e=78) was monitored with TE-150 multiple channel mass spectrometer and the spectra was recorded at the same time. Reaction pressure is 34 kPa.

3 Results and discussion

3.1 Reduction performance of Re/HZSM-5 in methane and in hydrogen flow

Catalytic features of Re_2O_7/HZSM-5-based catalyst for activating methane were investigated by TG-DTA-MS measurement. When Re_2O_7/HZSM-5-based catalyst was

heated in methane flow by programmed temperature from 673 to 973 K, reduction process of Re_2O_7/HZSM-5 by methane first take place at about 873 K, and then benzene, naphthalene and ethene were produced on the reduced catalyst shortly as shown in figure 1. In the reduction process of Re_2O_7/HZSM-5 by methane, CO, H_2O, H_2 and a little C_2H_6 were given off, and a strong endothermic effect companying the reduction were identified by DTA as shown in fig 2. This is quite different from the reduction of Re_2O_7/HZSM-5 by H_2. It is shown for the reduction process of Re_2O_7/HZSM-5 by H_2 in fig 3 that the reduction starts at about 573 K and it is a exothermic process. To explain the different reduction performance of Re_2O_7 in methane and in hydrogen, we propose here that a new phase of rhenium carbide is formed by reduction of of Re_2O_7 in methane as shown in scheme 1. The carbide is stable in the atmosphere of methane and is active to catalyze the aromatization reaction of methane. The temperature for formation of rhenium carbide is about 100 K lower than that for molybdenum carbide formation at the same conditions, therefore, low-temperature activity of Re/HZSM-5 is better than that of Mo/HZSM-5-based catalyst.

3.2. Catalytic performance of Re/HZSM-5 for dehydro-dimerization and dehydro-aromatization of methane

The activity and the selectivity of Re/HZSM-5-based catalyst with different Re-loading for dehydro-dimerization and dehydro-aromatization of methane at 873 K is listed in table 1 and compared with that of Mo/HZSM-5-based catalyst. 10% Re/HZSM-5 shows high benzene selectivity and low coke selectivity. In addition, to compare with Mo/HZSM-5-based catalyst, Re/HZSM-5-based catalyst exhibits relatively much higher activity and selectivity for dehydro-dimerization of methane to form C_2 hydrocarbons and lower activity and selectivity for naphthalene production. The bimetal catalyst of Mo-Re/HZSM-5 shows a higher C_2 selectivity than Mo/HZSM-5 and a higher naphthalene selectivity than Re/HZSM-5.

Dependence of activity and selectivity of Re/HZSM-5 catalyst on reaction

temperature and specific velocity is given in table 2 and fig 4, respectively. Methane conversion and benzene selectivity increase sharply with increasing temperature from 873 to 1023 K as shown in fig 4. Naphthalene selectivity get the maximum value at 973 K and then decrease with further increase of temperature. Low reaction temperature lead to a high C_2 selectivity.

Benzene formation rate can be greatly enhanced by increasing specific velocity of methane. However, catalyst deactivates quickly at very high specific velocity of methane. So benzene formation rate can not be enhanced further by increasing SV from 5000 to 10000 ml/h/g-cat as show in fig 4.

3.3 Effect of H_2 pretreatment on catalytic performance of Re/HZSM-5

Fig 5 shows the effect of pretreating catalyst by hydrogen and methane on the activity of Re/HZSM-5 for benzene formation. It is shown in fig 5 that pretreatment of Re/HZSM-5 by hydrogen and methane lead to decrease of the starting temperature for benzene formation. The pretreated Re/HZSM-5 by hydrogen at a lower temperature of 573 or 623 K shows the best low-temperature activity for benzene formation and the starting temperature for producing benzene is about 773 K. The time on stream results in fig 6 also indicate that the stability and activity of Re/HZSM-5 catalyst for benzene formation is enhanced by H_2 pretreatment. This is quite different from the case of Mo/HZSM-5 type catalyst.

The products for the temperature-programmed reaction of methane on Mo/HZSM-5 are identified by a mass spectrometer and shown as in fig 7. The initial temperature for benzene formation is as high as about 950K. Pretreatment by hydrogen reduction and carburization also lead to decrease of the initial temperature for benzene formation as shown in fig 8.

3.4 Copling effect of Co in Re-Co/HZSM-5 catalyst

The activity of Re/HZSM-5 and Re-Co/HZSM-5 for benzene formation with time

on stream was compared in figs 9-11. It is indicated in figs9-11 that the activity of Re/HZSM-5 is evidently enhanced by addition of 0.5% Co to 10%Re/HZSM-5 at various reaction conditions. However, the Re-Co/HZSM-5 catalyst is not very stable with time on stream in the reaction conditions.

4 Conclusion

Re_2O_7/HZSM-5 is endothermically converted to its reduced state heat and it accompany with production of COx and loss of catalyst weight in methane flow before production of hydrocarbon products. The temperature for formation of rhenium active phase is about 100 K lower than that for molybdenum type catalyst. As a result, Re/HZSM-5-based catalyst exhibits a better low-temperature activity and a higher selectivity to C_2 hydrocarbons. In addition, activity and stability of Re/HZSM-5-based catalyst is also dependent on pretreatment conditions or addition of modifier such as Co to it. The pretreatment of Re/HZSM-5 by hydrogent lead to a better catalytic activity and stability. Addition of Co to Re/HZSM-5 is effective to enhance the activity.

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Cauptions of figures and tables:

Fig 1. TPR spectra of Re/HZSM-5 in methane flow

Fig 2. DTA spectra of Re/HZSM-5-based catalysts in methane flow

Fig 3. TG-DTA-MS spectra of Re/HZSM-5 in hydrogen flow

Table 1. Activity and selectivity of Re/HZSM-5 catalysts for dehydro-dimerization and dehydro-aromatization

Table 2. Dependence of activity and selectivity on reaction temperature for dehydro-dimerization and dehydro-aromatization

Fig 4. Dependence of benzene formation rate on methane specific velocity on 10% Re/HZSM-5

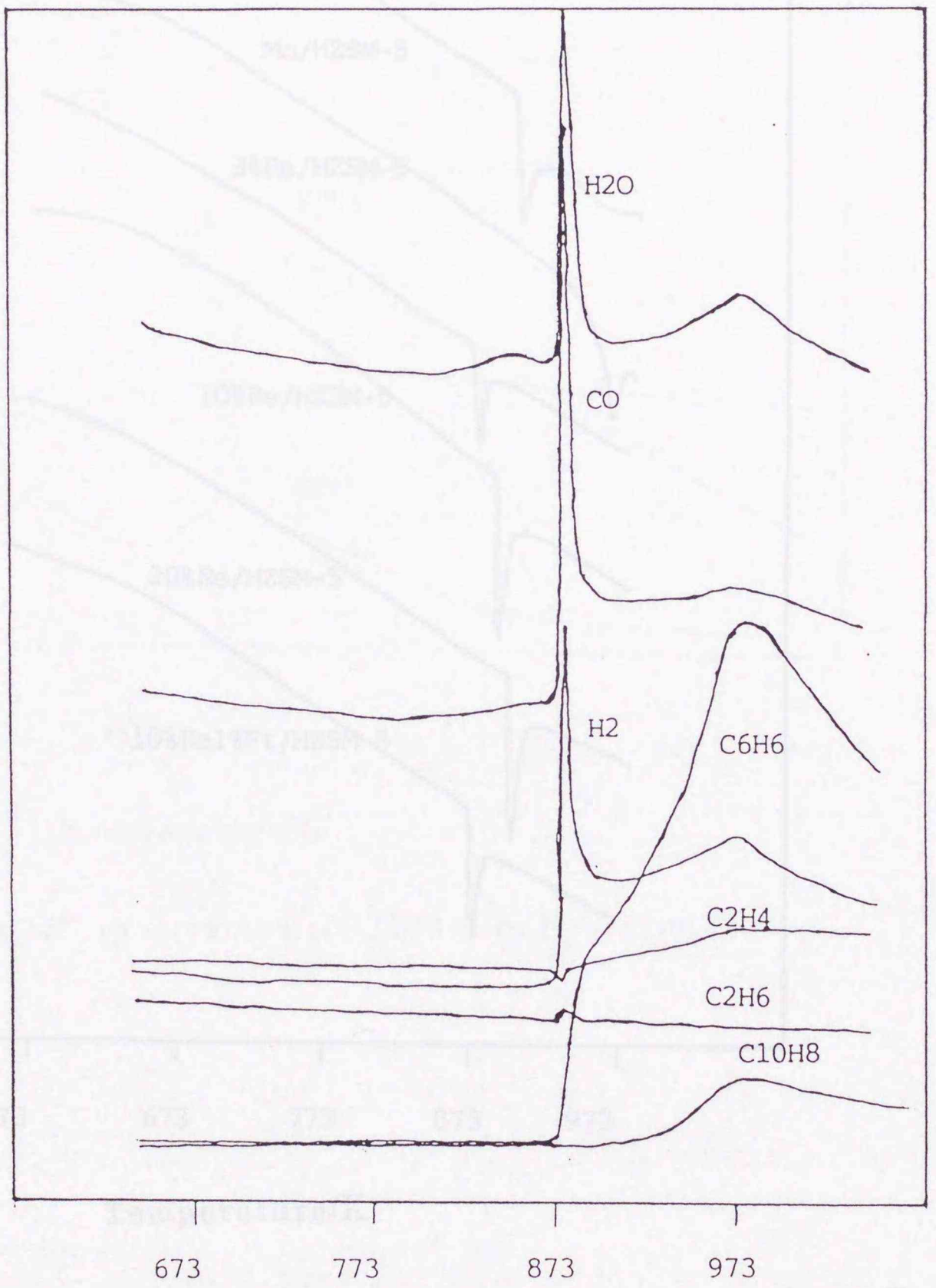
Fig 5. TPR spectra for benzene formation on pretreated 10% Re/HZSM-5 at different conditions

Fig 6. Effect of hydrogen pre-reduction on activity and stability of 10% Re/HZSM-5

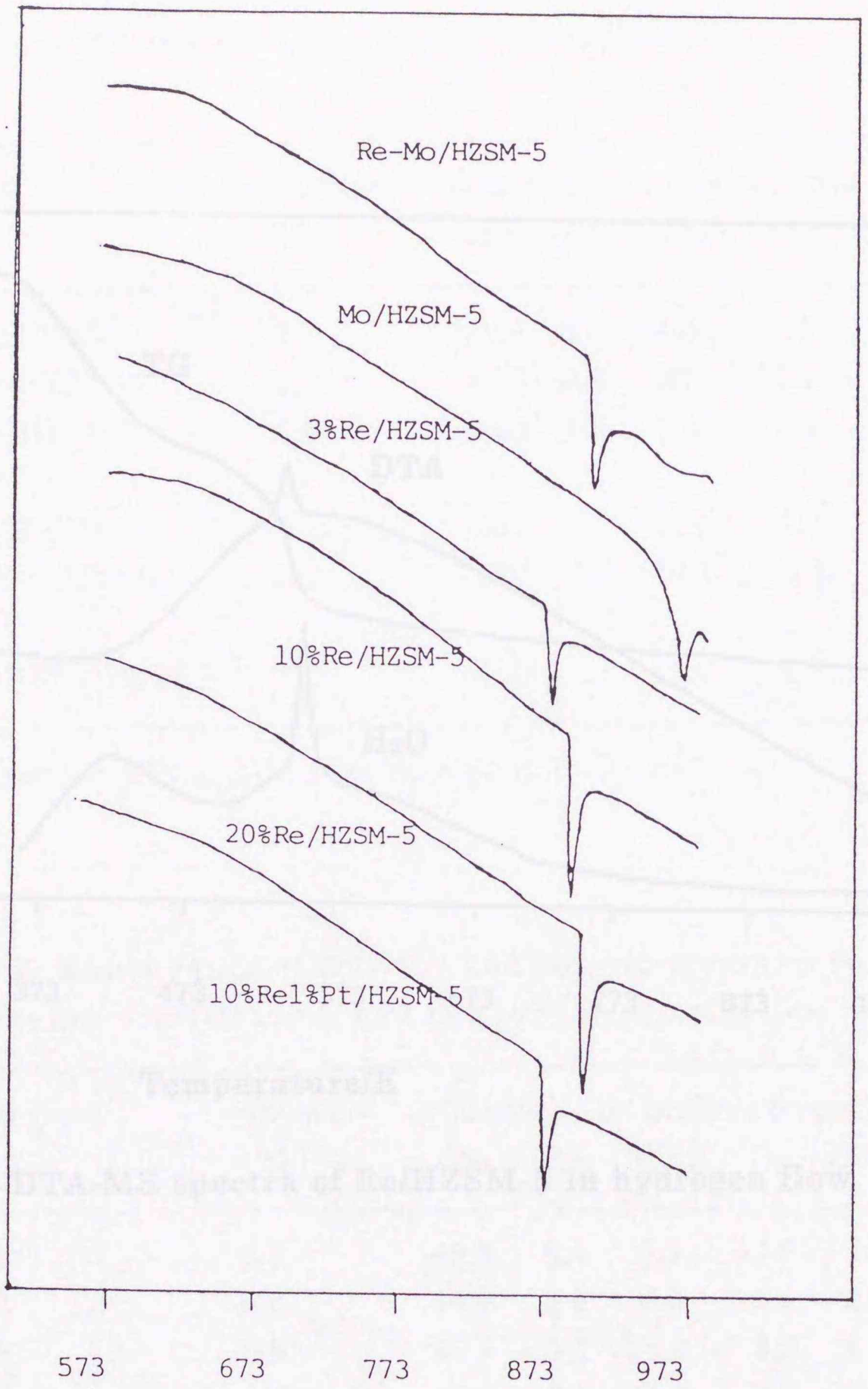
Fig 7. TPR spectra of Mo/HZSM-5 in methane flow

Fig 8. TPR spectra for benzene formation on pretreated 3% Mo/HZSM-5 at different conditions

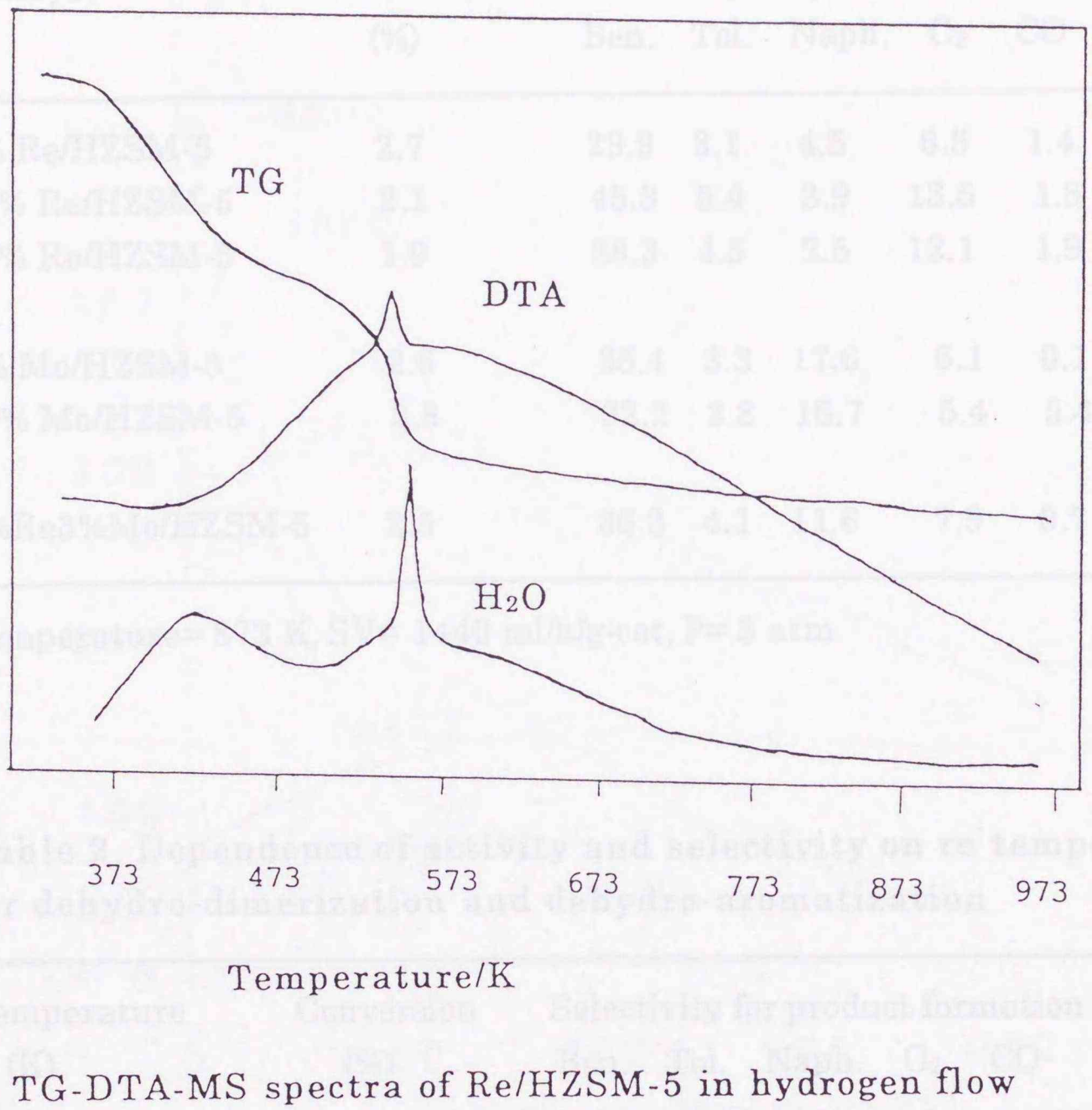
Fig 9. Effect of Co addition to Re/HZSM-5 on rate of benzene formation



TPR spectra of Re/HZSM-5 in methane flow



DTA spectra of Re/HZSM-5-based catalyst in methane flow



TG-DTA-MS spectra of Re/HZSM-5 in hydrogen flow

Table 1. Activity and selectivity of Re/HZSM-5 catalysts for dehydro-dimerization and dehydro-aromatization

Catalyst	Conversion (%)	Selectivity for product formation (%)					
		Ben.	Tol.	Naph.	C_2	CO	Coke
3% Re/HZSM-5	2.7	29.9	3.1	4.5	6.5	1.4	51
10% Re/HZSM-5	2.1	45.3	5.4	3.9	13.5	1.8	30
20% Re/HZSM-5	1.9	38.3	4.5	2.5	12.1	1.9	40
3% Mo/HZSM-5	2.6	35.4	3.3	17.6	6.1	0.1	37
15% Mo/HZSM-5	2.8	32.2	2.8	16.7	5.4	5.4	38
3%Re3%Mo/HZSM-5	2.5	36.3	4.1	11.6	7.9	0.7	39

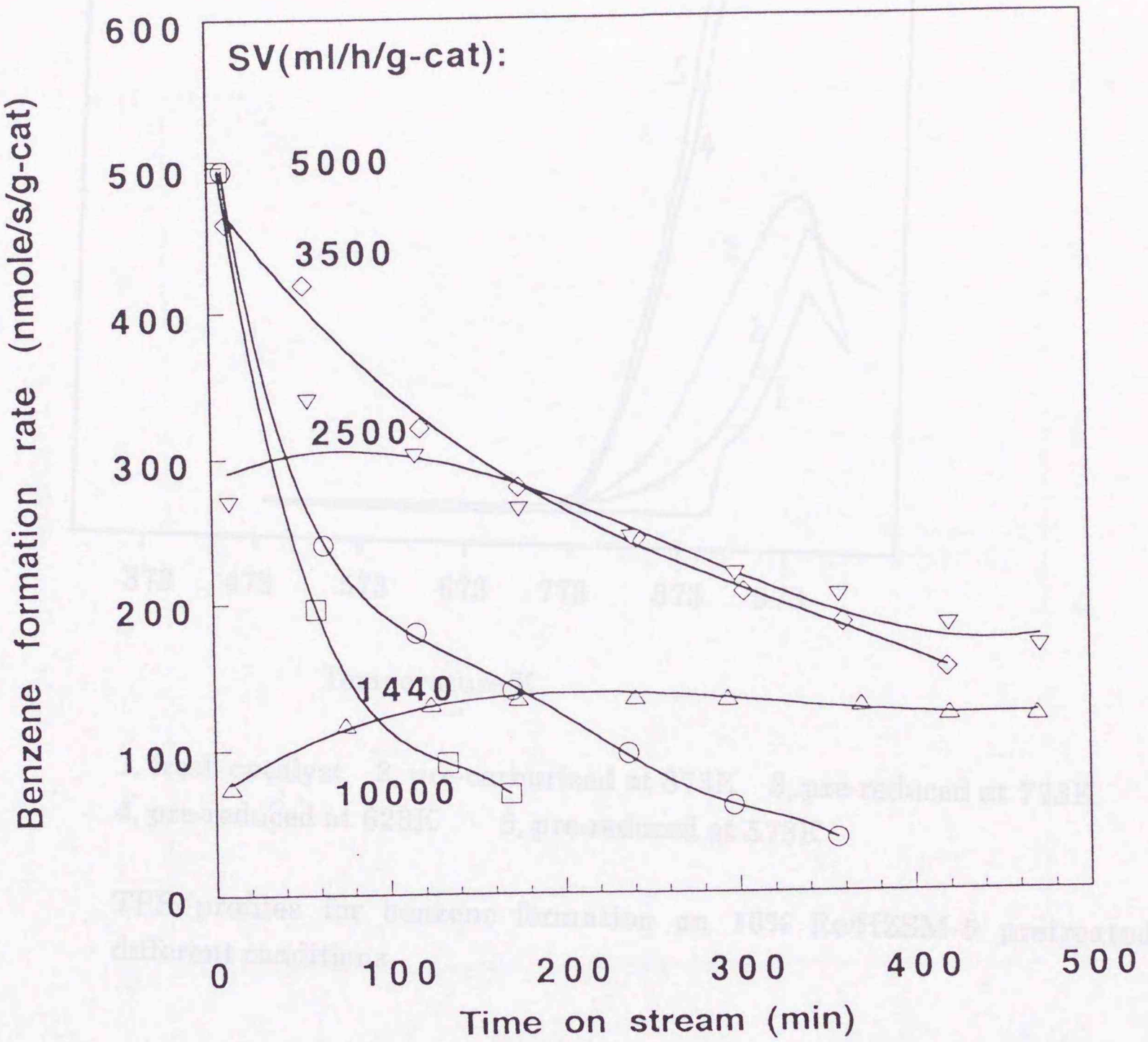
Temperature= 873 K, SV= 1440 ml/h/g-cat, P= 3 atm

Table 2. Dependence of activity and selectivity on re temperature for dehydro-dimerization and dehydro-aromatization

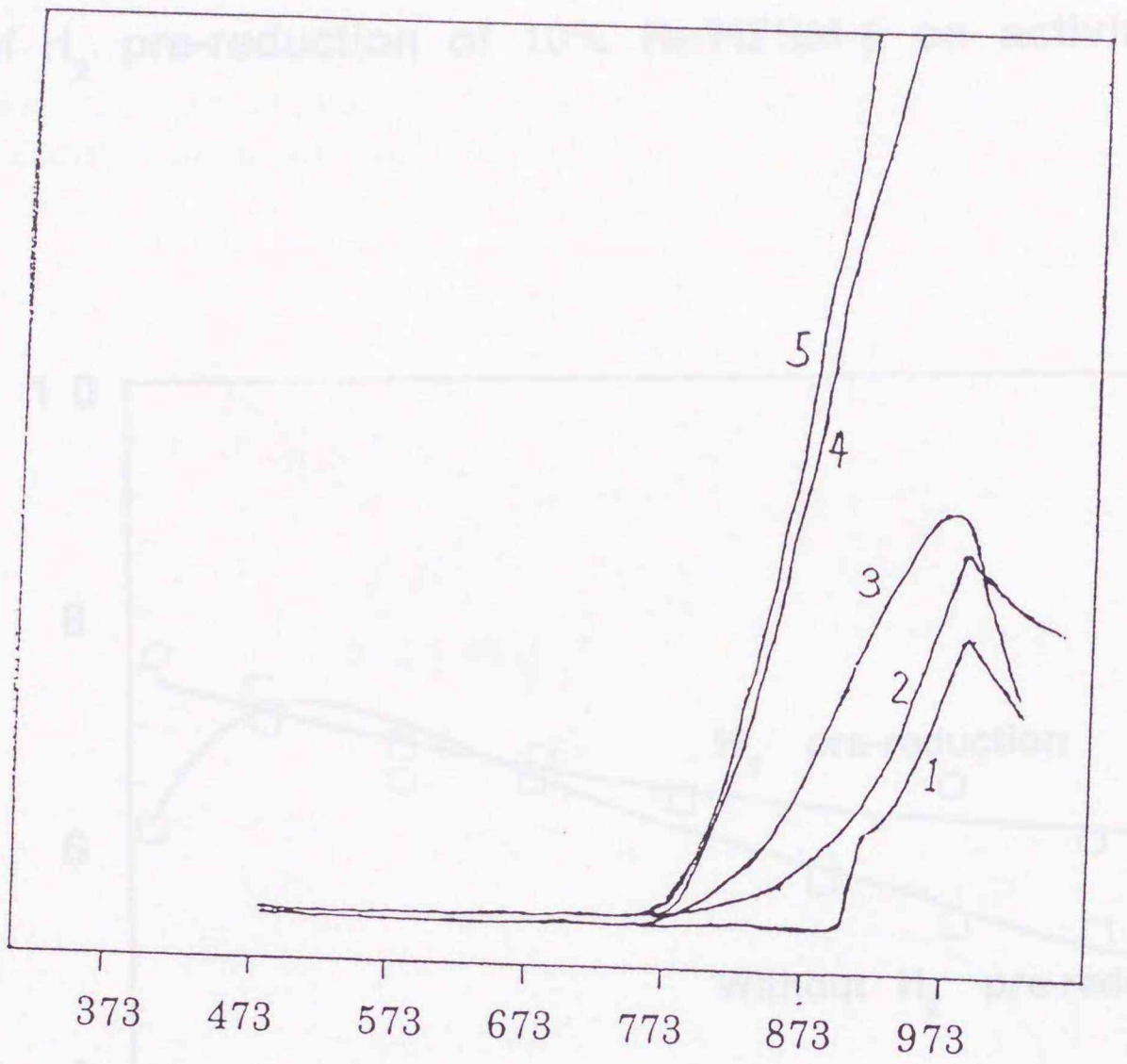
Temperature (K)	Conversion (%)	Selectivity for product formation (%)					
		Ben.	Tol.	Naph.	C_2	CO	Coke
873	2.1	45.3	5.4	3.9	13.5	1.8	30
923	4.2	43.0	3.8	8.3	5.9	0.9	42
973	6.8	47.6	3.3	11.4	3.9	0.2	33
1023	9.6	50.6	3.3	3.0	3.8	0	39

SV= 1440 ml/h/g-cat, P= 3 atm, catalyst: 10% Re/HZSM-5

Dependence of benzene formation rate on methane specific velocity (SV) on 10%Re/HZSM-5



T=1023K
P= 3atm

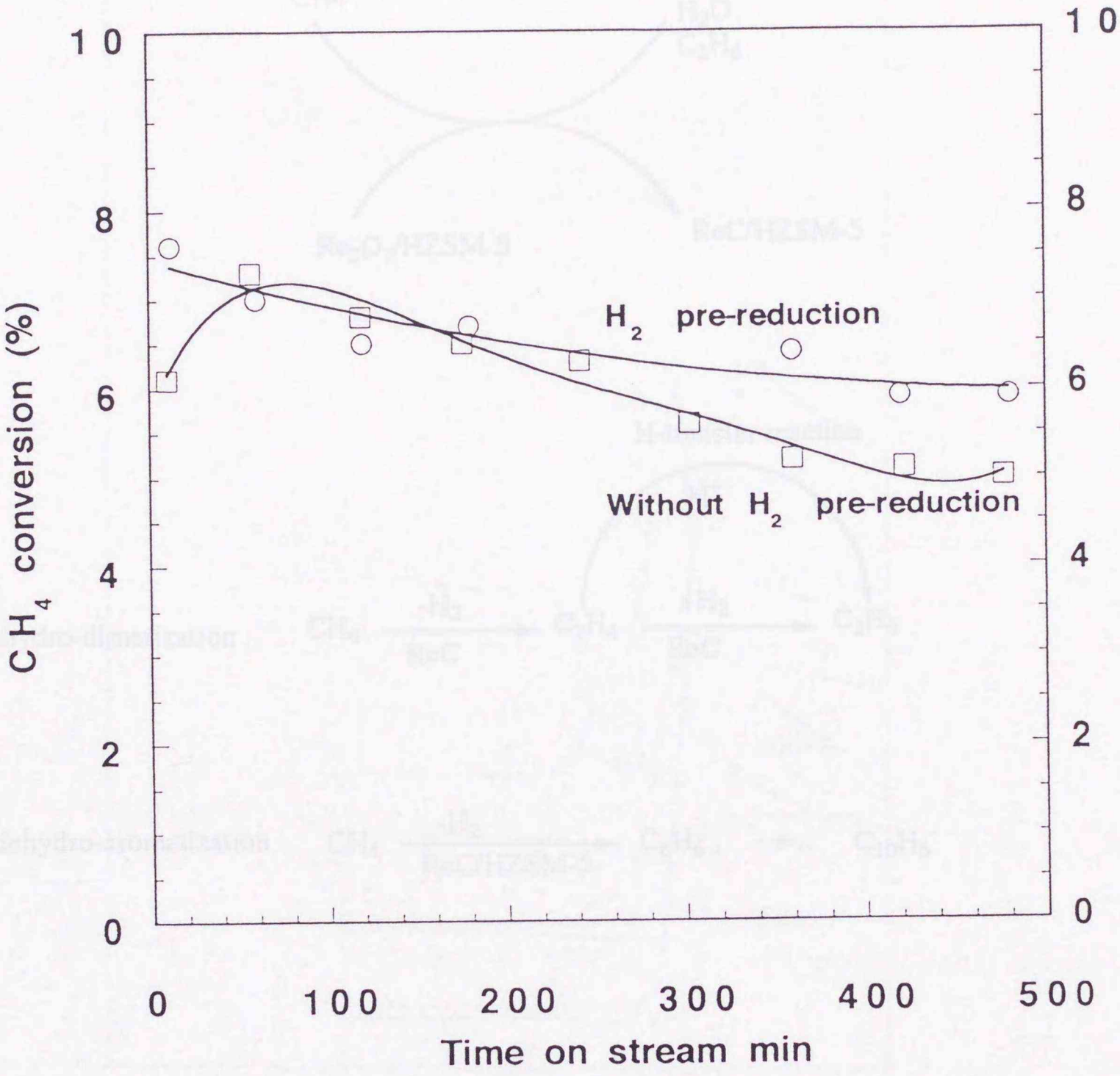


Temperature/K

1, fresh catalyst 2, pre-carburized at 873K 3, pre-reduced at 773K
4, pre-reduced at 623K 5, pre-reduced at 573K

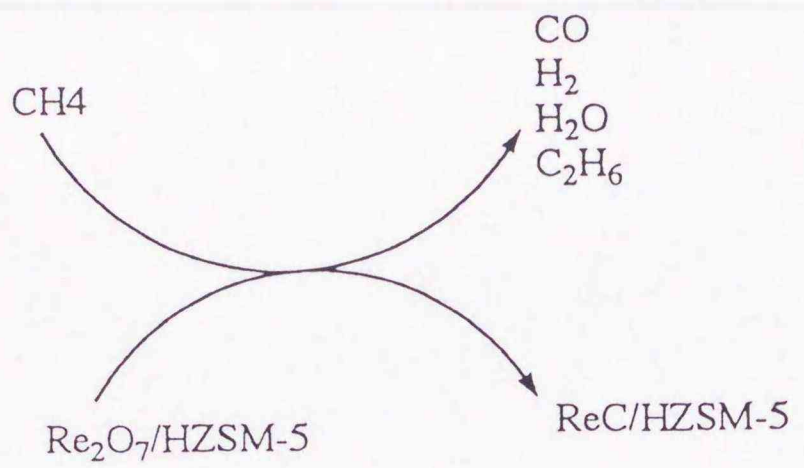
TPR profiles for benzene formation on 10% Re/HZSM-5 pretreated at different conditions

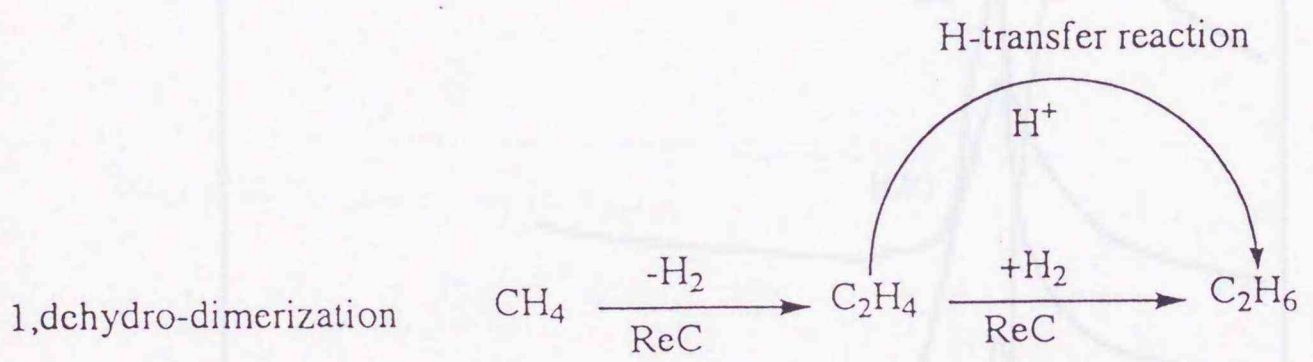
Effect of H_2 pre-reduction of 10% Re/HZSM-5 on activity and stability

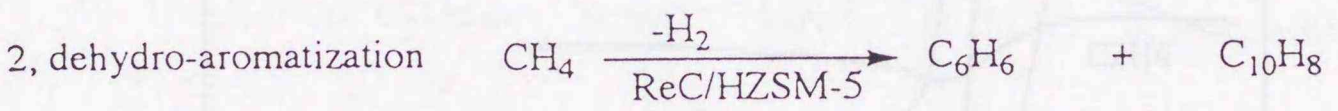


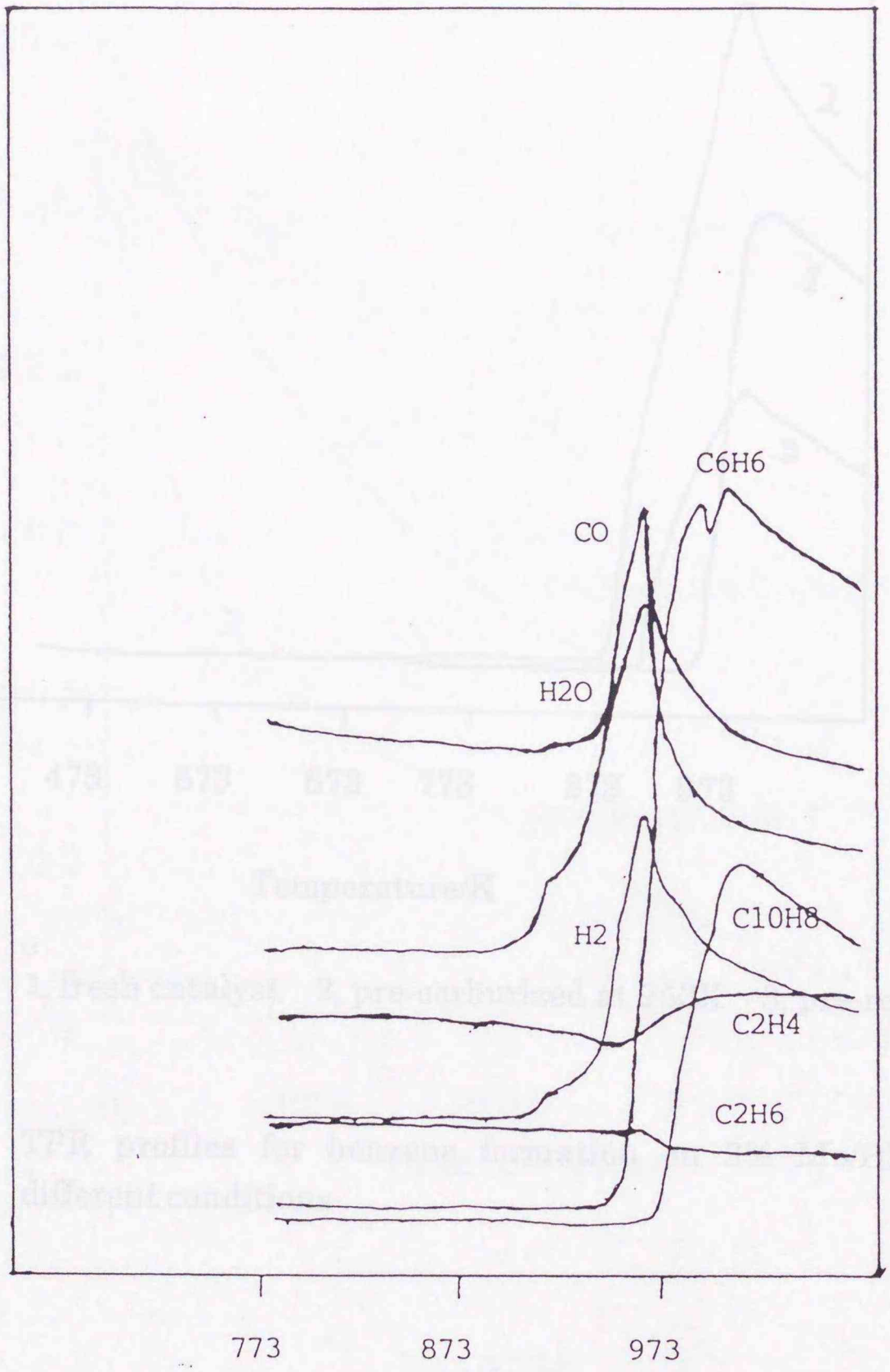
T= 973 K
P= 3 atm
SV = 1440 ml/h/g-cat

According to the obtained results, the process for formatio of rhenium carbide active phase and for production of C_2 and aromatics by dehydro-dimerizatio and dehydro-aromatization of methaneis schemed as follows,

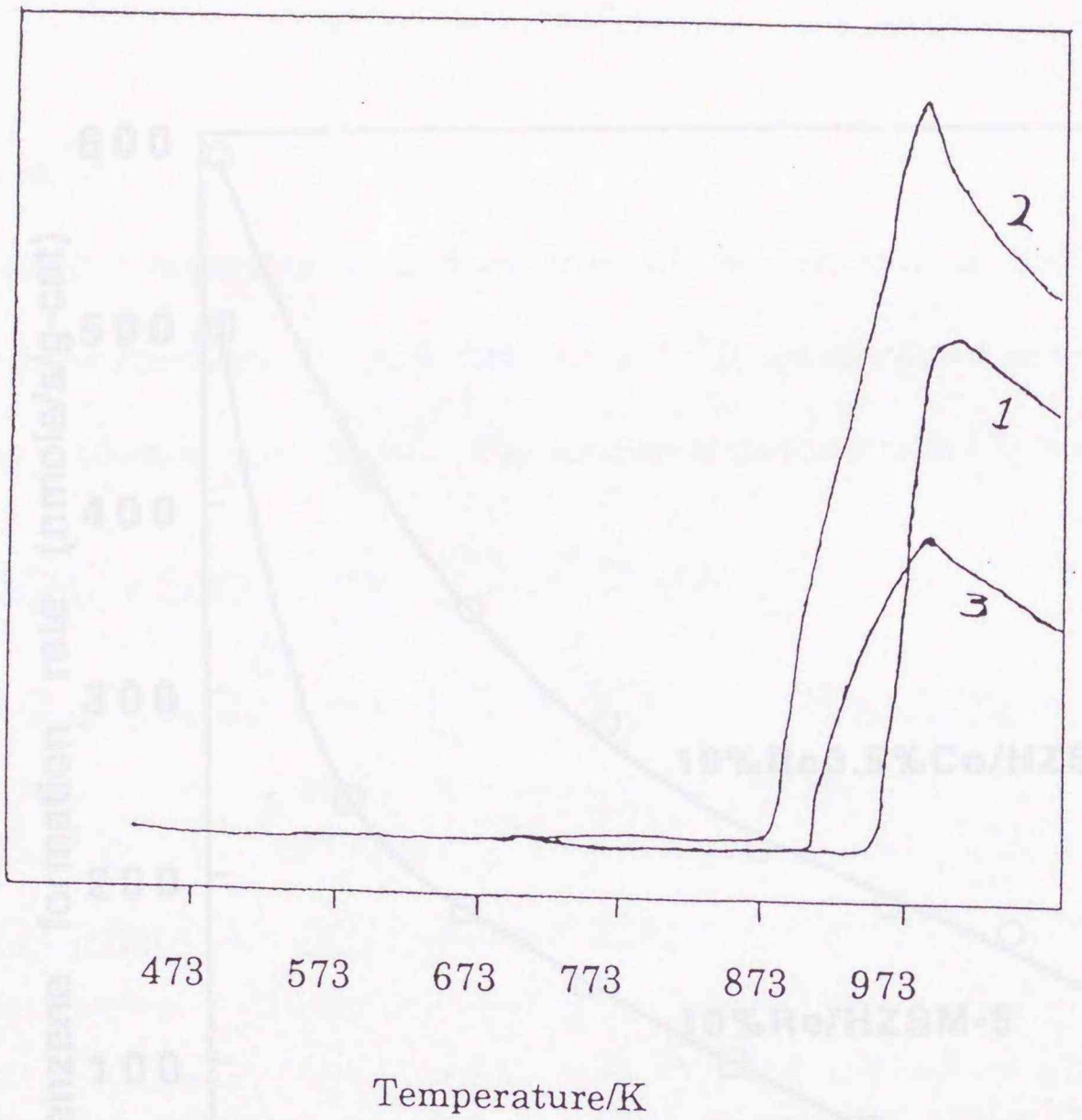








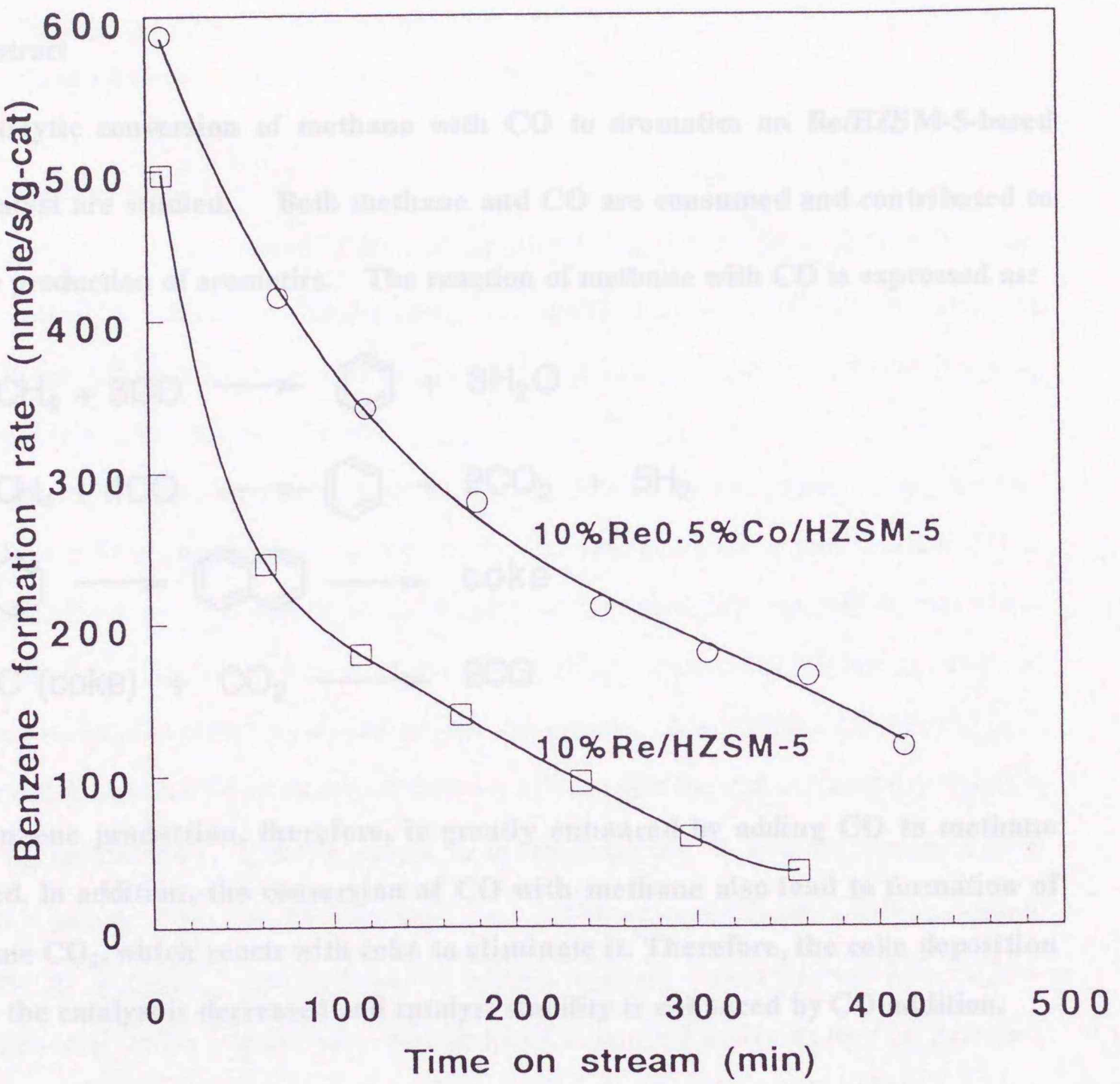
TPR spectra of Mo/HZSM-5 in methane flow



1, fresh catalyst 2, pre-carburized at 953K 3, pre-reduced at 973K

TPR profiles for benzene formation on 3% Mo/HZSM-5 pretreated at different conditions

Effect of Co addition to Re/HZSM-5 on rate of benzene formation

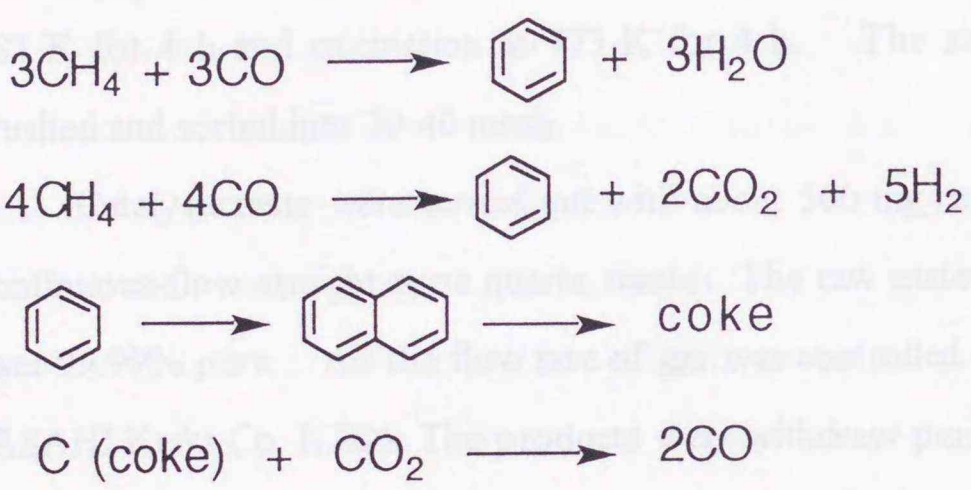


T=1023K
P= 3atm
SV= 5000 ml/h/g-cat

Chapter 9
Methane conversion with CO into aromatics on Re/HZSM-5 catalyst

Abstract

Catalytic conversion of methane with CO to aromatics on Re/HZSM-5-based catalyst are studied. Both methane and CO are consumed and contributed to the production of aromatics. The reaction of methane with CO is expressed as:



Benzene production, therefore, is greatly enhanced by adding CO to methane feed. In addition, the conversion of CO with methane also lead to formation of some CO_2, which reacts with coke to eliminate it. Therefore, the coke deposition on the catalyst is decreased and catalyst stability is enhanced by CO addition.

1 Introduction

The catalytic features of Re/HZSM-5-based catalysts for dehydrogenation and aromatization of methane was presented previously. Compared with Mo/HZSM-5, Re/HZSM-5 shows much better lower-temperature activity for production of aromatics. In the present research, methane conversion with CO to aromatics on Re/HZSM-5 is studied and a mechanism for the reaction is suggested.

2 Experimental

Re/HZSM-5 was prepared by impregnating NH_4ZSM-5 (SiO_2/AI_2O_3=40, Toso Co.) with $NH_4ReO_4 4H_2O$ (Kanto Chem. Co.) aqueous solution, followed by drying at 383 K for 4 h and calcination at 773 K for 4 h. The sample was finally pressed, crushed and sorted into 20-40 mesh.

Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow straight type quartz reactor. The raw materials of methane and CO is over 99.99% pure. All the flow rate of gas was controlled with mass flow controllers (ASAHI Keiki Co. LTD). The products were withdraw periodically from the outlet of reactor and analyzed by two on-line gas chromatography of Shimadazu GC-9A and GC-8A equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) respectively. Hydrocarbon products were separated by a 4 mm ×1m Porapak P column and Ar , CH_4, CO, CO_2, H_2 were analyzed by a 4 mm×1m active carbon column. 10.7% Ar in methane was employed as internal standard. Formation rate of products, methane conversion were calculated by an internal standard analyzing method described as previously. Below, the method is presented briefly. Even if the total flow rate changed at outlet from inlet of reactor (F_{Total}^{intlet} ,F_{Total}^{outlet}). Flow rate of non-reactive internal standard gas (F_{st}) doses not change.

$$F_{st} = F_{Total}^{outlet} \times X_{st}^{outlet} = F_{Total}^{inlet} \times X_{st}^{inlet}$$

Here, X_{st} refer to concentration of the internal standard gas.

Formation rate of i product (F_i) can be calculated as,

$$F_i = F_{Total}^{outlet} \times X_i^{outlet} = F_{st} \times X_i^{outlet} / X_{st}^{outlet}$$

By the same way, methane conversion ($C_{methane}$) can be calculated as,

$C_{methane} = (F_{methane}^{inlet} - F_{methane}^{outlet})/ F_{methane}^{inlet} = 1 - F_{methane}^{outlet}/ F_{methane}^{inlet}$

$=1 - F_{Ar} \times X_{methane}^{outlet}/X_{Ar}^{outlet} \times F_{methane}^{inlet}$

CO conversion (Cco) is calculated as, $Cco = (F_{CO}^{inlet} - F_{CO}^{outlet})/ F_{CO}^{inlet}$

HC selectivity is caiculated as S_{HC}= formation rate of HC/(consumption rate of methane + consumption rate of CO)

3 Results and discussion

3.1 Features of methane reaction with CO on Re/HZSM-5

The consumption rates of CO and methane as well as the formation rates of products with time on stream for methane conversion with CO on Re/HZSM-5 are shown in figs 1 and 2. The main products for reaction of methane and CO on the catalyst are benzene, naphthalene, C_2 and a little CO_2. The consumption rates of methane and CO initially is higher and then kept to be constant with time on stream after about 2 h. Formation rate of benzene is lower and CO_2 formation rate is higher in the initial stage and then kept to be stable. In addition, formation rate of CO_2 is much less than a half of CO consumption rate. Active carbon species and CO_2 is produced from Budart reaction of CO. We supposed that the active carbon species is contributed to the production of higher hydrocarbons by reaction with hydrogen or with methane which provide hydrogen source. On the other hand, coke deposition on the catalyst, which lead to decrease of catalyst activity, is inhibited by the reaction of coke with CO_2 to produce CO (coke + CO_2 = 2CO). Therefore, the amount of produced CO_2 is much less than what expected from Budart reaction (about a half of consumed CO).

3.2 Effect of CO/methane ratio

Dependence of benzene formation rate on the concentration of CO in methane feed is shown in fig 3. Rate of benzene formation is greatly enhanced and stabilized by increasing the concentration of CO in methane from 0 to 22.2%. Further increase of

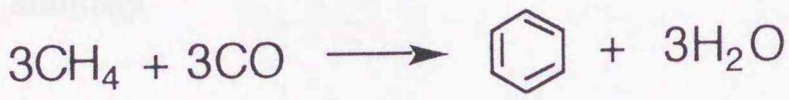
CO from 22.2 to 47.7% lead to decrease of catalyst stability. Conversion of methane and selectivity of total hydrocarbon products increase by addition of CO to methane feed as shown in fig 4. Therefore, both methane and CO are contributed to production of higher hydrocarbons. It also can be seen from fig 4 that CO conversion increases with increase of CO concentration in methane feed. Selectivity of total hydrocarbon products is maximized at a CO concentration of about 8.6% and benzene formation rate is maximized at a CO concentration of about 22.2%.

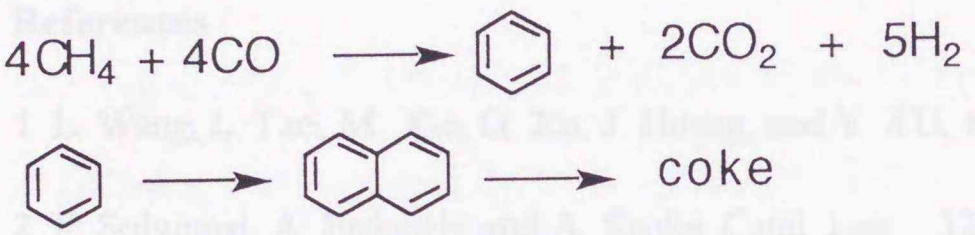
3.3 Effect of varying methane SV and reaction temperature

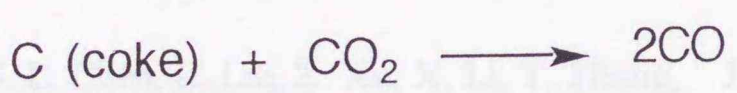
Dependence of conversion, selectivity and benzene formation rate on reaction temperature is shown in fig 5. Both methane conversion and selectivity of total higher hydrocarbon products are remarkably enhanced by increasing reaction temperature from 973 K to 1073 K, although CO conversion decreases a little at higher temperature. Benzene formation rate is almost doubled by increasing temperature from 973 K to 1023 K. This indicates that higher reaction temperature is more favorable for the catalytic conversion of methane with CO to higher hydrocarbon products on Re/HZSM-5. Fig 6 shows that Re/HZSM-5 catalyst for the reaction at high temperature is quite stable with time on stream. Rate of benzene formation increases and naphthalene is decreases a little with time on stream. Methane conversion almost keep constant within 500 min. Effect of methane specific velocity on conversion of methane and CO, formation rate of benzene and selectivity to total hydrocarbon products is shown in fig 7. Benzene formation rate increases by a order of magnitude by increasing methane SV from 1440 to 10000 ml/h/g-cat. However, methane conversion change little with increasing methane SV. Therefore, Re/HZSM-5 catalyst exhibits very high activity for methane aromatization with CO at high SV. Fig 8 indicates that a lower CO concentration of about 8.6% in methane feed lead to a higher activity and stability for benzene formation at high methane specific velocity.

3.4 The mechanism suggested for the catalytic conversion of methane with CO

According the analysis of products and consumption of methane and CO, the conversion of methane with CO on Re/HZSM-5 proceed as follows,

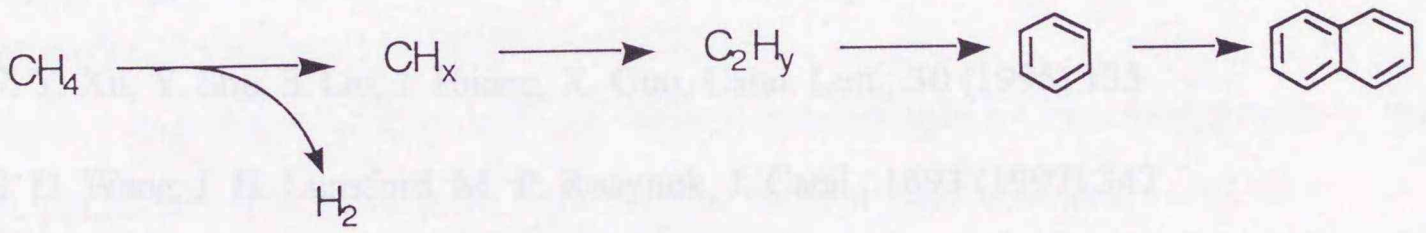


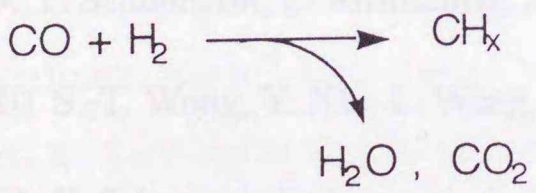


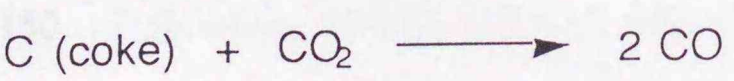


Contribution of CO on the production of aromatics and production of CO_2 are described by following mechanism,

Mechanism:







The role of CO addition for stabilizing catalyst is due to the reaction of produced CO_2 with coke to produce CO. Therefore, coke deposition on the catalyst is decreased.

4 Conclusion

Activity and stability of Re/HZSM-5 catalyst for methane aromatization is greatly enhanced by CO addition to methane feed. CO is contributed to the formation of benzene by interaction with methane on Re/HZSM-5 catalyst. In addition, a little CO_2 is also produced as a side product, which may play a role to enhance the catalytic stability.

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Caption of figures:

Fig 1. Consumption of CH_4 and CO and formation rate of CO_2 with time on stream for methane conversion with CO on 10% Re/HZSM-5

Fig 2. Conversion and product formation rate with time on stream for methane conversion with 22.2% CO on 10%Re/HZSM-5 at 1023 K and 3 atm

Fig 3. Benzene formation rate with time on stream for methane conversion with different CO concentration on 10%Re/HZSM-5

Fig 4. Conversion of CH_4 and CO, Selectivity of higher hydrocarbon products and formation rate of benzene as a function of CO concentration in methane feed

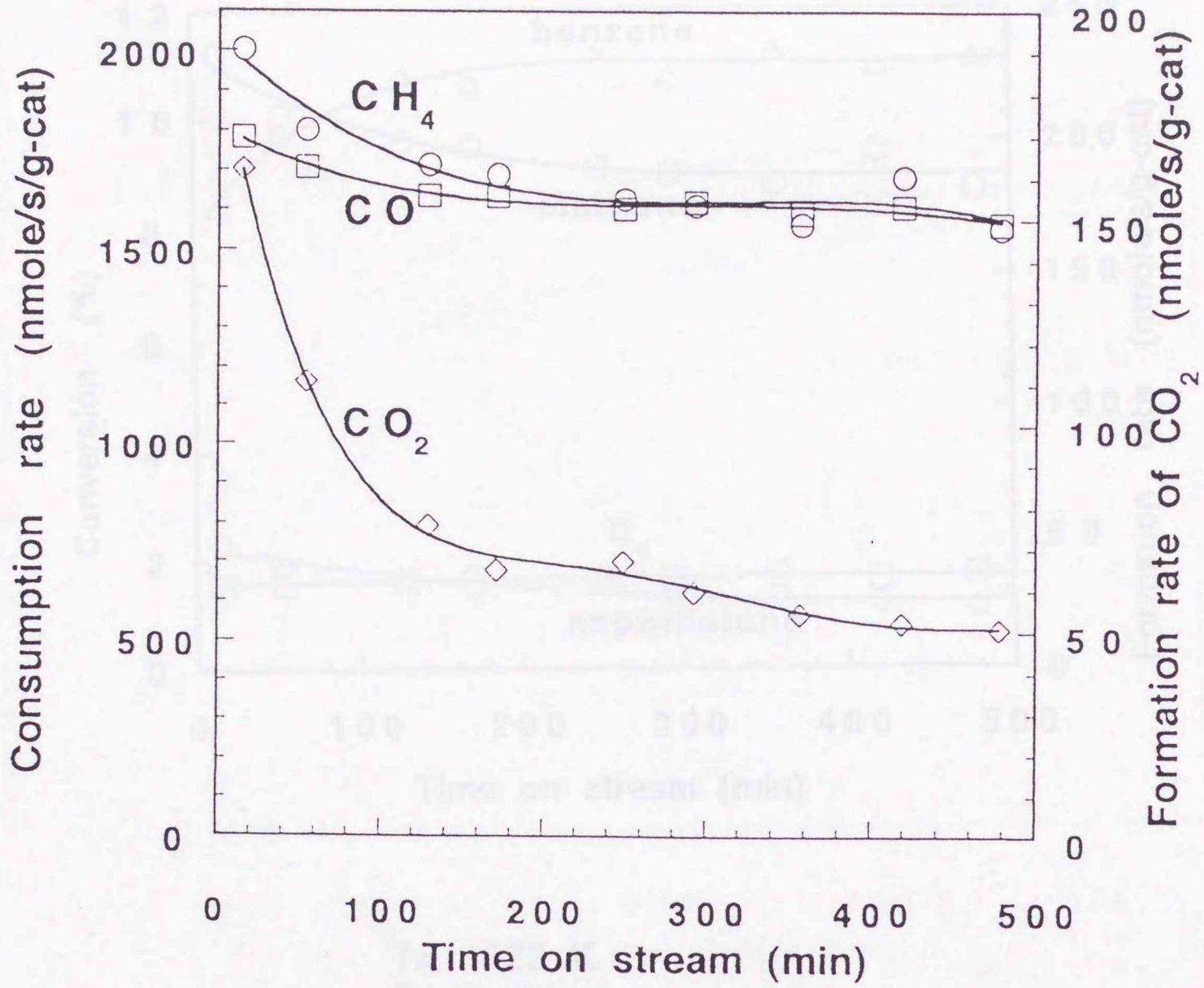
Fig 5. Conversion of CH_4 and CO, Selectivity of higher hydrocarbon products and formation rate of benzene as a function of reaction temperature

Fig 6. Conversion and formation rate of products with time on stream for methane conversion with 22.2% CO

Fig 7. Conversion of CH_4 and CO, Selectivity of higher hydrocarbon products and formation rate of benzene as a function of methane specific velocity

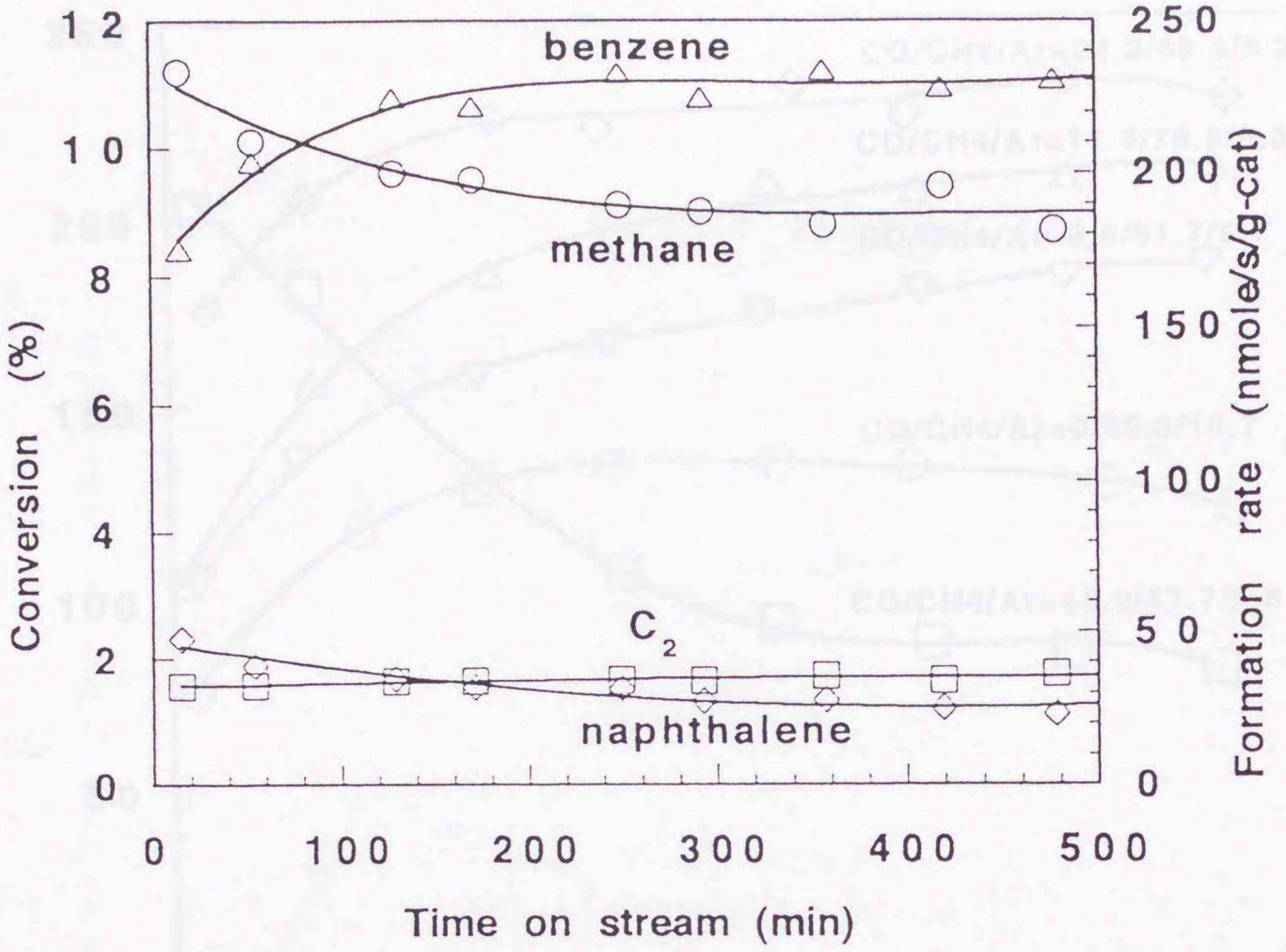
Fig 8. Benzene formation rate with time on stream for methane conversion with different CO concentration at a higher methane SV

Fig 1. Consumption rate of CH_4 and CO and formation rate of CO_2 with time on stream for methane conversion with CO on 10% Re/HZSM-5



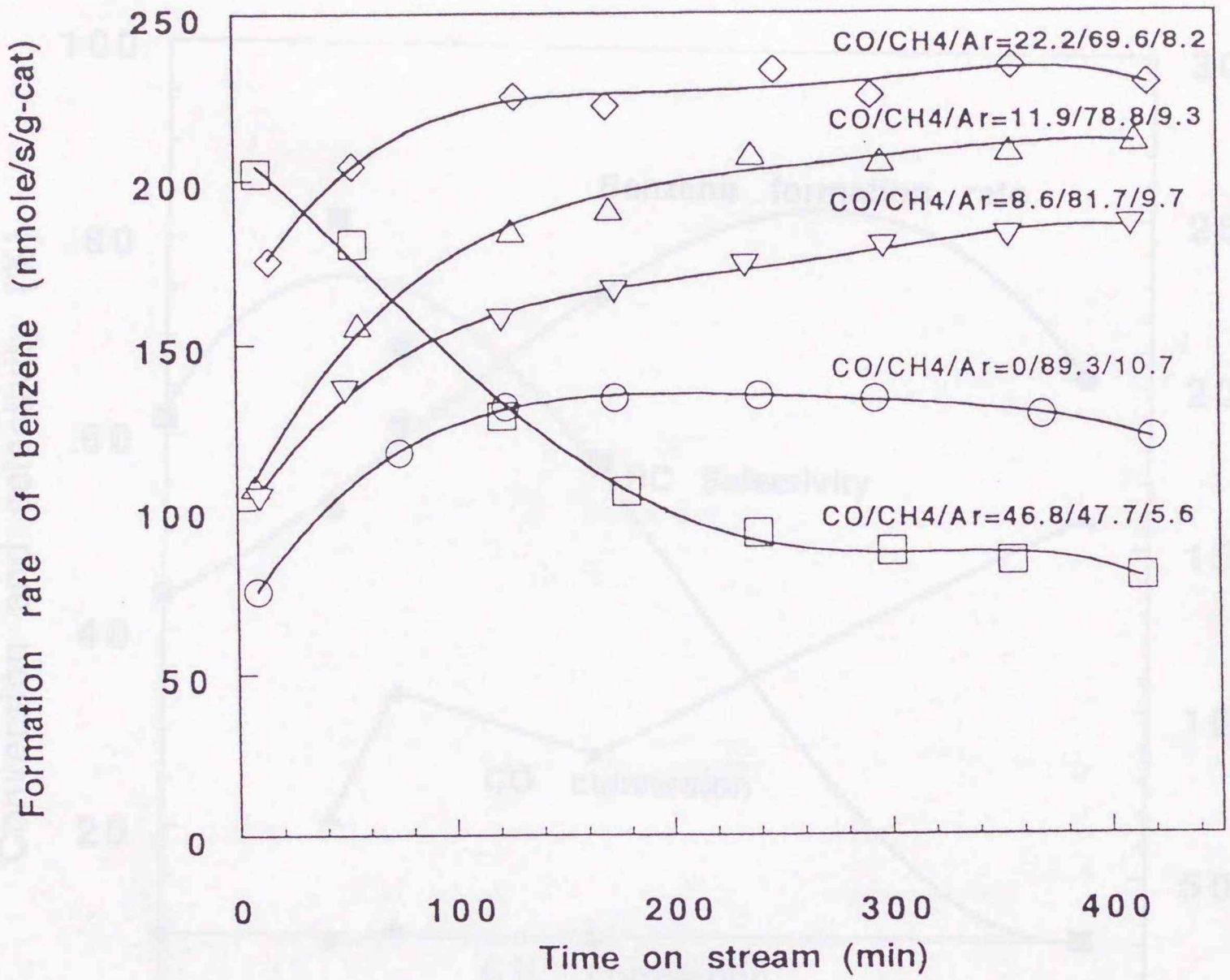
T=1023 K
P= 3 atm
SV=1440 ml/h/g-cat
CO/CH4/Ar= 22.2/69.6/8.2

Fig 2. Conversion and formation rate of products with time on stream for methane conversion with 22.2% CO on 10% Re/HZSM-5



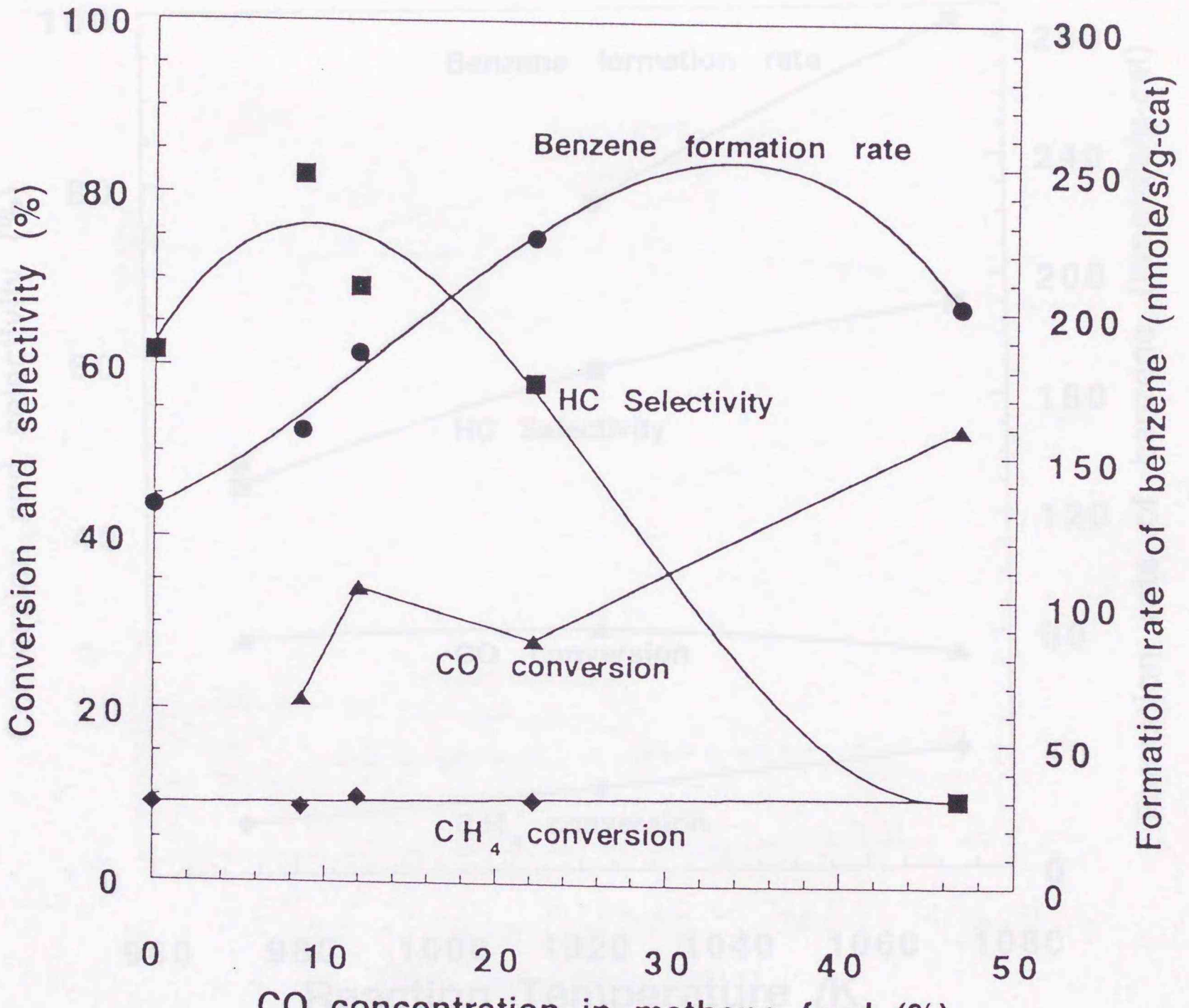
T= 1023 K
P= 3 atm
SV= 1440 ml/h/g-cat

Fig 3. Benzene formation rate with time on stream for methane conversion with different CO concentration on10%Re/HZSM-5



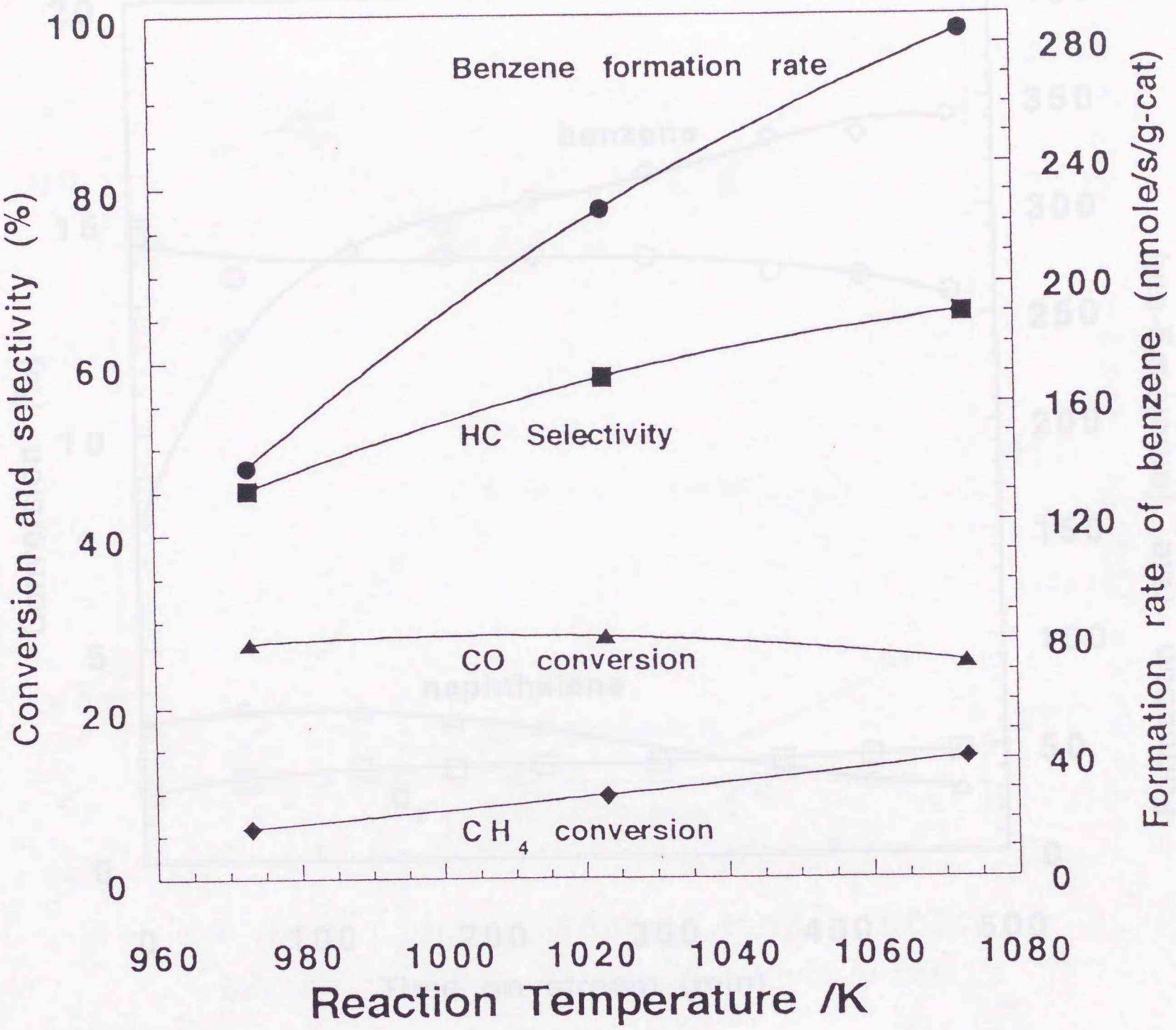
SV= 1440 ml/h/g-cat
T= 1023 K
P = 3 atm

Fig 4. Conversion of CH4 and CO, selectivity of hydrocarbon products and formation rate of benzene as a function of CO concentration



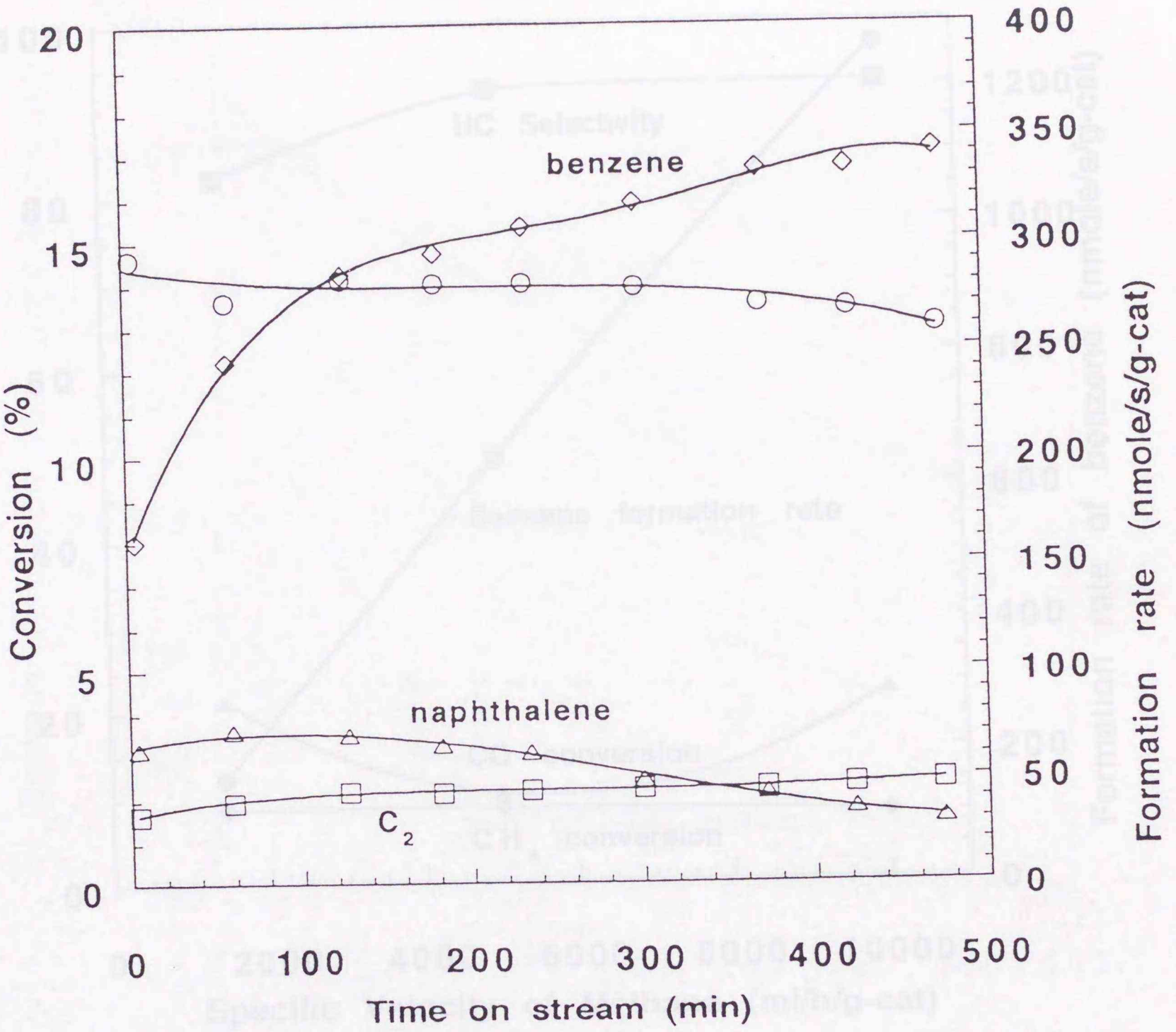
T= 1023 K
P= 3 atm
SV= 1440 ml/h/g-cat

Fig 5. Conversion of CH_4 and CO, selectivity of higher hydrocarbon products and formation rate of benzene as a function of reaction temperatures



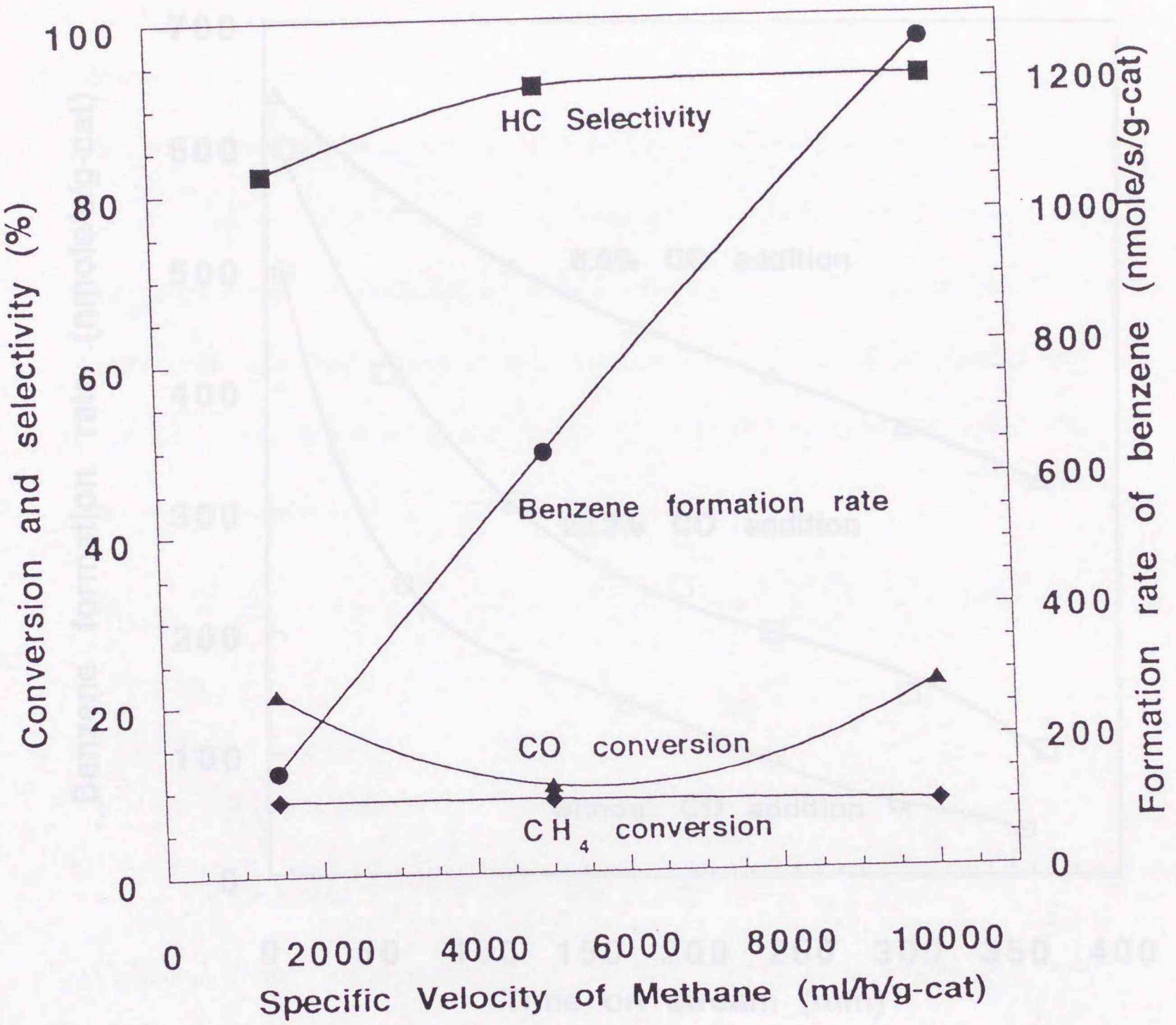
P= 3 atm
SV= 1440 ml/h/g-cat
$CO/CH_4/Ar$= 22.2/69.6/8.2

Fig 6. Conversion of and formation rate of products with time on stream for methane conversion with 22.2% CO on 10% Re/HZSM-5 at 1073 K



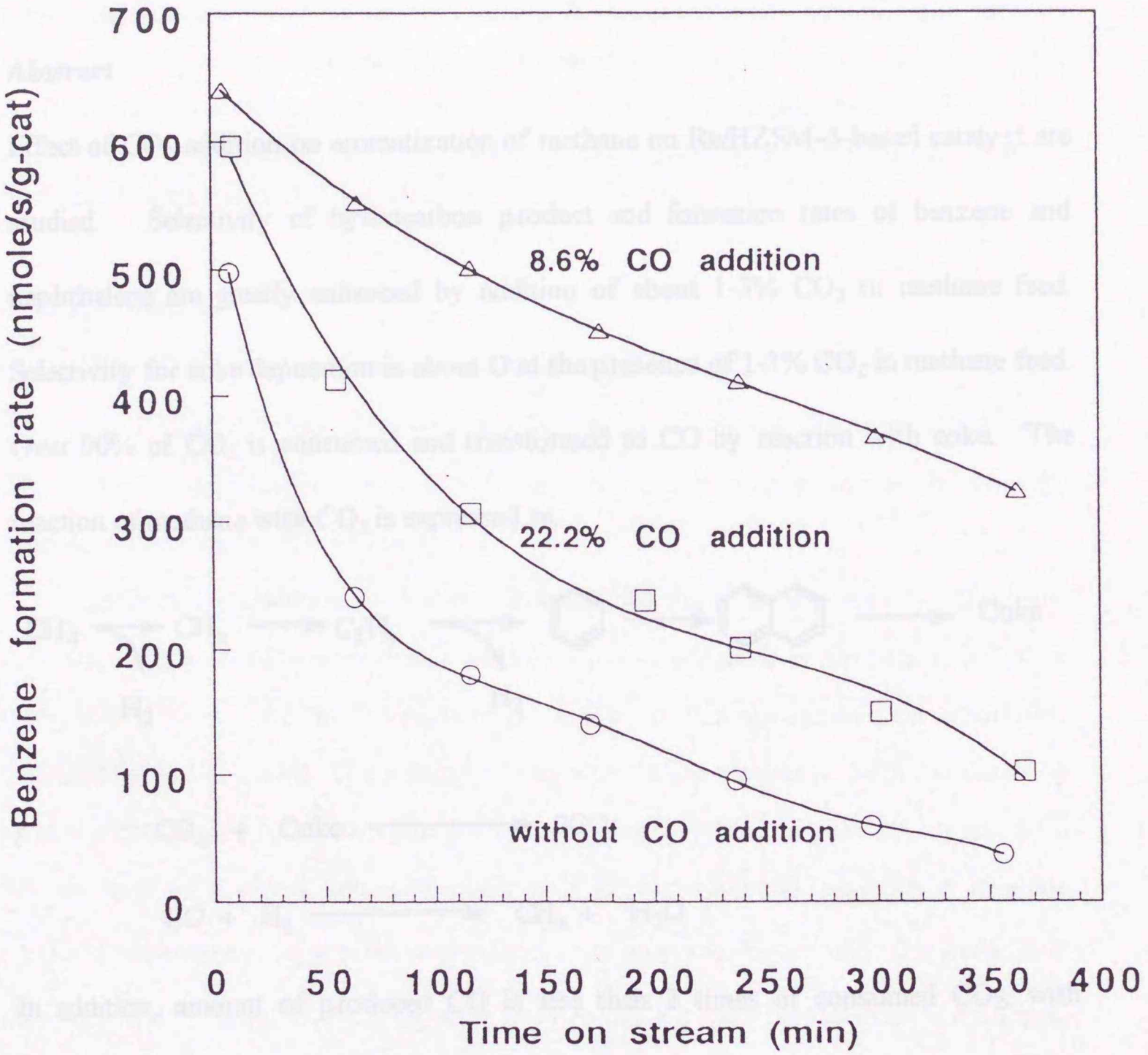
Catalyst: 10% Re/HZSM-5
Temperature = 1073 K
Pressure = 3 atm
SV=1440ml/h/g-cat

Fig 7. Conversion of CH4 and CO, selectivity of higher hydrocarbon products and formation rate of benzene as a function of methane specific velocity



T= 1023 K
P= 3 atm
$CO/CH_4/Ar=8.6/81.7/9.7$

Fig 8. Benzene formation rate with time on stream for methane conversion with CO of deifferent concentration on 10%Re/HZSM-5 at a higher SV of methane

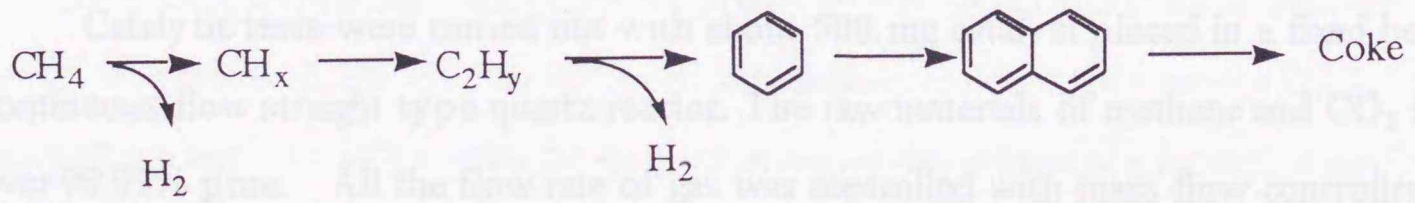


T=1023K
P= 3atm
SV= 5000 ml/h/g-cat

Chapter 10
Methane aromatization with CO_2 on Re/HZSM-5 catalyst

Abstract

Effect of CO_2 addition on aromatization of methane on Re/HZSM-5-based catalyst are studied. Selectivity of hydrocarbon product and formation rates of benzene and naphthalene are greatly enhanced by addition of about 1-3% CO_2 to methane feed. Selectivity for coke deposition is about O at the presence of 1-3% CO_2 in methane feed. Over 90% of CO_2 is consumed and transformed to CO by reaction with coke. The reaction of methane with CO_2 is expressed as:



$$CO_2 + Coke \longrightarrow 2CO$$

$$CO + H_2 \longrightarrow CH_x + H_2O$$

In addition, amount of produced CO is less than 2 times of consumed CO_2, with methane also lead to formation of some CO_2. Therefore, a part of produced CO is secondarily react with hydrogen to produce hydrocarbon products, which is responsible for the increase of hydrocarbon selectivity.

1 Introduction

The catalytic features of Re/HZSM-5-based catalysts for dehydrogenation and aromatization of methane and effect of CO addition to methane feed on the catalytic reaction were discussed previously. Compared with Mo/HZSM-5 [1-20], Re/HZSM-5 shows much better lower-temperature activity for production of aromatics and different selectivity to C_2 and naphthalene [21]. In the case of CO addition to methane feed, both methane and CO are consumed and contributed to production of aromatics on Re/HZSM-5 [22]. In the present research, effect of CO_2 addition to methane on methane aromatization on Re/HZSM-5 is studied.

2 Experimental

Re/HZSM-5 was prepared by impregnating NH_4ZSM-5 (SiO_2/AI_2O_3=40, Toso Co.) with $NH_4ReO_4 4H_2O$ (Kanto Chem. Co.) aqueous solution, followed by drying at 383 K for 4 h and calcination at 773 K for 4 h. The sample was finally pressed, crushed and sorted into 20-40 mesh.

Catalytic tests were carried out with about 500 mg catalyst placed in a fixed bed continuous-flow straight type quartz reactor. The raw materials of methane and CO_2 is over 99.99% pure. All the flow rate of gas was controlled with mass flow controllers (ASAHI Keiki Co. LTD). The products were withdraw periodically from the outlet of reactor and analyzed by two on-line gas chromatography of Shimadazu GC-9A and GC-8A equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) respectively. Hydrocarbon products were separated by a 4 mm×1m Porapak P column and Ar , CH_4, CO, CO_2, H_2 were analyzed by a 4 mm×1m active carbon column. 10.7% Ar in methane was employed as internal standard. Formation rate of products, methane conversion were calculated by an internal standard analyzing method described as previously. Below, the method is presented briefly. Even if the total flow rate changed at outlet from inlet of reactor (F_{Total}^{intlet} ,F_{Total}^{outlet}). Flow rate of non-reactive internal standard gas (F_{st}) doses not change.

$$F_{st} = F_{Total}^{outlet} \times X_{st}^{outlet} = F_{Total}^{inlet} \times X_{st}^{inlet}$$

Here, X_{st} refer to concentration of the internal standard gas.

Formation rate of i product (F_i) can be calculated as,

$F_i = F_{Total}^{outlet} \times X_i^{outlet} = F_{st} \times X_i^{outlet} / X_{st}^{outlet}$

By the same way, methane conversion ($C_{methane}$) can be calculated as,

$C_{methane} = (F_{methane}^{inlet} - F_{methane}^{outlet}) / F_{methane}^{inlet} = 1 - F_{methane}^{outlet} / F_{methane}^{inlet}$

$= 1 - F_{Ar} \times X_{methane}^{outlet} / X_{Ar}^{outlet} \times F_{methane}^{inlet}$

CO_2 conversion (C_{CO2}) is calculated as, $C_{CO2} = (F_{CO2}^{inlet} - F_{CO2}^{outlet}) / F_{CO2}^{inlet}$

HC selectivity is caiculated as S_{HC}= formation rate of HC/consumption rate of methane

Coke selectivity = (consumed CH_4 + consumed CO_2 - produced HC - produced CO)/consumed methane.

3 Results and discussion

3.1 Achievement of high and stable benzene formation by addition of CO_2

Benzene formation rate with time on stream is very stable and a stable formation rate of benzene is about 130 nmole/s/g-cat for methane aromatization on Re/HZSM-5 catalyst at a methane SV of 1440 ml/h/g-cat. A higher rate of benzene formation can be obtained by increasing methane specific velocity. However, benzene formation rate with time on stream is not stable as shown in fig 1. Benzene formation rate at the initial stage is about 500 nmole/s/g-cat at a methane SV of 5000 ml/h/g-cat and decreases very quickly with time on stream. To solve this problem, some CO_2 with different concentration is added to methane feed. A high and stable rate of benzene formation with time on stream has been attained for methane aromatization with adding a little CO_2 to methane feed on Re/HZSM-5 at a high methane SV of 5000 ml/h/g-cat as shown in fig 2. 1-3% CO_2 addition in methane feed is important for obtaining a high a stable formation rate of benzene. A higher CO_2 concentration of 8.6% in methane feed lead to a suppression of benzene formation rate. In addition, benzene formation rate can be increased further by increasing methane SV and reaction temperature. About 1600 nmole/s/g-cat of benzene formation rate is achieved for methane aromatization with

about 2.1% CO_2 on 10%Re/HZSM-5 at 1073K and methane SV of 10000 ml/h/g-cat.

3.2. Conversion of CH_4 and CO_2 and analysis of products

The results for conversion of CH_4 and CO_2 and analysis of products by employing CH_4 with 2% CO_2 as feed are shown in figs 4 and 5. It is shown in fig 4 that over 90% CO_2 is converted to CO. Formation rate of CO is more than consumption rate of CO_2, but less than 2 times of CO_2 cosumption rate. This indicate that some methane is also contributed to the formation of CO. It is shown in fig 5 that major hydrocarbon product is benzene and formation rate of naphalene, C_2 and T+X are much less than formation rate of benzene. In addition, it is also clear in fig 5 that methane conversion is high and benzene formation rate is lower in initial stage and then become stable with time on stream. Therefore, there is a introduce period for methane conversion with CO_2.

3.3 The role of CO_2 in enhancing HC selectivity and inhibiting coke deposition

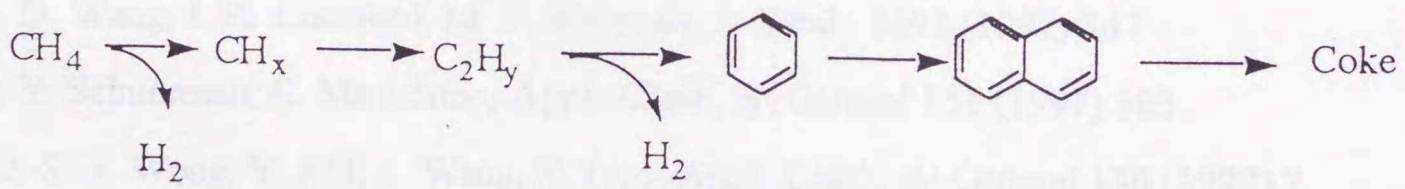
Product selectivity is analyzed and results are shown in fig 6. It is clear in fig 6 that the selectivity of hydrocarbon products is evidently enhanced by addition of 1-2% CO_2. It is quite important that selectivity for coke deposition on the catalyst is about 0 when 1-3% CO2 is added to methane feed as shown in fig 6. In addition, benzene formation rate is maximized at 1-2% CO_2 in methane feed. Higher concentration of CO_2, for instance, 8.6% CO_2 in methane feed lead to a sharp suppression of benzene formation. As soon as coke is deposited on the catalyst from methane aromatization, it will react with CO_2 to produce CO through reaction: CO2 + C(coke) = 2CO. This reaction is responsible for inhibition of coke deposition on the catalyst and that the coke selectivity is about 0. On the other hand, the produced CO may further react with hydrogen and is partially contributed to the production of benzene. Therefor, selectivity of hydrocarbon products is high when 1-2% CO_2 is added to methane feed.

3.4 Effect of reaction temperature and methane SV

The results in fig 7 indicate that CH4 conversion and benzene formation rate increase remarkably with increase of reaction temperature. HC selectivity and CO_2 conversion are maximized at a reaction temperature of 1023 K. At a selected reaction temperature of 1023 K, methane conversion with 2.1% CO_2 is conducted by varying methane specific velocity. Conversion of CH4 and CO_2, selectivity of hydrocarbon products and formation rate of benzene as a function of methane SV is shown in fig 8. It is indicated in fig 8 that CH_4 conversion change little with increase of methane SV. However, benzene formation rate increases by one order of magnitude by increasing methane SV from 1440 to 10000 ml/h/g-cat. HC selectivity and CO_2 conversion also increase a little by increasing methane SV. So, Re/HZSM-5 catalyst is quite active for methane conversion with CO_2.

3.5 The mechanism for the reaction of methane with CO_2

Based on the above results, the role of CO_2 in enhancing selectivity of hydrocarbon products and inhibiting coke deposition is described as below,



$$CO_2 + Coke \longrightarrow 2CO$$

$$CO + H_2 \longrightarrow CH_x + H_2O$$

The reaction of CO_2 with coke to produce CO and the secondary reaction of produced CO with hydrogen to produce CHx species are responsible for the low coke selectivity and high hydrocarbon selectivity.

4 Conclusion

High and stable rate of benzene formation is achieved at a high SV of methane on Re/HZSM-5 type catalyst by addition of about 1-3% CO_2 to methane feed. A little

amount of CO_2 in methane feed is very effective to suppress coke deposition on the catalyst and selectivity of hydrocarbon products is greatly improved by addition of CO_2 to methane feed. The reaction of CO_2 with coke to produce CO and the secondary reaction of produced CO with hydrogen to produce CHx species are responsible for the low coke selectivity and high hydrocarbon selectivity.

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20. D. Wang, J. H. Lunsford, M. P. Rosynek, Topics Catal., 3 (1996) 289

21. unpublished results

22. unpublished results

Caption of figures:

Fig 1. Benzene formation rate with time on stream for methane aromatization on 10%Re/HZSM-5 at various methane specific velocity

Fig 2. Benzene formation rate with time on stream for methane aromatization with different CO_2 concentration on 10%Re/HZSM-5

Fig 3. Conversion and product formation rate with time on stream for methane aromatization with 2.1% CO_2 on 10%Re/HZSM-5 at 1073 K and methane SV of 10000ml/h/g-cat

Fig 4. Consumption rate and conversion of CO_2 and formation rate of CO with time on stream for methane aromatization with 2%CO_2 on 10% Re/HZSM-5

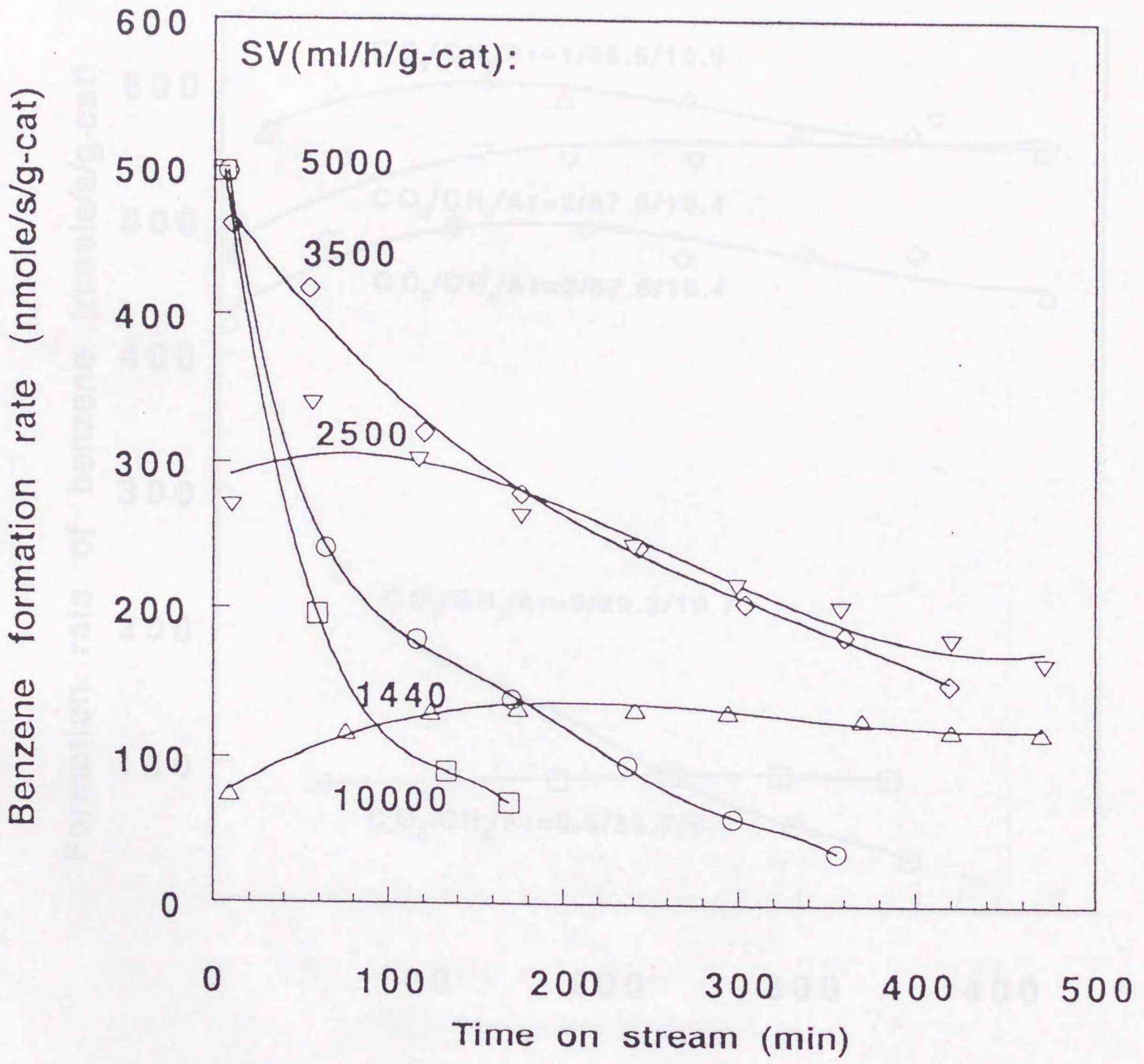
Fig 5. Conversion and product formation rate with time on stream for methane aromatization with 2% CO_2 on 10%Re/HZSM-5

Fig 6. Conversion of CH_4 and CO_2, selectivity of higher hydrocarbon products and formation rate of benzene as a function of CO_2 concentration in methane feed

Fig 7. Conversion of CH_4 and CO_2, selectivity of higher hydrocarbon products and formation rate of benzene as a function of reaction temperature

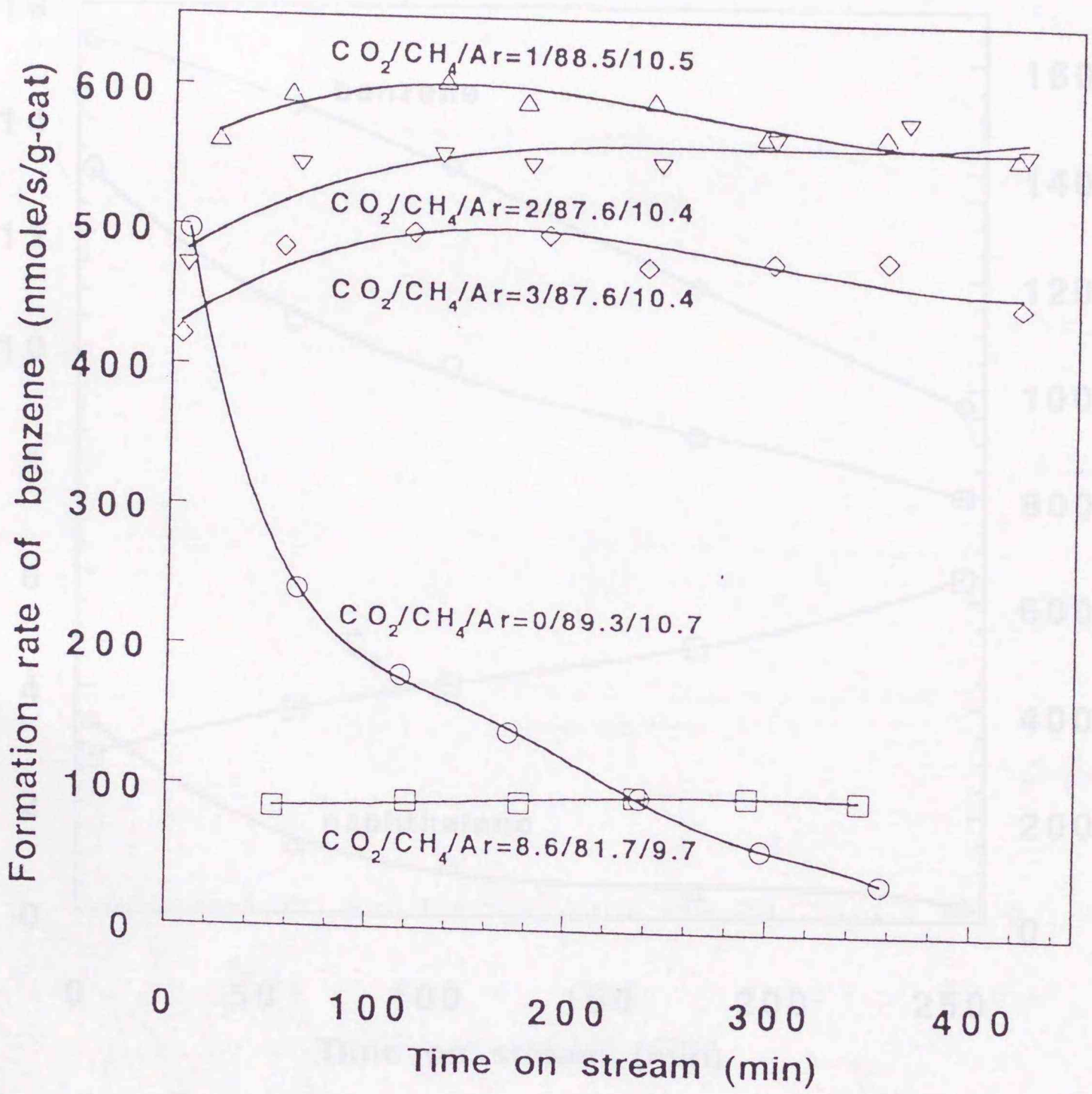
Fig 8. Conversion of CH_4 and CO_2, selectivity of higher hydrocarbon products and formation rate of benzene as a function of methane specific velocity

Fig 1. Benzene formation rate with time on stream for methane aromatization at different specific velocity (SV) of methane on 10%Re/HZSM-5



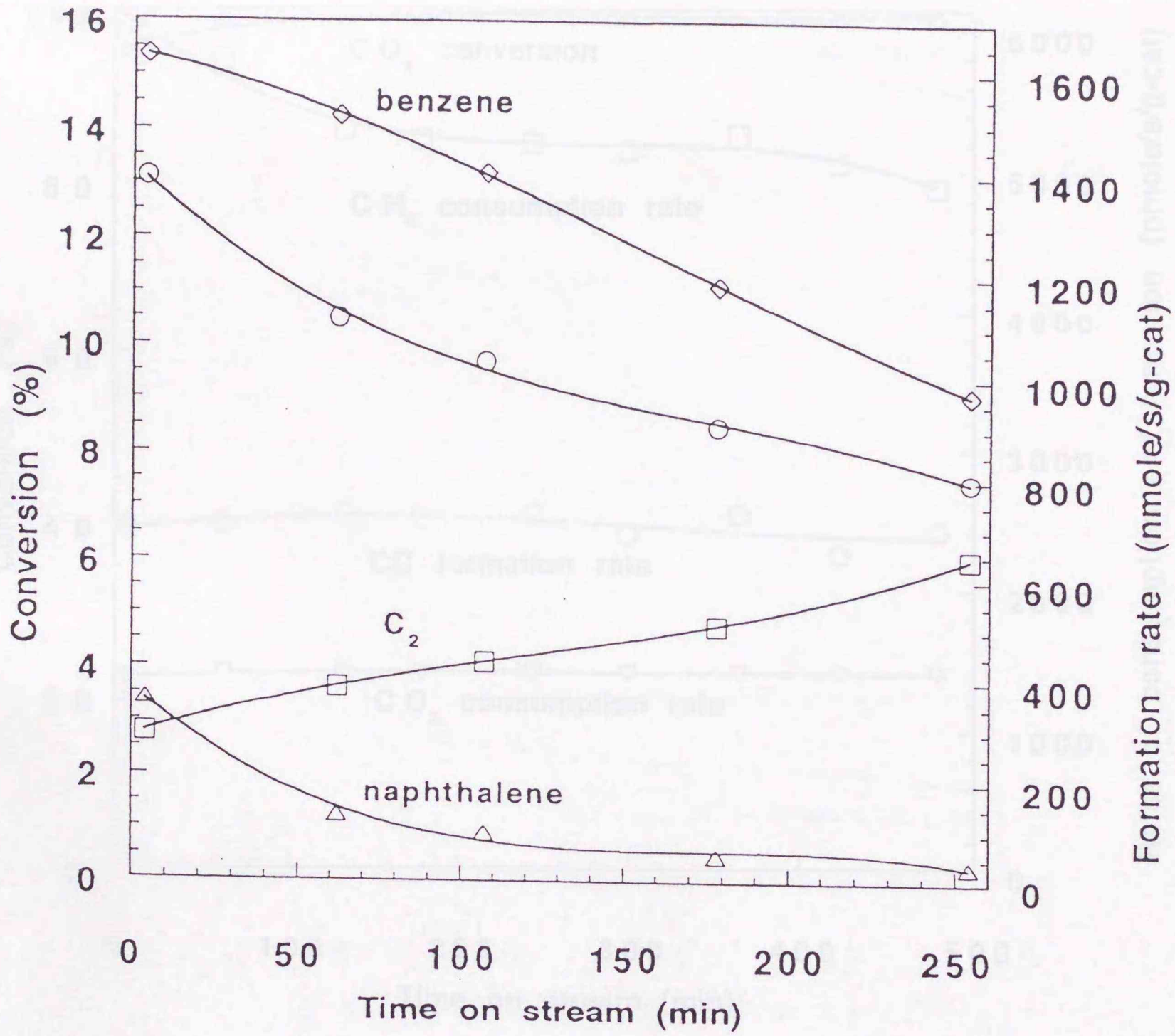
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Fig 2. Benzene formation rate with time on stream for methane aromatization with various CO_2 concentration in methane feed



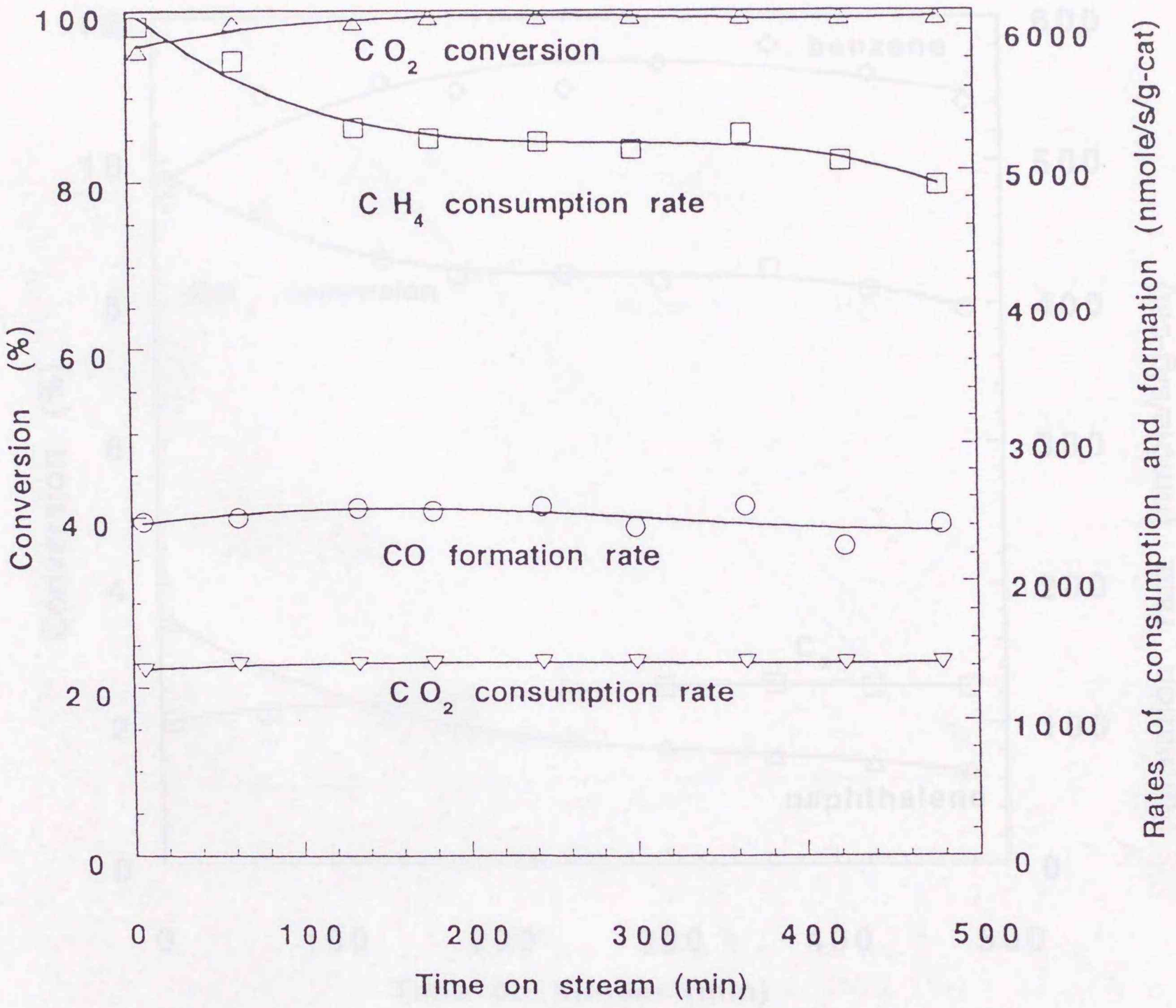
T= 1023K
P= 3 atm
SV= 5000 ml/h/g-cat

Fig 3. Conversion and product formation rate with time on stream for aromatization of methane with 2.1% CO_2 at 1073 K and methane SV of 10000 ml/h/g-cat



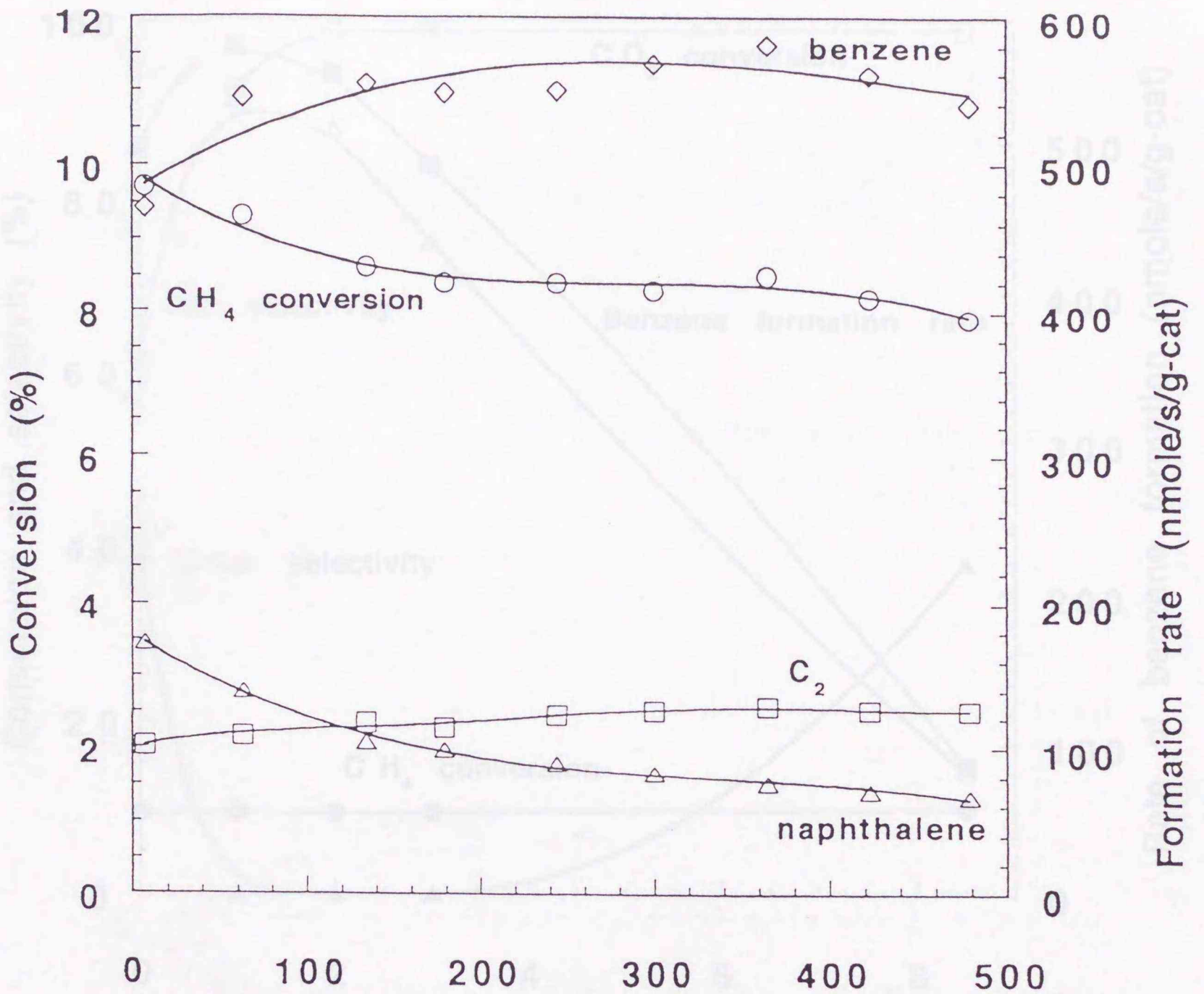
Catalyst: 10% Re/HZSM-5
Temperature = 1073 K
Pressure = 3 atm
SV=10000ml/h/g-cat

Fig 4, Consumption rate and conversion of CO_2 and CH_4, formation rate of CO with time on stream for methane aromatization with 2% CO_2 on10%Re/HZSM-5



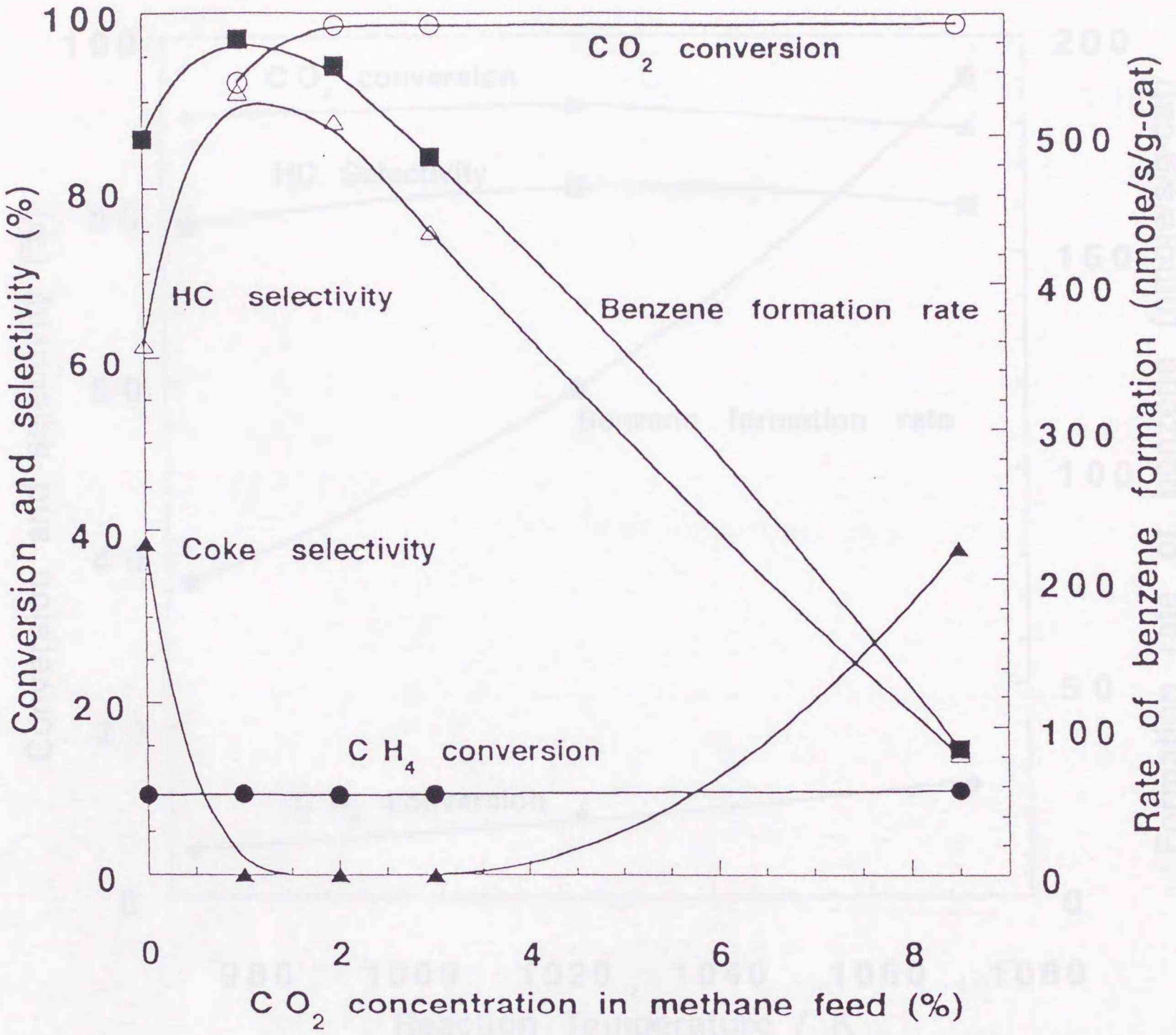
T=1023 K
P=3atm
SV=5000ml/h/g-cat

Fig 5. Conversion and product formation rate with time on stream for aromatization of methane with 2% CO_2



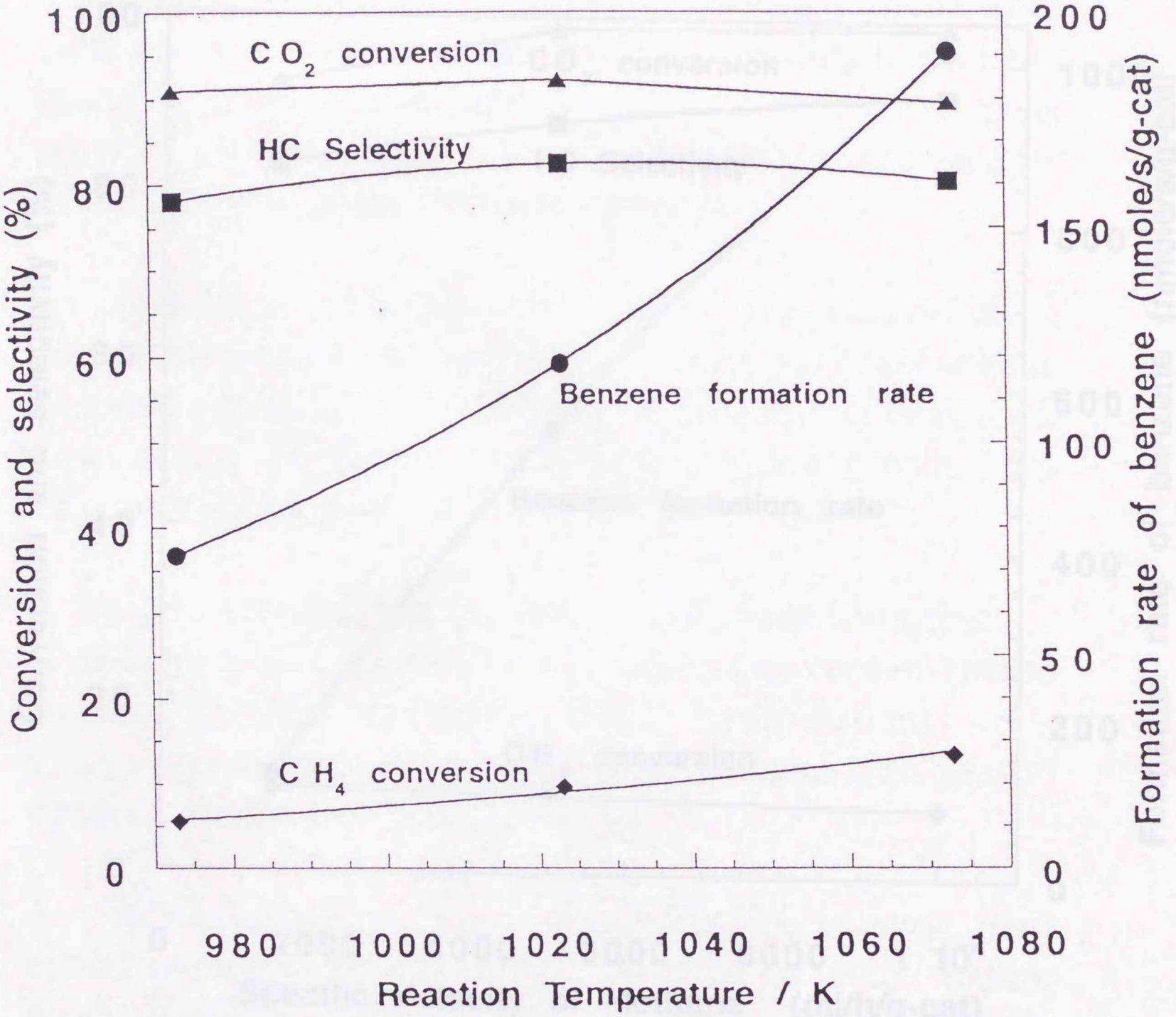
Catalyst: 10% Re/HZSM-5
Temperature = 1023 K
Pressure = 3 atm
SV=5000ml/h/g-cat

Fig 6. Conversion of CH4 and CO_2 , selectivity of HC and coke, formation rate of benzene as a function of CO_2 in methane feed on 10% Re/HZSM-5



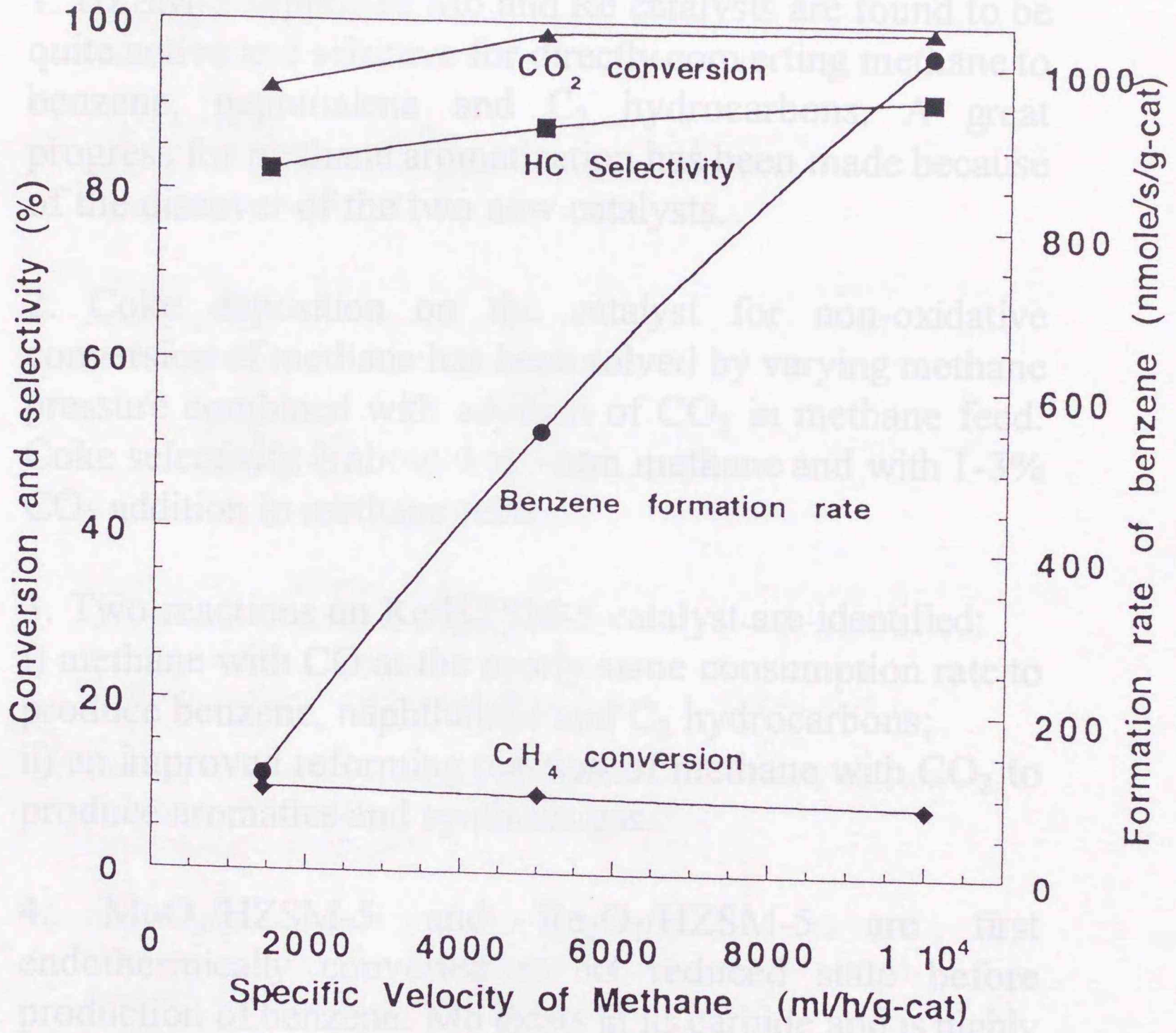
Reaction temperature = 1023 K
SV of methane = 5000 ml/h/g-cat
P= 3 atm

Fig 7. Conversion of CH_4 and CO_2, HC selectivity and formation rate of benzene as a function of teaction temperature



P= 3 atm
SV= 1440 ml/h/g-cat
$CO_2/CH_4/Ar$ = 2.1/87.5/10.4

Fig 8. Conversion of CH_4 and CO_2, selectivity of hydrocarbon products and formation rate of benzene as a function of methane SV



T= 1023 K
P= 3 atm
$CO_2/CH_4/Ar$=2.1/87.5/10.4

Conclusion

1. HZSM-5 supported Mo and Re catalysts are found to be quite active and selective for directly converting methane to benzene, naphthalene and C_2 hydrocarbons. A great progress for methane aromatization has been made because of the discover of the two new catalysts.

2. Coke deposition on the catalyst for non-oxidative conversion of methane has been solved by varying methane pressure combined with addition of CO_2 in methane feed. Coke selectivity is about 0 at 3 atm methane and with 1-3% CO_2 addition in methane feed.

3. Two reactions on Re/HZSM-5 catalyst are identified:
i) methane with CO at the nearly same consumption rate to produce benzene, naphthalene and C_2 hydrocarbons;
ii) an improved reforming reaction of methane with CO_2 to produce aromatics and synthesis gas.

4. MoO_3/HZSM-5 and Re_2O_7/HZSM-5 are first endothermically converted to its reduced state before production of benzene. Mo exists in its carbide and is highly dispersed on the HZSM-5 support.

LIST OF PUBLICATIONS

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1. Linsheng Wang,Longxiang Tao,Maosong Xie,Guifen Xu,Jiasheng Huang,Yide Xu, Dehydrogenation and aromatization of methane under non-oxidizing conditions, **Catalysis Letters**, 21(1993)35-41

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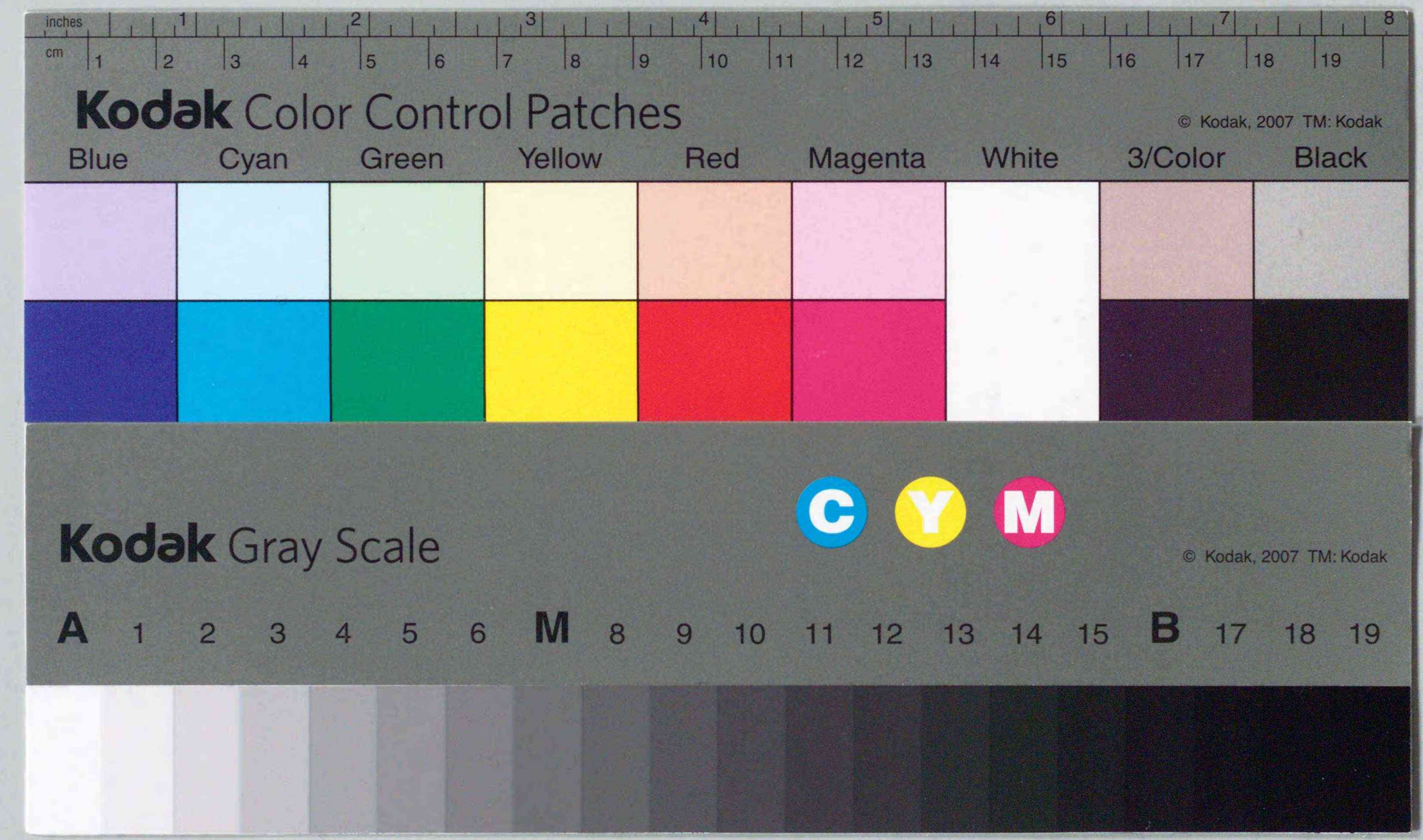
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