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Oxidation and Hydrogenation Reactions over
Supported Platinum Catalysts

担持白金触媒による酸化および水素化反応

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TABLE OF CONTENTS

Chapter 1. General Introduction	1
1.1. Mesoporous materials	1
1.2. Supported metal catalyst	2
1.3. Complete oxidation of ethylene	3
1.3.1. Ethylene	3
1.3.2. Effects of ethylene on plants	5
1.3.3. Approach of inhibition or elimination of ethylene	9
1.3.4. Removal of ethylene with precious metal catalysts	11
1.4. Selective hydrogenation of phenylacetylene	13
1.5. Purpose of the present work	15
Reference	16
 Chapter 2. Low-Temperature Oxidation of Ethylene over Pt Nanoparticles	
Supported on Mesoporous Silica	26
2.1. Introduction	26
2.2. Experimental	27
2.2.1. Synthesis of supports	27
2.2.2. Preparation of catalysts	28
2.2.3. Catalyst characterization	29
2.2.4. Ethylene oxidation	30
2.3. Results and discussion	32
2.3.1. Catalyst characterization	32
2.3.2. Catalyst screening	41
2.3.3. Ethylene oxidation at low temperature	43
2.4. Conclusion	46
Reference	46

Chapter 3. Mechanism Study on Ethylene Oxidation over Supported Pt Catalysts

.....	49
3.1. Introduction.....	49
3.2. Experimental.....	50
3.2.1. DRIFT measurements	50
3.2.2. Ethylene oxidation	51
3.3. Results and discussion	52
3.3.1. Catalyst characterization.....	52
3.3.2. Catalytic activity	52
3.3.3. Mechanistic study of ethylene oxidation over Pt catalysts	53
3.3.3.1. Pt/MCM-41	53
3.3.3.2. Pt/SiO ₂	59
3.3.3.3. Pt/Al ₂ O ₃	64
3.3.3.4. Pt/ZrO ₂	71
3.3.3.5. Pt/TiO ₂	78
3.3.3.6. Pt/ CeO ₂	85
3.4 Conclusion	91
Reference	91

Chapter 4. The Influence of Structure of Silica and the Doping of Heteroatoms on Ethylene Oxidation over Pt Catalysts

.....	96
4.1. Introduction.....	96
4.2. Experimental.....	97
4.2.1. Synthesis of supports	97
4.2.2. Preparation of catalysts	99
4.2.3. Catalyst characterization.....	99
4.2.4. Ethylene oxidation	101
4.3. Results and discussion	102
4.3.1. The effect of silica with different pore structure and surface silanol group	102

TABLE OF CONTENTS

4.3.2. The effect of SBA-15 with different metal doping	108
4.4. Conclusion	115
Reference	115
 Chapter 5. Selective Hydrogenation of Phenylacetylene by Pt Catalyst Supported on Zeolite-Templated Carbon	 119
5.1. Introduction.....	119
5.2. Experimental.....	120
5.2.1. Catalysts preparation.....	120
5.2.2. Phenylacetylene hydrogenation	120
5.3. Results and discussion	121
5.4. Conclusion	126
Reference	127
 Chapter 6. General Conclusions	 132
 List of Publication	 135
 Acknowledgement	 137

Chapter 1. General Introduction

1.1 Mesoporous materials

According to the IUPAC notation, porous materials are divided into several kinds by their size. Microporous materials have pore diameters of less than 2 nm and macroporous materials have pore diameters of larger than 50 nm; the mesoporous materials contains the pore with sizes between 2 and 50 nm.[1] Materials with disordered or ordered mesostructure can be categorized as mesoporous materials.

MCM-41, which stands for Mobil Composition of Matter No. 41, shows a highly ordered hexagonal array of unidimensional pores with a very narrow pore size distribution. It was prepared by scientist in Mobil Oil Corporation in 1992.[2] Since then many new mesoporous solids were developed based on templating mechanisms related to the procedure for the original MCM-41 preparation. There are lots of prospective applications of mesoporous silica in sorption, gas sensing, ion exchange, catalysis. Figure 1-1 shows that the intrinsic silanol groups of mesoporous silica play an important role in preferential oxidation of carbon monoxide in excess hydrogen.

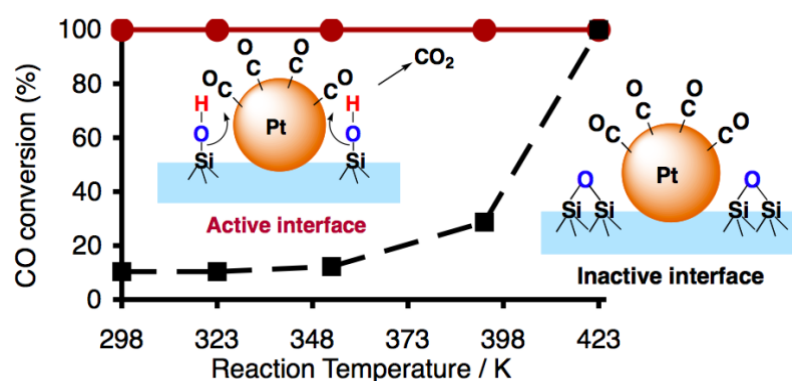


Figure 1-1. Intrinsic catalytic role of mesoporous silica in preferential oxidation of carbon monoxide in excess hydrogen.[3]

1.2 Supported metal catalyst

Supported metal catalysts on various supports (Al_2O_3 , SiO_2 , TiO_2 , CeO_2 , Co_3O_4 , and carbon et al.) can be divided into two types: one is base metal catalyst (Cu, Co, Ni et al.) and the other is precious metal (Pt, Pd, Ru, Au, Ag et al.) catalyst. Base metal catalyst has often been used in carbon dioxide hydrogenation, sulfur dioxide reduction, water-gas shift reaction, oxidation of hydrocarbons and preferential oxidation of carbon monoxide in the presence of excess hydrogen.[4-8] Attractive features of supported base metal catalyst are their low costs and potential commercial benefits. A major practical drawback of base metal catalyst is lower activity compared with that of noble metal catalysts. On the other hand, although the cost of precious metal catalysts is high, their high activity, selectivity and stability in catalysis under various conditions made them has been widely applied in many industries, including both oxidation and hydrogenation reactions, such as refinery, petrochemicals, chemicals, polymer, synthetic fibers, pharmaceuticals and environment. For instance, most of noble metal catalysts are effective for catalytic hydrogenation of pyrolysis gasoline and oxidation of hydrocarbons and CO.[7-10] Because of the high catalytic activities of supported precious metal catalysts on catalytic reactions, I chose study on the catalytic effect of supported noble metal catalysts on complete oxidation of ethylene as oxidation catalysis reaction and selective hydrogenation of phenylacetylene as reduction catalysis reaction. The reasons are explained in the following sections.

1.3 Complete oxidation of ethylene

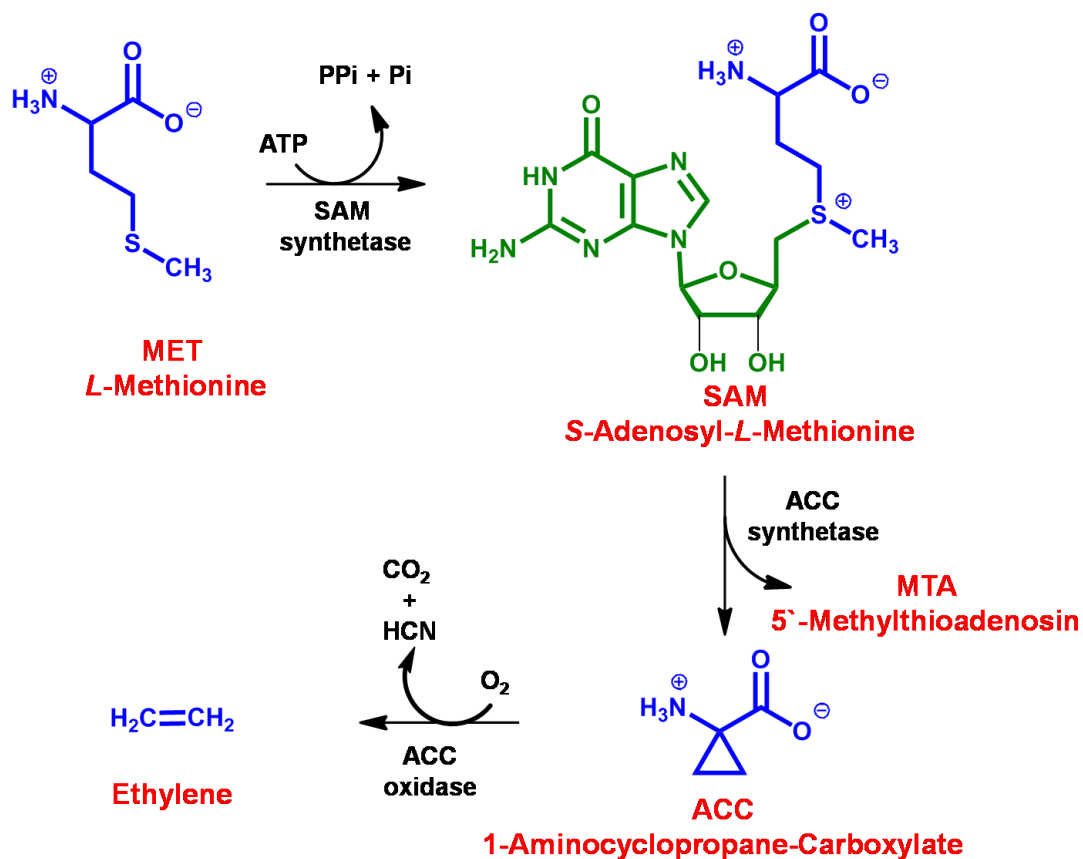
1.3.1 Ethylene

Ethylene (C_2H_4 , also known as IUPAC name: ethene), a colorless, flammable, gaseous organic compound that is the simplest of alkene chemical structures (alkenes contain a carbon-carbon double bond) and the simplest unsaturated hydrocarbon after acetylene (C_2H_2).

Ethylene is also a gaseous plant hormone. It was noted in the 19th century that the leakage from illumination gas street lighting systems caused premature senescence and defoliation of plants in the greenhouse and of trees near gas lines,[11] In 1901, Neljubov provided chemical proof that the active component in illuminating gas to be ethylene but it was not until 1934 that Gane identified that ethylene can be synthesized in ripe apples and in 1935 Crocker proposed ethylene to be the hormone responsible for fruit ripening and senescence of vegetative tissues.[11-13] Since then ethylene has been found to be produced from all parts of higher plants, such as leaves, stems, roots, flowers, fruits tubers, and seedlings. Otherwise, it has been shown that ethylene has an important role in many plant development processes, ranging from germination to senescence, including seed germination, vegetative growth, leaf abscission, flowering, senescence and fruit ripening. Ethylene also plays a role in response to water stress, chilling and mechanical injury.[14]

In the second half of the 20th century, a number of studies were focused on the pathway of ethylene biosynthesis. As reviewed in reference 4, lots of compounds were proposed as the precursors for producing ethylene, such as linolenic acid, propanal, β

-alanine, and methionine et al. Ultimately, it is found by Yang et al. that methionine gives rise to ethylene that needs three key enzymatic reactions. As shown in Scheme 1-1, methionine is firstly converted to SAM (S-Adenosyl-L-Methionine) by SAM synthetase, then, ACC (1-Aminocyclopropane-Carboxylate) synthetase converts SAM to ACC, and the last, ACC oxidase degrades ACC to release ethylene. In this process, the formation of ACC is often cited as the rate limiting step in the pathway; therefore, regulation of this enzyme is the key to the ethylene biosynthesis. The final step requires oxygen and involves the action of the enzyme ACC oxidase, which catalyzed by an oxidative enzyme called ethylene forming enzyme. The control of ethylene production has received considerable study. Study of ethylene has focused around the synthesis promoting effects of auxin, wounding, and drought as well as aspects of fruit-ripening.[14-15]



Scheme 1-1. Pathway of ethylene biosynthesis in plants.

1.3.2 Effects of ethylene on plants

Ethylene, as introduced above biosynthesized from plants plays a significant role in plants. Table 1-1 summarized the plant responses to ethylene. It is shown that ethylene stimulates all of the process in the plant growth from seeds germination to fruit ripening.

Table 1-1. Plant responses to ethylene.[16-20]**Ethylene stimulates**

Stimulates the release of dormancy.

Stimulates shoot and root growth and differentiation (triple response)

Synthesis of ethylene in ripening climacteric fruit.

Ripening of fruit.

Pigment synthesis.

Induction of femaleness in dioecious flowers.

Stimulates flower opening.

Chlorophyll destruction and yellowing.

Seed germination.

Adventitious root formation.

Respiration.

Phenylpropanoid metabolism.

Flowering of bromeliads.

Abscission.

Senescence.

Ethylene inhibits

Ethylene synthesis in vegetative tissue and non- climacteric fruit.

Flower development in most plants.

Auxin transport.

Shoot and root elongation (growth).

Normal orientation of cell wall microfibrils.

Table 1-2. Beneficial and detrimental effects of ethylene on the quality of fresh fruits and vegetables.[16]

Benefits

Promotes color development in fruit.
 Stimulates ripening of climacteric fruit.
 Promotes de-greening of citrus.
 Stimulates dehiscence in nuts.
 Alters sex expression in the cucurbitaceae.
 Promotes flowering in bromeliaceae (e.g. pineapple).
 Reduces lodging of cereals by inhibiting stem elongation.

Detriments

Accelerates senescence.
 Stimulates chlorophyll loss (e.g. yellowing).
 Enhances excessive softening of fruits.
 Stimulates sprouting of potato.
 Promotes abscission of leaves and flowers.
 Stimulates phenylpropanoid metabolism.
 Promotes discoloration (e.g. browning).
 Hastens toughening of vegetables.

Ethylene has often been applied in orchard or greenhouse to growing or post harvesting plants because of its beneficial role in vegetables or fruits as shown in Table 1-2. Deteriorative effects (Table 1-2) are often caused by unintentional exposure of the harvested commodity to ethylene, especially, when plants are grown or stored in confined spaces such as greenhouses, cold storage rooms or refrigerator, or transportation (e.g. ship, truck,). However, it is difficult to simply conclude which response is beneficial or detrimental, because the same ethylene response can play a

beneficial effect on one system and make a detrimental effect on another. Table 1-3 takes examples of ethylene response such as accelerating chlorophyll loss, promoting ripening and stimulating phenylpropanoid metabolism, which are viewed as beneficial in degreening of citrus, ripening of climacteric fruit and defense against pathogens, whereas considered as deleterious in yellowing of green vegetables, overly softening fruit and making a bitter taste.[16] Therefore, it is very necessary to take an advantage of beneficial effect of ethylene, but to eliminate the detrimental effect of ethylene in horticulture, storage room (e.g. warehouse and refrigerator) and transportation (e.g. shipping, truck).

Table 1-3. Examples of how the same ethylene response can be beneficial in one system and detrimental in another.[16]

Example of benefit	Ethylene response	Example of detriment
Degreening of citrus	Accelerates chlorophyll loss	Yellowing of green vegetables
Ripening of climacteric fruit	Promotes ripening	Overly soft and mealy fruit
Defense against pathogens	Stimulates metabolism	Browning and bitter taste

1.3.3 Approach of inhibition or elimination of ethylene

Various methods summarized in Table 1-4 were designed to reduce the deleterious effects of ethylene on plants (e.g. the abscission of flowers, softening of fruits and the senescence of vegetables).

Table 1-4. Strategies to inhibit or eliminate ethylene gas for reducing the detrimental effect of ethylene on plants.

Environmental inhibition

Increasing CO₂ concentration, decreasing O₂ concentration.[21-23]

Lowering storage temperature.[21-25]

Scrubbers.[26]

Chemical inhibition

STS (Silver thiosulfate).[22-23]

2,5-NBD (2,5-Norbornadiene).[23, 27-28]

DACP (Diazocyclopentadiene).[23]

1-MCP (1-Methylcyclopropene).[23, 29-30]

Adsorbent

KMnO₄.[31]

Zeolite.[32]

Carbon.[33]

Biotechnology materials

Soil bacteria, dry biobed and biofilter.[34-43]

Photocatalytic elimination

TiO₂ or Pt/TiO₂.[44-46]

Metal catalytic elimination

Au catalyst.[47-50]

Pt catalyst.[51]

Environmental inhibition of ethylene including increasing carbon dioxide,

decreasing oxygen concentrations and lowering storage temperature are well known antagonists of ethylene action and various packaging and storage methods for fresh horticultural products. They are usually used for storage many types of fruit, however, they are restricted for storage of flowers or potted plants.[21-25] Scrubbers are widely used in storage facilities.[26] The limitation of the scrubbers is the high operation costs and replenishing the ethylene-removing agent. STS as an effective inhibition of ethylene for cut flowers was reviewed by Serek et al., however, it is incompatible with food crops because of the poison of Ag ion as a heavy metal.[22-23] Sisler et al. has reported that NBD was an effective ethylene antagonists, which was limited for commercial use because of its disagreeable odor and continuously presenting for competing ethylene effects.[23, 27-28] DACP has been also applied in different ornamental crops because of its strong ethylene action inhibitor, however, it is an unlikely candidate for commercial use due to its instability and explosive character.[23] Extensive literature have been reported about the effect of 1-MCP on plants, whereas it still restricted for commercial use in two reasons: one is that the issues of 1-MCP application in edible horticultural crops is still under investigation , the other is that much commercially relevant research on its effects is proprietary and public research is used only as required to investigate longer-term problems.[23, 29-30] Absorbent such as KMnO_4 , Zeolite and carbon were also chosen for removing ethylene from the air to reduce the damage the plants. It has been found KMnO_4 is very effective for ethylene elimination, however, its chemical properties makes easily contaminates food products and the waste disposal may be an additional issue.[31-33] In addition, biotechnological

materials such as soil bacteria, dry biobed and biofilter were also applied in ethylene removing.[34-43] However, high cost for its production and its inefficiency in removal of trace ethylene remained as drawbacks. Some photocatalysts were also prepared for complete oxidation of ethylene,[44-46] they were limited due to the more complicated working conditions. Therefore, in order to overcome the disadvantages above mentioned, more environmental friendly and effectively method should be developed.

1.3.4 Removal of ethylene with precious metal catalysts

Gold is not found as an effective catalyst until Haruta et al. discovered in 1987 that the small size of the AuNPs ($< 5\text{nm}$) supported on semiconduction transition-metal oxides, such as iron oxide could efficiently catalyze the oxidation of carbon monoxide to carbon dioxide at low temperature.[52] The surprising discovery made nano-gold has been widely studied for decades. Both academic and industry have paid more attention to nano-gold catalysts and predicted more extensive and increasing application prospects.[53] As summarized in Table 1-4, supported Au catalysts has been applied in complete oxidation of ethylene at high temperature by Ahn's group.[47] For efficient elimination of trace ethylene at low temperature, Hao's group made lots of efforts on preparing Au catalysts. Firstly, Au nanoparticle supported on various metal oxides such as ZnO, Fe₂O₃, TiO₂ and Co₃O₄ were prepared by the deposition-precipitation method. It is found that Au/Co₃O₄ is the most effective catalyst for elimination of trace ethylene at room temperature. However, the conversion of ethylene at 20°C is only 7.4% from a relatively low concentration.[48] Au nanoparticles supported on mesoporous Co₃O₄ were later prepared by a nanocasting method. It was reported that mesoporous Co₃O₄,

with reactive planes $\{110\}$ producing the surface-active oxygen species easily, are more active than Co_3O_4 nanosheets with $\{112\}$ planes which is corresponded with the results for CO oxidation that Co_3O_4 nanorod with high exposure of $\{110\}$ plane including lots of Co^{3+} active site inducing high catalytic activity as shown in Figure 1-2.[54] But the catalytic activity was still insufficient for complete removal of trace (50 ppm) ethylene at 0°C .[49] Au nanoparticles supported on Co_3O_4 nanorod, nanopolyhedra and nanocubes were also prepared for studying the morphology effects of Co_3O_4 on the catalytic activity of Au/ Co_3O_4 catalysts for complete oxidation of trace ethylene. It has been observed that Co_3O_4 nanorod shows the highest catalytic activity because its exposition crystal plane is $\{110\}$, while the dominant exposed planes of Co_3O_4 -nanopolyhedra and -nanocubes are $\{011\}$ and $\{001\}$ planes. Compared with $\{011\}$ and $\{001\}$ planes, $\{110\}$ shows the maximum amount of oxygen vacancies.[50]

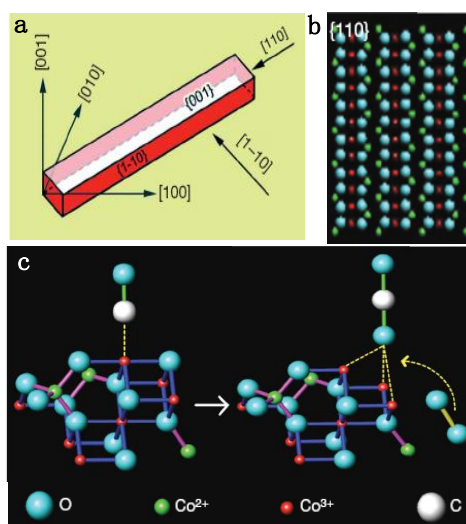


Figure 1-2. Possible reaction pathway for CO oxidation on Co_3O_4 nanorod. a, Shape of the nanorod, where red represents the catalytically active planes. b, The surface atomic configurations in the $\{110\}$. c, A ball-and-stick model for CO adsorption and oxidation on the active Co^{3+} site. [54]

Pt catalyst has been extensively applied in various chemical reactions. Its using in automobiles as a catalytic converter is the most important application, which allows the complete combustion of low concentrations of unburned hydrocarbons from the exhaust into carbon dioxide and water vapor. Platinum catalysts are also employed in the petroleum industry in a number of separate processes, especially in catalytic reforming. In addition, Pt catalyst has also been widely applied in CO oxidation in catalytic converters, the decomposition of hydrogen peroxide into water and oxygen gas and H_2/O_2 reaction in fuel cells.[55] Lots of work has been made to prepare Pt catalyst for removing the ethylene gas in VOC at higher temperature or kinetic study of the support effect on the catalytic activity of ethylene oxidation.[56] Manaka et al. made efforts to decrease the reaction temperature for eliminating ethylene less than 100°C by preparation of Pt nanoparticles supported on $\text{Ce}_{0.64}\text{Zr}_{0.16}\text{Bi}_{0.20}\text{O}_{1.90}/\gamma\text{-Al}_2\text{O}_3$. [51] However, lots of work need to do to overcome the completely remove ethylene at lower temperature (e.g. room temperature or 0°C).

1.4 Selective hydrogenation of phenylacetylene

Phenylacetylene is a poisoning impurity in styrene feedstocks that causes deactivation of the styrene polymerization catalyst and degrades polystyrene properties. Therefore, removal of phenylacetylene to styrene by selective hydrogenation is an important industrial process. The phenylacetylene semihydrogenation can be carried out under very mild conditions; consequently, it has been often applied as a model reaction for testing of hydrogenation catalysts.[57-59] Up to now, both homogeneous

[60-62] and heterogeneous catalysts [63-68] have been employed for selective hydrogenation of alkynes. Homogenous catalysts contain a monomeric metal ion coordinated by various ligands. In this system, the catalyst and the reactant are in the same phase. The main advantage of homogenous catalysts is that the activity and selectivity can be controlled by changing the catalyst's molecular properties. The main drawback is the problem of catalyst separation and recovery, which prevents scientific successes from becoming commercial ones. However, Compared with homogeneous catalysts, heterogeneous catalysts are consist of metal nanoparticles supported or immobilized on solid supports. They can be easily recovered and reused reflecting the robustness of the catalysts. Most of the catalysts used in practical application are heterogeneous catalysts.

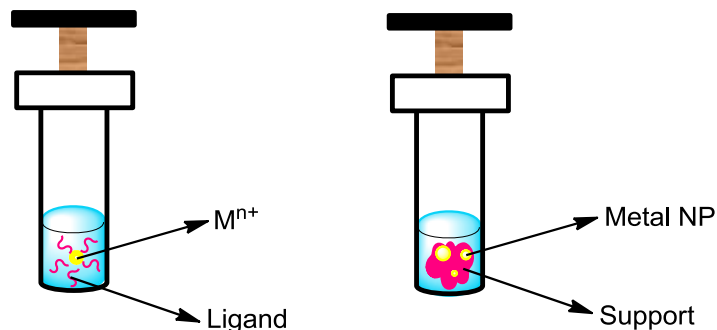


Figure 1-3. Homogenous (left) and heterogeneous (right) catalyst.

It is well known that in heterogeneous catalytic reaction, metal-support effect plays a key role in activity and selectivity. Zeolite-templated carbon (ZTC) [69] is a carbon replica obtained from a zeolite as a template (shown in Figure 1-4), giving ordered three-dimensional micropores consisting of nano-sized graphene units. It has been extensively studied as attractive materials for storage of hydrogen,[70]

electrochemical capacitors and lithium ion batteries,[71] its application in catalysis has been limited to the studies related with fuel cell.[72-73] Herein, it is interesting to using ZTC as support for preparation of Pt catalyst with its application in the semihydrogenation of phenylacetylene.

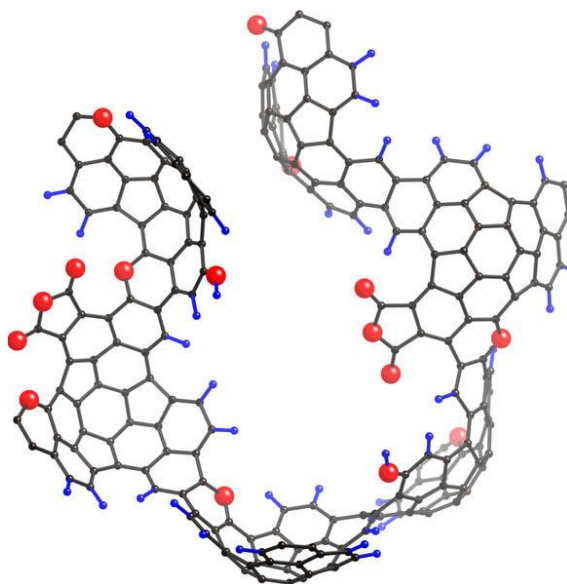


Figure 1-4. An idealized model of ZTC.

1.5 Purpose of the present work

The aims of this thesis include two parts: one is the development of active catalysts for the elimination of ethylene at low temperature; the other is the study of selective hydrogenation of phenylacetylene into styrene by using novel Pt/ZTC catalyst. This thesis is divided in six parts. The main core of this text is composed of the Chapters II, III and IV.

Chapter II consists in the screening of metal and supports effects for the oxidation of ethylene. In addition, the most effective catalyst was applied in low-temperature elimination of trace ethylene.

Chapter III describes the mechanistic study of the supports effects on the catalytic oxidation of ethylene by *in-situ* DRIFTS. The detailed reaction pathways of Pt catalysts supported on different metal oxides such as MCM-41, SiO₂, Al₂O₃, ZrO₂, TiO₂ and CeO₂ were also investigated.

Chapter IV investigates the pore structure and surface silanol group of silica and metal doping in SBA-15 effect on the catalytic activity of ethylene oxidation.

Chapter V is dedicated to the application of novel ZTC supported Pt catalyst on selective hydrogenation of phenylacetylene to styrene. The influence of precursors and supports on the catalytic activity was investigated.

Chapter VI summarizes and integrates the main conclusions withdrawn from this work.

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Chapter 2. Low-Temperature Oxidation of Ethylene over Pt Nanoparticles Supported on Mesoporous Silica

2.1 Introduction

Ethylene is a gaseous volatile organic compound (VOC) that works as a plant hormone to inhibit or promote plant growth. Ethylene released from fruits, vegetables and flowers can accelerate aging and spoiling of plants even in refrigerators at low temperature. Consequently, the elimination of trace amounts of ethylene at low temperature (ca. 0°C) is imperative.

Previously, biotechnological materials such as soil bacteria, dry biobeds and biofilters were applied for removal of ethylene.[1-4] However, high production costs and inefficiency in removing trace amounts of ethylene were drawbacks of these methods. Several photocatalysts have also been used,[5-8] but this resulted in limited application due to the requirement for more complicated working conditions.

Many attempts have been made by Hao et al. to develop Au catalysts supported on Co_3O_4 for removal of ethylene at low temperature. First, 2 wt% Au/ Co_3O_4 catalyst prepared by a deposition-precipitation method showed only 7.4% conversion of ethylene at 20°C from a relatively low concentration (1050 ppm).[9] A more active catalyst, 2.5 wt% Au nanoparticles supported on mesoporous Co_3O_4 , was later prepared by a nanocasting method, but the catalytic activity was still insufficient for complete removal of trace (50 ppm) ethylene at 0°C despite the complicated preparation method.[10] Au nanoparticles supported on Co_3O_4 rods recently prepared by a

hydrothermal method solved the time-wasting problem in catalyst preparation; however, the method afforded no significant improvement in catalytic activity.[11] Therefore, further catalyst screening is still necessary to find sufficiently active catalysts for removal of low concentrations of ethylene.

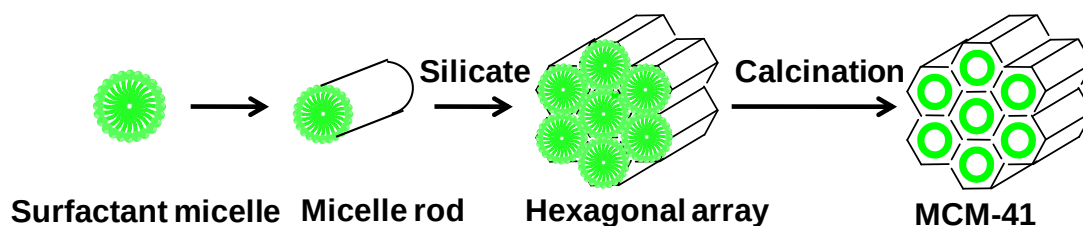
Herein, we report our work on the catalytic performance of Pt nanoparticles supported on mesoporous silica MCM-41 in ethylene oxidation under low temperature conditions. This study has revealed the influence of metals (Pt, Pd, Au and Ag) and supports (MCM-41, SiO₂, Al₂O₃, ZrO₂, TiO₂ and CeO₂) on the catalytic performance. The Pt nanoparticles supported on MCM-41 exhibited the highest activity and demonstrated excellent durability in prolonged reaction time or recycle use. The conversion of 50 ppm ethylene over 1 wt% Pt/MCM-41 at 0°C was >99.8%. To the best of our knowledge, this is the highest conversion of ethylene oxidation at low temperature reported to date.

2.2 Experimental

2.2.1 Synthesis of supports

MCM-41 was synthesized according to the reported method.[12] Sodium silicate (Kanto, 35~38 wt% SiO₂, 17~19 wt% Na₂O) was used as a silica source, and the silica source was firstly diluted by water, then added dropwise to the clear solution of *n*-hexadecyltrimethylammonium bromide (C₁₆TMABr) at room temperature with vigorous stirring. The molar composition of the resulting mixture is C₁₆TMABr: SiO₂: Na₂O: H₂O = 1: 4.3: 1.6: 302. After stirring at room temperature for 1 h, the gel mixture

was heated at 100°C for 24 h. Then the mixture was cooled to room temperature, and the pH was adjusted to 10 by using acetic acid. The mixture was then heated at 100°C for 48 h. The pH adjustment and heating procedures were repeated twice. The precipitated solid was filtered and washed thoroughly with 3000 mL deionized water. The solid was dried at 100°C in an oven and calcined in air at 550°C to remove the surfactant. The detailed procedure has been shown in Scheme 1.



Scheme 2-1. The procedure for preparation of MCM-41.

The procedure for preparing mesoporous ZrO_2 was similar to that in literature.[13] A micellar solution was prepared by dissolving P123 (10 wt%) and Brij56 [$\text{C}_{16}(\text{EO})_{10}$] (10 wt%) in distilled water at room temperature with stirring for more than 3 h. An appropriate amount of zirconium propoxide [$\text{Zr}(\text{OC}_3\text{H}_7)_4$] was added dropwise into the above solution to give a surfactant-to-Zr molar ratio of 0.35. After further stirring for 1 h, the mixture was transferred into a Teflon-lined autoclave and heated at 130°C for 12 h. The product was filtered three times, dried at 110°C for 12 h and then calcined in air at 500°C for 6 h to remove the surfactant.

2.2.2 Preparation of catalysts

All the catalysts were prepared by using the impregnation method. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, PdCl_2 , $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, and AgNO_3 were used as metal precursors. MCM-41, SiO_2 (Fuji

Silysia, Cariat Q-10), γ -Al₂O₃ (Nishio Kogyo, A-11), mesoporous ZrO₂, TiO₂ (JRC-TIO-4) and CeO₂ (JRC-CEO-2) were used as catalyst supports. Typically, 1.0 g of support material was impregnated with 50 mL aqueous solution containing the required amount of metal precursor salts. The mixture was stirred for 18 h, evaporated and dried under vacuum overnight. The resulting solid was calcined under O₂ flow at 200°C for 2 h, and then reduced under H₂ flow at 200°C for 2 h.

2.2.3 Catalyst characterization

X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were obtained by a Rigaku diffractometer (Rigaku Miniflex) with Cu K α radiation ($\lambda = 0.15418$ nm). The scanning rate of the diffractometer is 2° min⁻¹. The measurement was carried out by an X-ray generator with a voltage of 30 kV and a current of 15 mA.

Nitrogen adsorption

The nitrogen adsorption/desorption isotherms at about -196°C were obtained by a Belsorp mini II (BEL Japan) after heating the samples at 120°C under vacuum for 6 h, the specific surface area and the pore-size distribution were calculated by Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively, where the range of a P/P° is changed from 0.05 to 0.995.

Transmission electron microscopy (TEM)

The microstructure of the metal particles was investigated by a transmission electron microscopy (TEM, JEM-2100F) with accelerating voltage of 200 kV. The samples for TEM measurements were prepared by placing a drop of dilute ethanol

suspension of supported metal particles onto a copper grid and allowing ethanol to be evaporated in air.

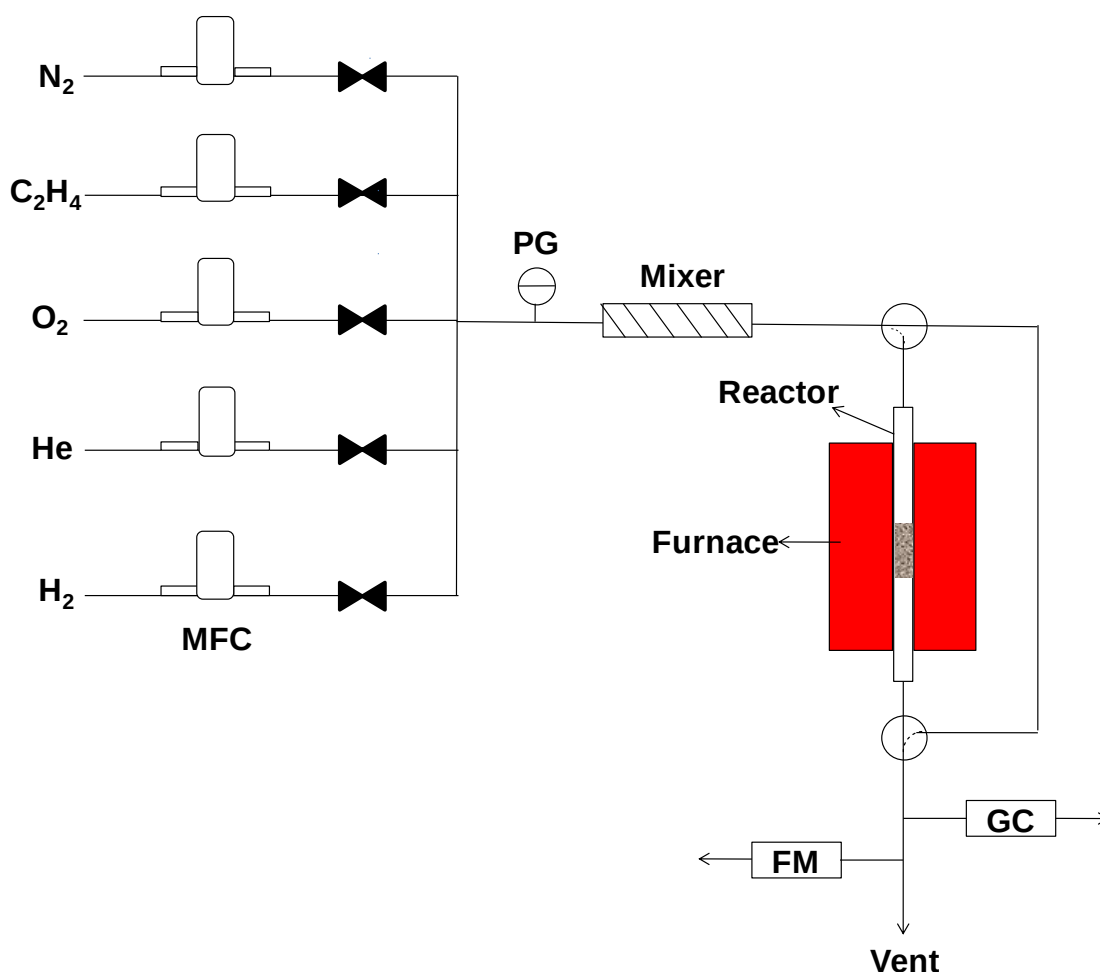
CO chemisorption

The dispersions of the Pt nanoparticles were measured by CO chemisorption on a BELCAT-A (BEL Japan). Prior to each chemisorption experiment, a sample was reduced by H₂ with a flow rate of 30 mL min⁻¹ at 200°C for 2 h, followed by cooling to 50°C under He flow. The chemisorption of CO was performed at 50°C (with 10% CO in He), where an equilibrium was assumed when no further CO adsorption was observed. Pt dispersions were obtained based on the amount of CO adsorbed and assuming 1:1 ratio for Pt:CO.

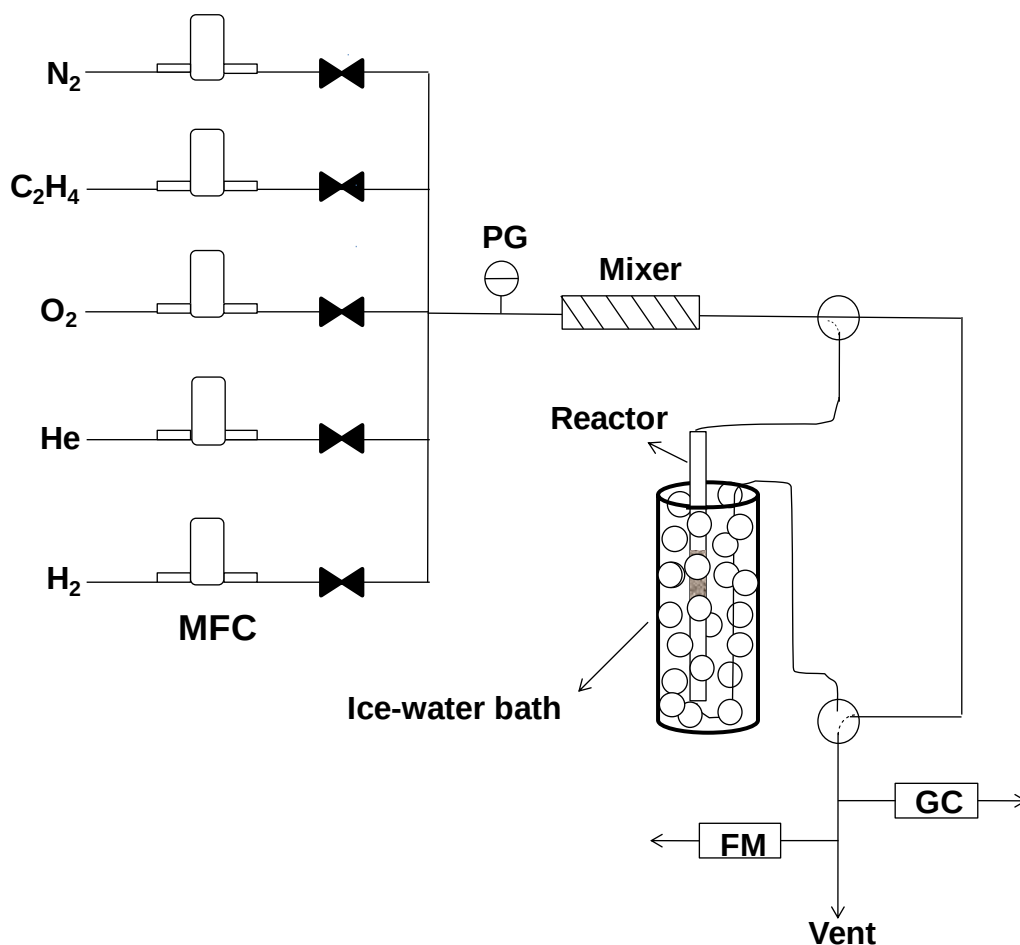
2.2.4 Ethylene oxidation

The catalytic oxidation of C₂H₄ was performed in a stainless steel tubular fixed-bed reactor (i.d. = 4 mm) under atmospheric pressure in a flow apparatus (Scheme 2-2) which consists of a feed unit, the reactor and an analysis unit utilizing on-line gas chromatography. Each catalyst (0.20 g, 40-60 mesh) loaded in the reactor was pretreated under a H₂ stream (30 mL min⁻¹) at 200°C for 1 h before use. The reactant gas mixture [C₂H₄ (99.99%) 0.32 vol%, O₂ (99.999%) 20 vol%, N₂ (99.999%) 5 vol%, He (99.999%) balance] was fed to the reactor using mass flow controllers to achieve the desired flow rates. After reaching a steady state, typically in ca. 1 h, the reaction temperature was gradually increased from room temperature to 200°C (1°C min⁻¹), and the outlet gas was analyzed at every 5°C interval using an on-line gas chromatograph [Agilent 3000A Micro GC equipped with thermal conductivity detector

(TCD) and a column of molecular sieves 5A (10 m) and Plot U (8 m)]. The catalytic performance of 1 wt% Pt/MCM-41 (0.40 g, 40-60 mesh) was also investigated at 0°C with 50 ppm of C₂H₄. Scheme 2-3 shows the experimental apparatus for ethylene oxidation at low temperature, first the catalyst was pretreated in furnace at 200°C for 1h, and then the reactor was put in ice-water bath for 0°C reaction. The detection limit of C₂H₄ was 0.1 ppm in the present analysis. The C₂H₄ conversions ($\chi_{C_2H_4}$) were calculated as follows: $\chi_{C_2H_4} = ([C_2H_4]_{in} - [C_2H_4]_{out}) / [C_2H_4]_{in} \times 100$ (%), where [C₂H₄]_{in} and [C₂H₄]_{out} is the concentration of C₂H₄ introduced to the reactor and that detected after the reactor, respectively.



Scheme 2-2. Schematic representation of the experimental apparatus for high-temperature reaction.



Scheme 2-3. Schematic representation of the experimental apparatus for low-temperature reaction.

2.3 Results and discussion

2.3.1 Catalyst characterization

All of the catalysts were prepared by using a typical wet impregnation method. Characterization of the catalysts was conducted by various physicochemical methods. The structural parameters such as BET surface area (S_{BET}), BJH pore size, particle size calculated by the Scherrer equation (D_x), Particle size calculated from TEM images (D_{TEM}), uptake of CO on Pt surface in the pulse mode and Particle size calculated based on CO uptake (D_c) are summarized in Table 2-1.

Table 2-1. Structural parameters of supports and catalysts.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^[a]	Pore size (nm) ^[b]	D_x (nm) ^[c]	D_{TEM} (nm) ^[d]	CO/Pt ^[e]	D_c (nm) ^[f]
MCM-41	1006	2.9	—	—	—	—
SiO ₂	256	22	—	—	—	—
Al ₂ O ₃	128	3.8	—	—	—	—
ZrO ₂	77	5.8	—	—	—	—
TiO ₂	48	—	—	—	—	—
CeO ₂	129	8.1	—	—	—	—
Pd/MCM-41	889	2.8	3.7	—	—	—
Ag/MCM-41	770	2.8	23	—	—	—
Au/MCM-41	822	2.8	35	—	—	—
Pt/MCM-41	913	2.9	2.4	2.9 ± 0.7	0.38	3.0
Pt/ SiO ₂	270	18	5.8	4.3 ± 1.2	0.25	4.6
Pt/Al ₂ O ₃	143	3.1	—	2.0 ± 1.0	0.44	2.6
Pt/ZrO ₂	72	4.9	—	1.2 ± 0.5	0.50	2.3
Pt/TiO ₂	52	—	—	2.8 ± 1.1	0.20	5.7
Pt/CeO ₂	99	6.2	—	2.1 ± 0.6	0.29	4.0
Pt/MCM-41	820	2.8	1.7	2.0 ± 0.6 ^[g]	0.51	2.2
				2.1 ± 0.5 ^[h]		

[a] BET (Brunauer-Emmett-Teller) surface area.

[b] Pore diameter by the BJH (Barrett-Joyner-Halenda) method.

[c] Particle size calculated by the Scherrer equation.

[d] Particle size calculated from TEM images.

[e] Uptake of CO on Pt surface in the pulse mode.

[f] Particle size calculated from $D_c = 1.13/D$, where D is the metallic dispersion (CO/Pt) based on CO uptake.

[g] Before reaction.

[h] After reaction

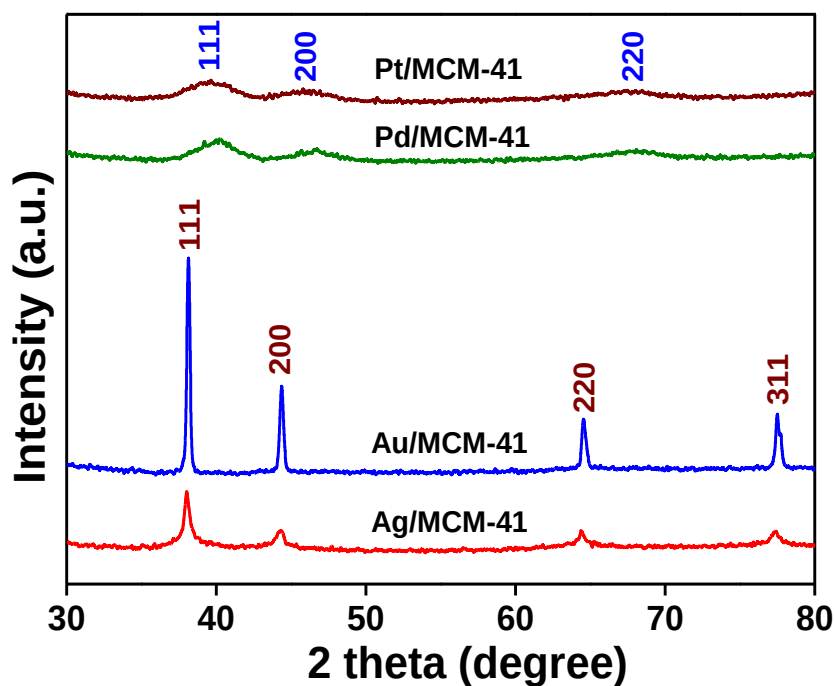


Figure 2-1. Wide angle XRD patterns of different metal catalysts supported on MCM-41.

Figure 2-1 shows the wide angle XRD patterns of different metal catalysts supported on MCM-41. By comparison with the JCPDS card (No. 04-0802), the three diffraction peaks of wine line at 2θ of 40° , 46° , and 67° respectively, could be indexed as (111), (200) and (220) Bragg's reflections of face-centered cubic (fcc) structure of Pt. The similar three peaks of olive line appeared at 40° , 47° , and 68° respectively, are assigned to (111), (200) and (220) Bragg's reflections of face-centered cubic (fcc) structure of Pd, which are corresponded with the JCPDS card (No. 89-4897). On the other hand, comparison of the JCPDS card (No. 89-3697 and No. 89-3722, respectively), the four peaks of blue and red lines centred at 38° , 44° , 64° , 77° , which can be assigned to the (111), (200), (220) and (311) reflections of face-centered cubic (fcc) Au and Ag crystal. The particle size of Pt, Pd, Au and Ag calculated by Scherrer

equation are 2.4, 2.7, 23, 35nm, respectively, as summarized in Table 2-1.

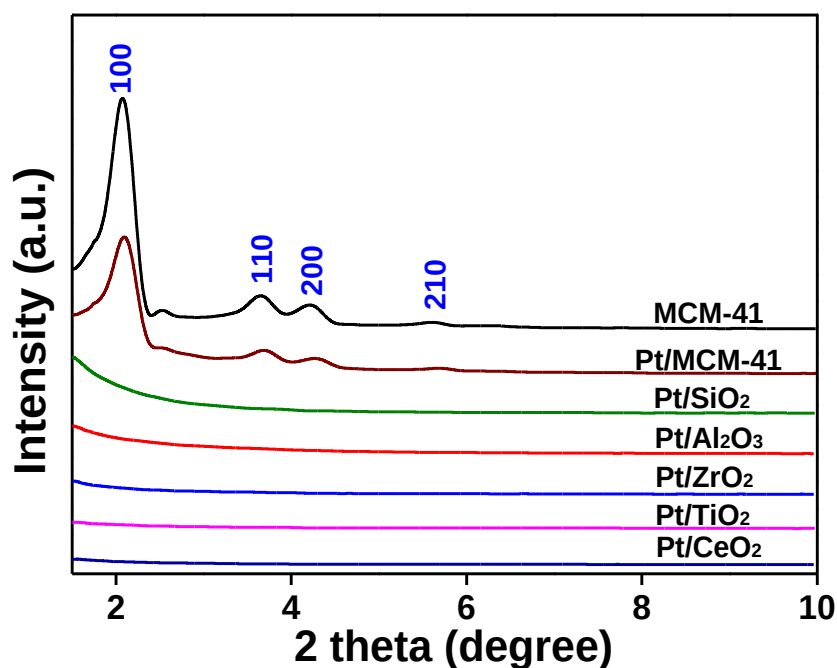


Figure 2-2. Small angle XRD patterns of Pt catalysts over different supports.

Figure 2-2 shows the small angle XRD patterns of MCM-41 and 5 wt% Pt/MCM-41, which are consistent with the reported literature.[14] The peaks appeared at (100), (110) and (200), are characteristic of a typical two-dimensional hexagonal structure of mesopores in MCM-41. This indicates that the mesoporous structure remains unchanged after incorporation of Pt nanoparticles. However, no such peaks were present in Pt/SiO₂, Pt/Al₂O₃, Pt/ZrO₂, Pt/TiO₂ and Pt/CeO₂, showing the absence of ordered structures.

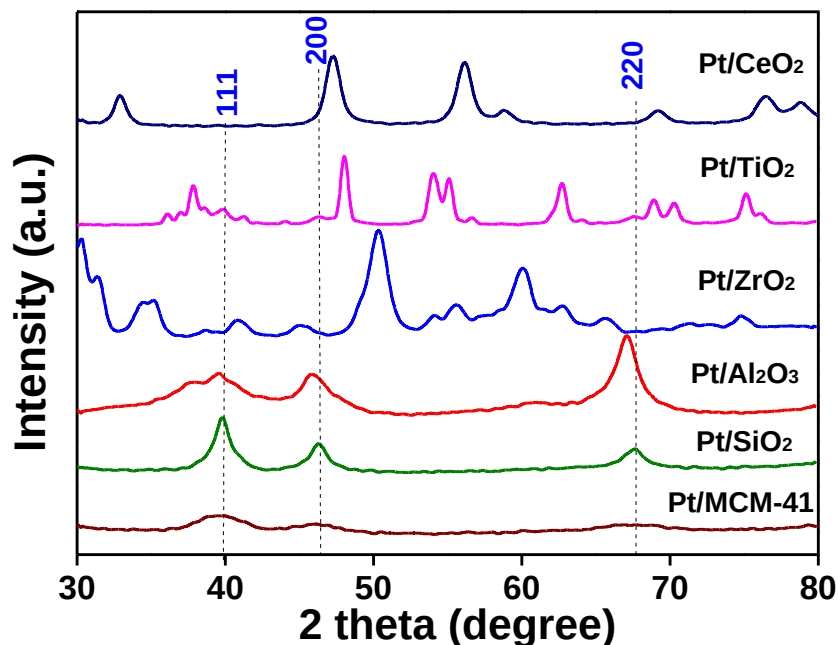


Figure 2-3. Wide angle XRD patterns of Pt catalysts over different supports.

In the wide angle region (Figure 2-3), Pt/MCM-41 and Pt/SiO₂ have three characteristic XRD peaks at 40°, 46°, and 67°, which can be assigned to (111), (200) and (220) reflections of face-centered cubic (fcc) Pt crystals as described in Figure 2-1. The particle sizes of Pt for Pt/MCM-41 and Pt/SiO₂ estimated by the Scherrer equation with the (111) peaks are 2.4 and 5.8 nm, respectively. In contrast, no Pt peak was observed in XRD patterns of Pt/Al₂O₃, Pt/ZrO₂, Pt/TiO₂ and Pt/CeO₂, which may be due to the smaller Pt particle size formed on the four supports as shown in the TEM images (Figure 2-6).

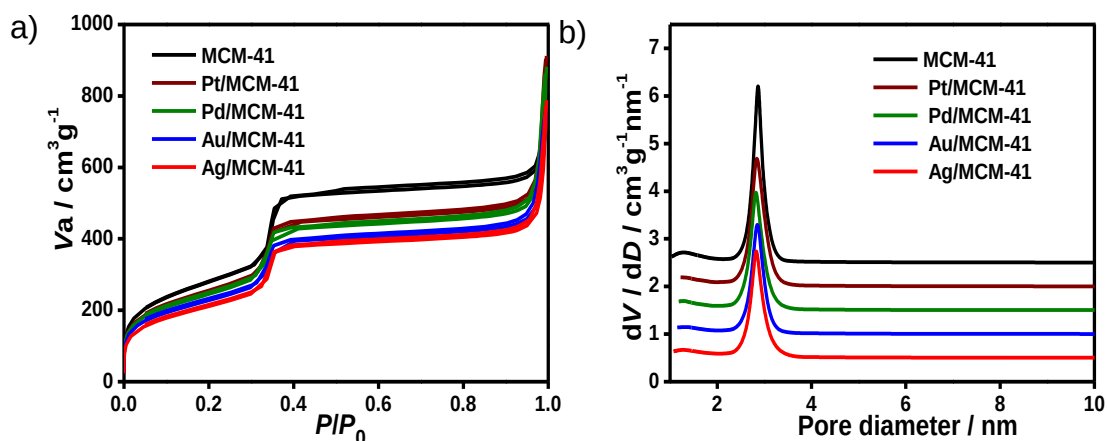


Figure 2-4. The nitrogen adsorption/desorption isotherms a) and BJH pore size distributions b) of MCM-41 and different metal catalysts supported on MCM-41.

The nitrogen adsorption/desorption isotherms and BJH pore size distributions of MCM-41 and Pt, Pd, Au and Ag catalysts supported on MCM-41 were shown in Figure 2-4. All of the curves in Figure 2-4a display typical type IV adsorption isotherms, indicating the mesoporous structure of each material. The pore structure of each catalyst has not been changed as represented in Figure 2-4b. As summarized in Table 2-1, the BET surface areas of MCM-41, Pt/MCM-41, Pd/MCM-41, Au/MCM-41 and Ag/MCM-41 are 1006, 913, 889, 822 and 770 $\text{m}^2 \text{g}^{-1}$, respectively, which illustrates the BET surface areas are decreased with the metal particle size increasing. The corresponded pore sizes are 2.9, 2.9, 2.8, 2.8 and 2.8 nm, respectively, indicating the no change of the pore structure and no plugging of the pores by metal nanoparticles.

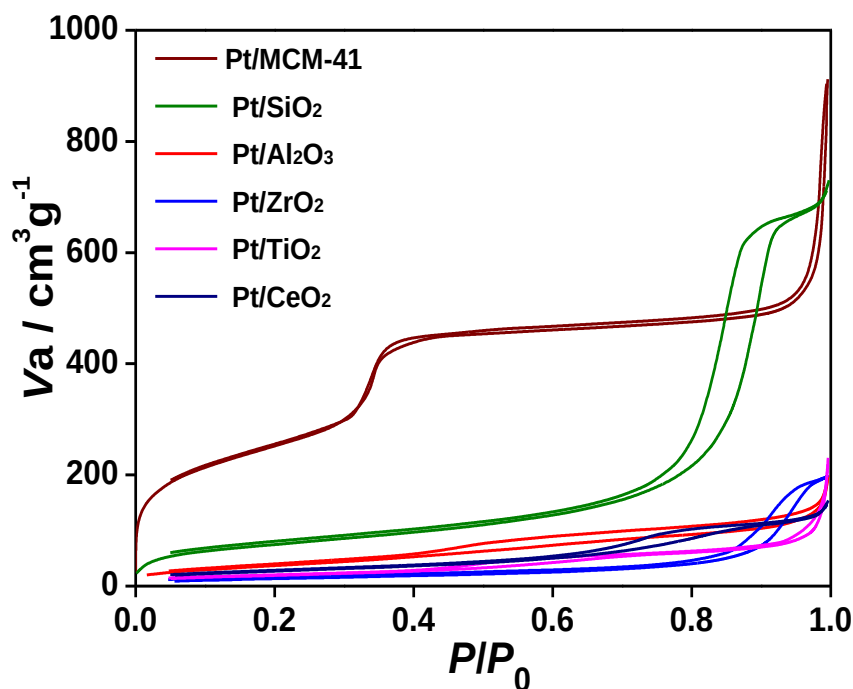
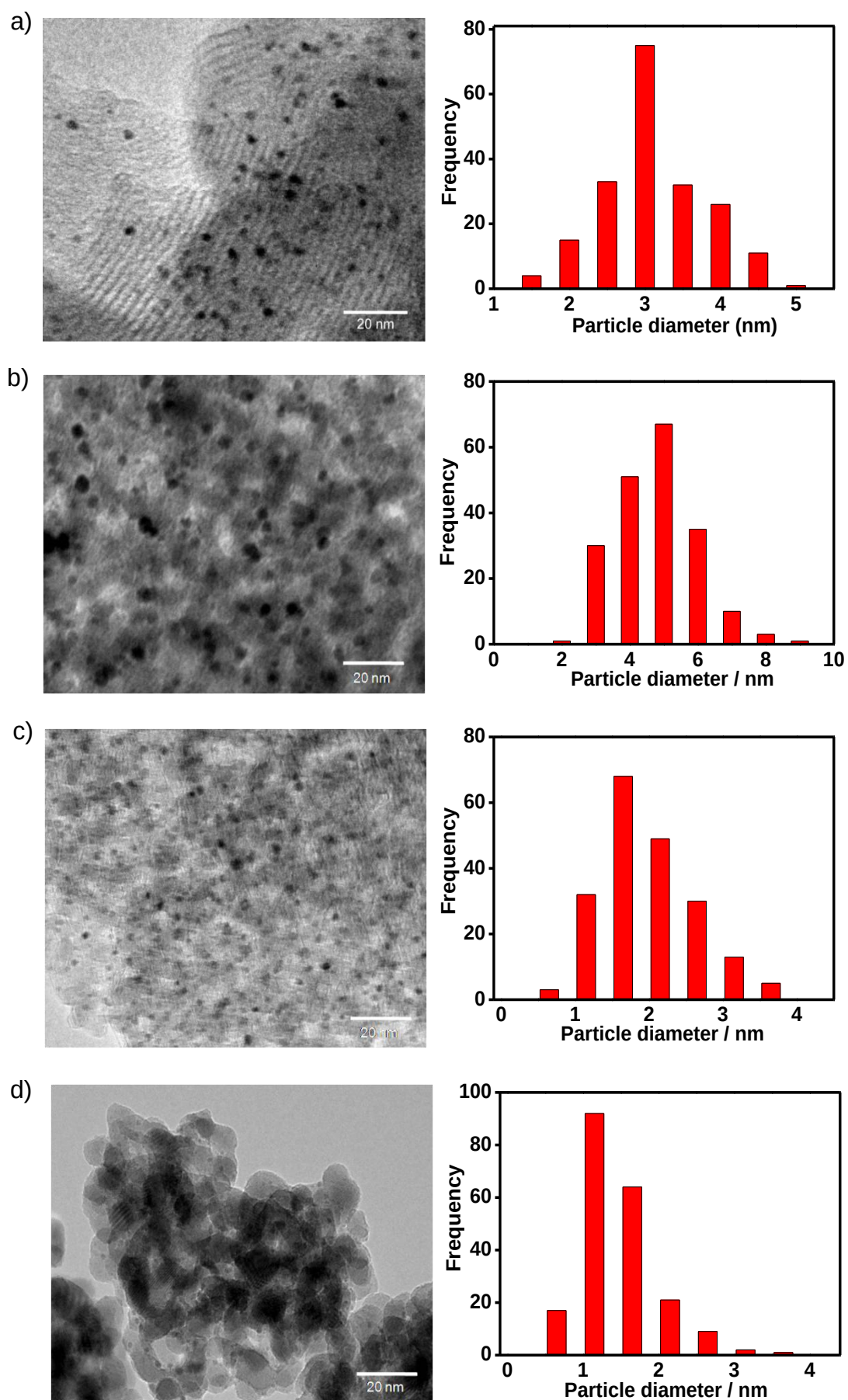


Figure 2-5. The nitrogen adsorption/desorption isotherms of Pt catalysts supported on various metal oxides.

Figure 2-5 reveals the nitrogen adsorption/desorption isotherms of various Pt catalysts. It is found that the type IV adsorption isotherms of Pt catalysts can be observed, which displays the mesoporous structure of each catalyst. The different shape of the curves may be due to the different structure of each catalyst. The BET surface areas and pore sizes of the supports and Pt catalysts are also listed in Table 2-1. The surface areas and pore sizes of the Pt catalysts were almost the same as the pure supports, indicating high homogeneity of the pore size and no plugging of the pores by Pt nanoparticles.



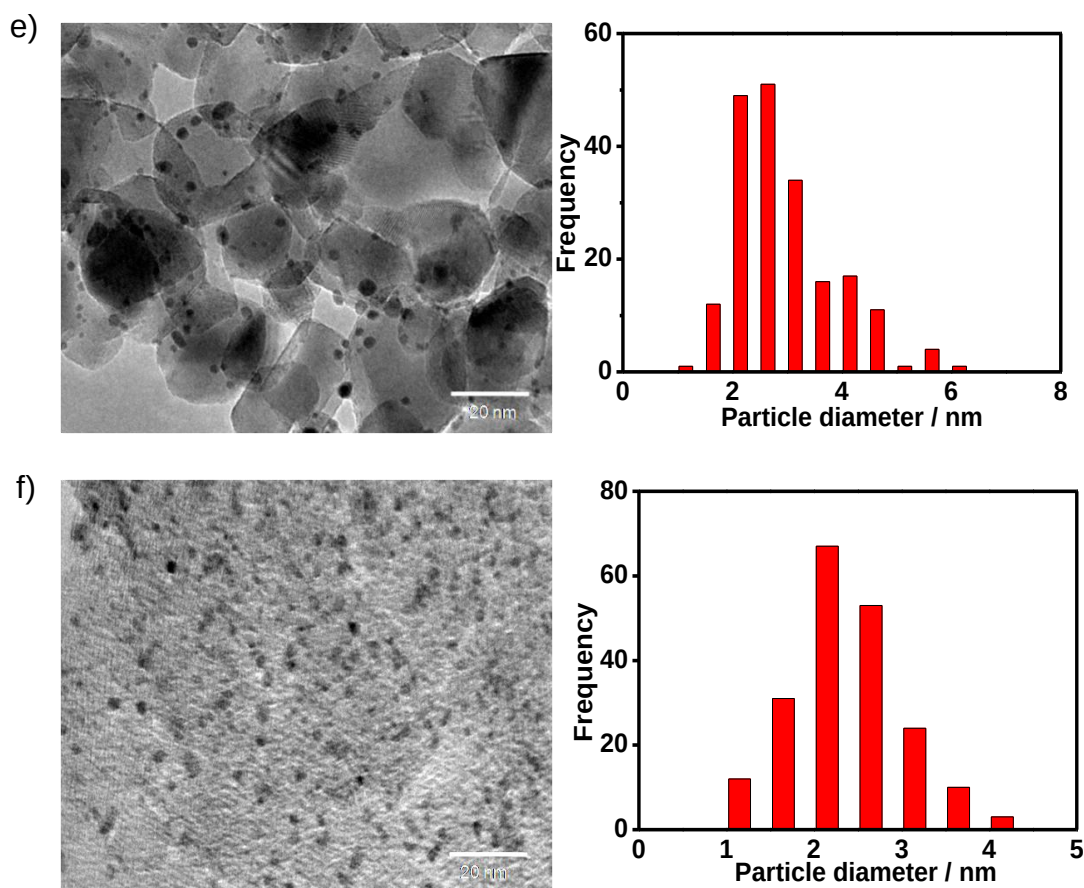


Figure 2-6. TEM images and Pt particle size distributions of a) 5% Pt/MCM-41, b) 5% Pt/SiO₂, c) 5% Pt/Al₂O₃, d) 5% Pt/ZrO₂, e) 5% Pt/TiO₂ and f) 5% Pt/CeO₂.

Typical TEM images of supported Pt catalysts are shown in Figures 2-6 with the corresponding particle size distribution from more than two hundred particles. Ordered mesoporous channels and highly dispersed Pt nanoparticles were observed for Pt/MCM-41 in Figure 2-6a. The Pt particle sizes in TEM are in the range of 1.2-4.3 nm (Table 2-1). Similarly, the corresponding particle sizes (D_c) based on CO chemisorption is 2.3-5.7 nm, which were calculated by the literature method.[15,16] Therefore, in these samples, we deduce most of the Pt surface is exposed to the gas phase.

2.3.2 Catalyst screening

Figure 2-7 shows the light-off curves of ethylene conversion over different metals on MCM-41. Complete oxidation of ethylene was observed on Pt/MCM-41 over a wide range of reaction temperatures (25-200°C). However, ethylene conversion was less than 40% for Pd/MCM-41 and Au/MCM-41 at 25-50°C. An increase in reaction temperature afforded >99.8% conversion over 145°C for Pd/MCM-41 and 96% conversion at 200°C for Au/MCM-41. At any given temperature, Ag/MCM-41 catalyst provided only 40% ethylene conversion. From these results, it can be concluded that Pt is the most effective metal for ethylene oxidation under these conditions.

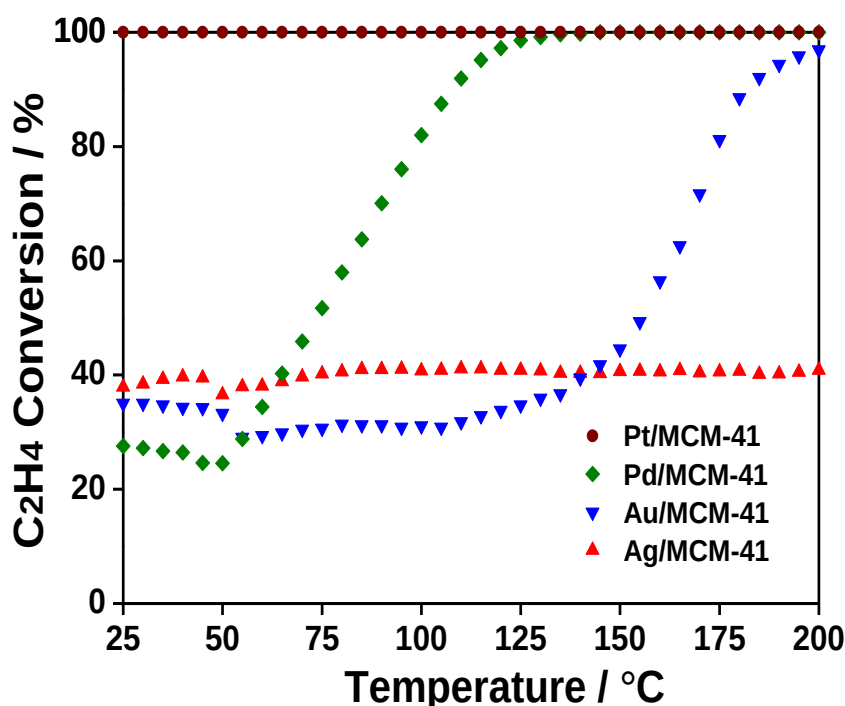


Figure 2-7. Light-off curves of catalytic ethylene conversion over different metals supported on MCM-41. Pt loading: 5 wt%; space velocity (SV): 1500 mL h⁻¹ g⁻¹; catalyst: 0.2 g; C₂H₄: 0.32 vol%; O₂: 20 vol%; N₂: 5 vol%; He balance.

The effect of the support was also investigated using Pt catalysts supported on MCM-41, SiO₂, Al₂O₃, ZrO₂, TiO₂ and CeO₂ (Figure 2-8). The catalytic activities were ranked as follows: Pt/MCM-41 > Pt/SiO₂ > Pt/Al₂O₃ > Pt/TiO₂, Pt/ZrO₂ > Pt/CeO₂. The difference in catalytic activity between Pt/MCM-41 and Pt/SiO₂ might be attributed to the difference in particle size and surface area of Pt. As shown in Table 2-1, the particle size of Pt for Pt/MCM-41 is smaller than that for Pt/SiO₂. Normally, higher BET surface areas afford smaller Pt particles, which induce higher catalytic activities.[17] In this regard, it is interesting that extremely low ethylene elimination efficiency was obtained with Pt catalysts supported on Al₂O₃, ZrO₂, TiO₂ and CeO₂, where particle sizes are smaller than active Pt/MCM-41 and Pt/SiO₂ catalysts.

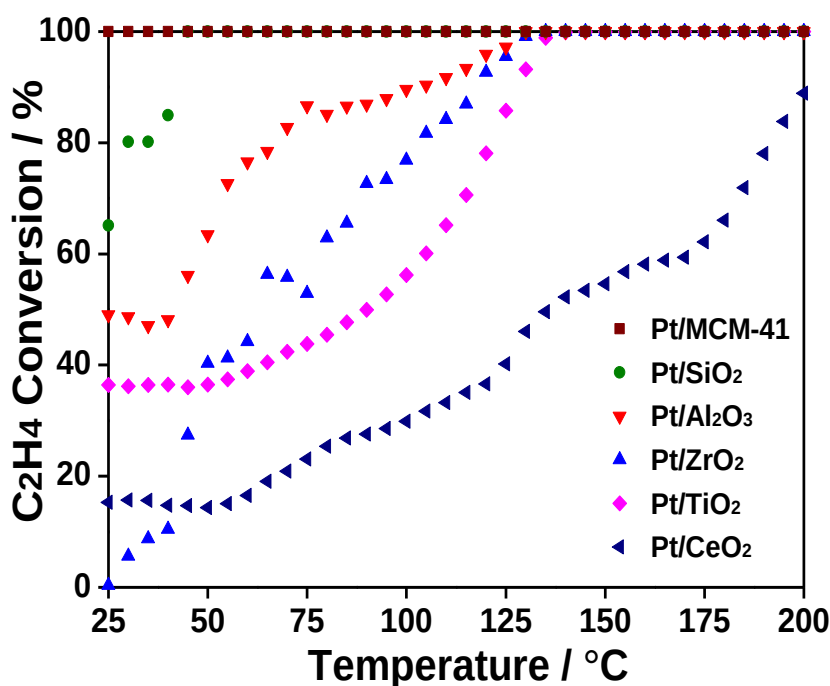


Figure 2-8. Light-off curves of catalytic ethylene conversion over Pt nanoparticles on different supports. Pt loading: 5 wt%; space velocity (SV): 1500 mL h⁻¹ g⁻¹; catalyst: 0.2 g; C₂H₄: 0.32 vol%; O₂: 20 vol%; N₂: 5 vol%; He balance.

2.3.3 Ethylene oxidation at low temperature

In this study, 2 wt% and 1 wt% Pt/MCM-41 were also prepared for investigation under more practical conditions with trace ethylene (50 ppm) at ambient or lower temperature (25 or 0°C). As shown in Table 2-2, the ethylene conversion reached 97% by using 2 wt% Pt/MCM-41, which was higher than the reported data under almost the same reaction conditions.[10,11] The conversion of 50 ppm ethylene with 1 wt% Pt/MCM-41 remained ca. 100% for more than 12 h at 25°C, showing great potential applicability to warehouse storage (Figure 2-9).

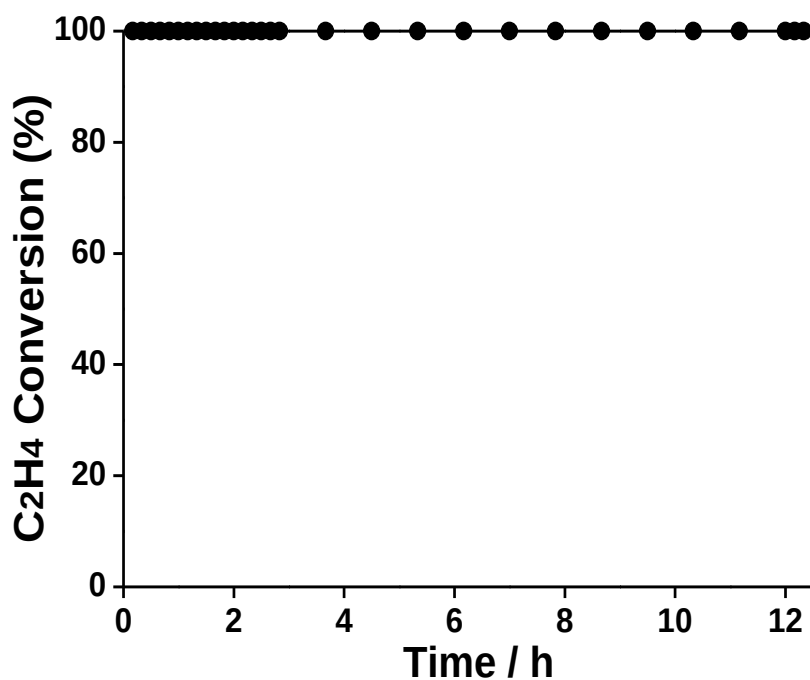


Figure 2-9. Catalytic performance and durability of Pt/MCM-41 at 25°C. Pt loading: 1 wt%; SV: 1500 mL h⁻¹ g⁻¹; catalyst: 0.40 g; C₂H₄: 50 ppm; O₂: 20 vol%; N₂: 5 vol%; He balance.

Table 2-2. Comparison of catalytic performance.

Catalyst	Metal loading (wt%)	Conversion (%)	T (°C)	Ethylene (ppm)	SV (mL h ⁻¹ g ⁻¹)	Ref.
Au/Co ₃ O ₄	2.5	76	0	50	14400	[10]
Au/Co ₃ O ₄	1.95	93.7	0	50	9000	[11]
Pt/MCM-41	1.95	96.8	0	50	9000	This study

In addition, we applied 1 wt% Pt/MCM-41 catalyst for ethylene oxidation at 0°C (Figure 2-10). Notably, >99.8% ethylene conversion was also accomplished under the conditions and perfect conversion of ethylene was maintained for more than 1 h.

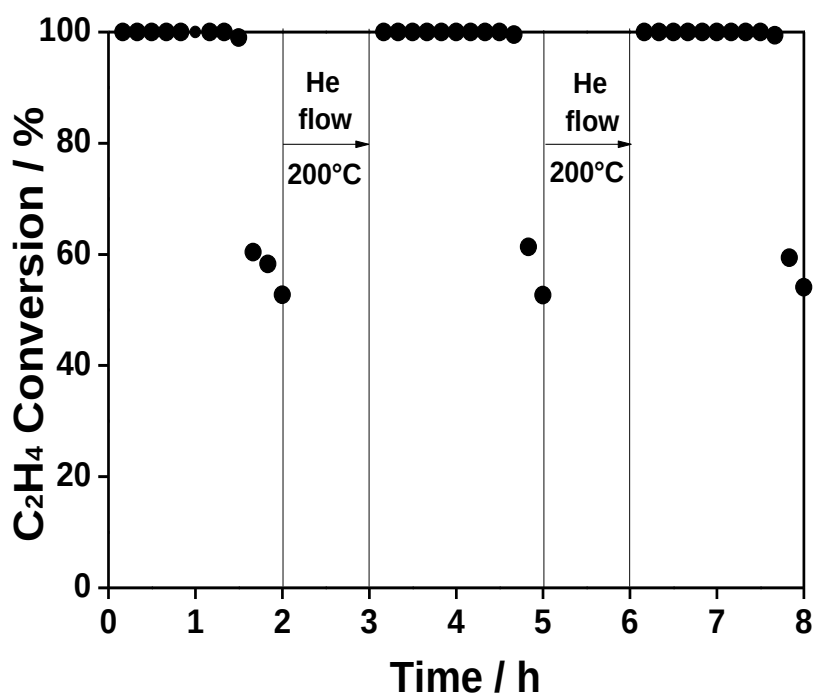


Figure 2-10. Regeneration of Pt/MCM-41 at 0°C. Pt loading: 1 wt%; SV: 1500 mL h⁻¹ g⁻¹; catalyst: 0.40 g; C₂H₄: 50 ppm; O₂: 20 vol%; N₂: 5 vol%; He balance.

The gradual deactivation observed in Figure 2-10 is attributed to adsorption of water on the catalyst surface, but high catalytic activity was recovered by heating the catalyst at 200°C under a He flow for 1 h. No size or structural change was observed for the spent catalyst in XRD (Figure 2-11) and TEM (Figure 2-12) analysis.

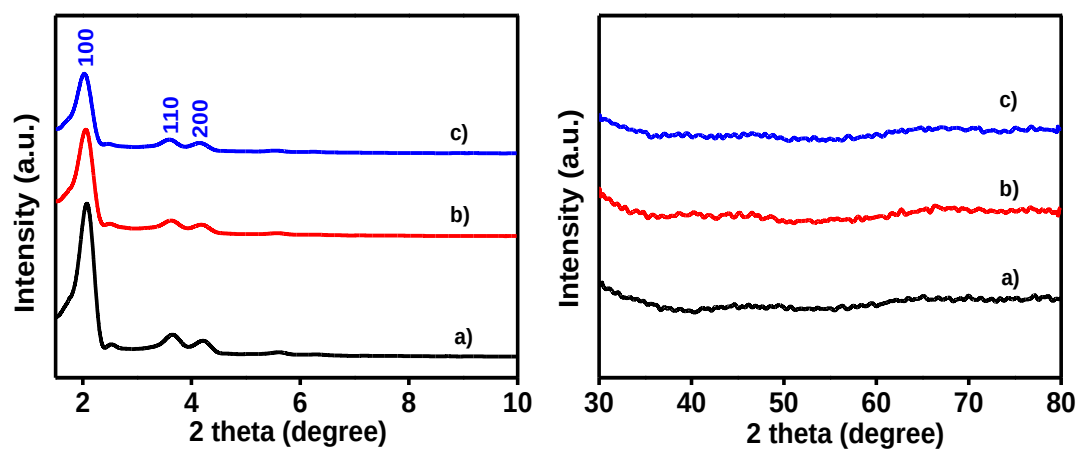
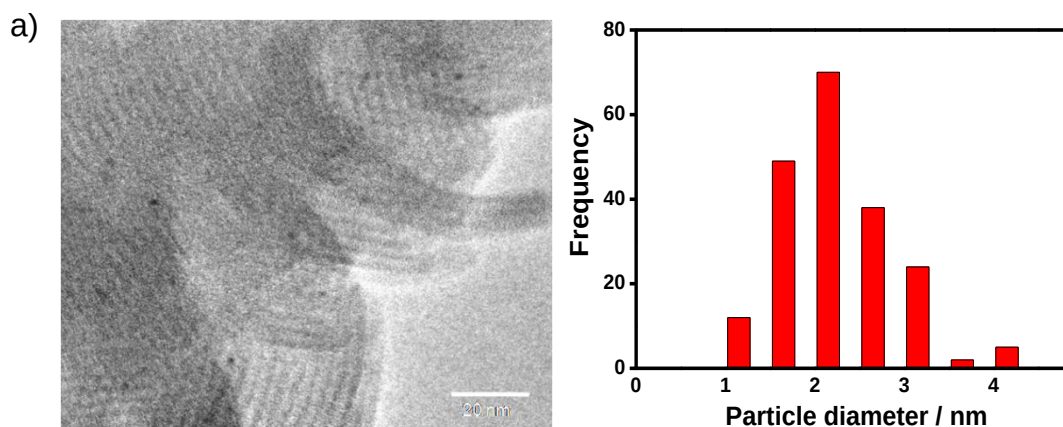


Figure 2-11. XRD patterns of a) MCM-41, b) 1% Pt/MCM-41 before reaction and c) 1% Pt/MCM-41 after reaction.



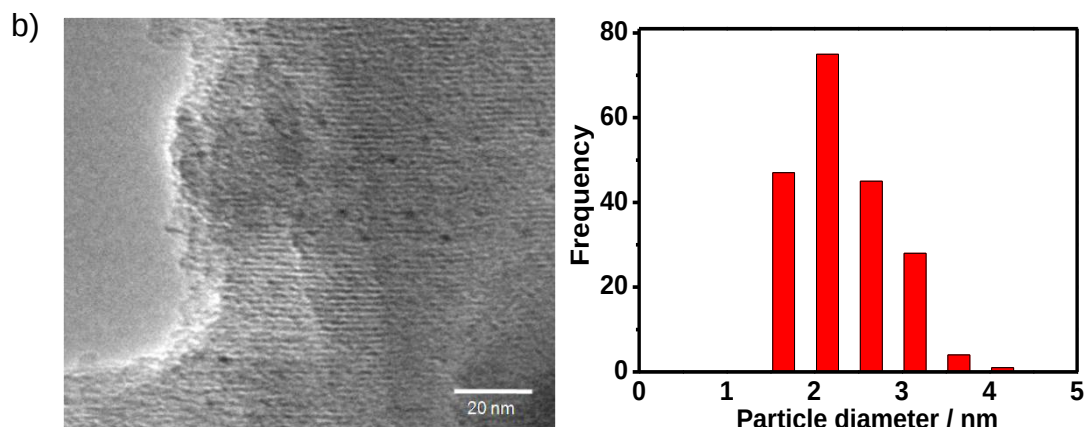


Figure 2-12. TEM images and Pt particle size distributions (insets) of 1% Pt/MCM-41 a) before and b) after reaction.

2.4 Conclusion

In conclusion, after screening of the metal and supports effects, we have found that Pt nanoparticles supported on mesoporous silica MCM-41 serve as an excellent catalyst for complete oxidation of ethylene at low temperature with high activity and durability. As a typical demonstration under practical conditions, the conversion of ethylene over 1 wt% Pt/MCM-41 at 0°C was >99.8%, which is higher than any previously reported results.

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Chapter 3 Mechanism Study on Ethylene Oxidation over Supported Pt Catalysts

3.1 Introduction

In our previous work, we have already found that the conversion of 50 ppm ethylene over 1wt% Pt/MCM-41 at 0°C was > 99.8%, which is, to the best of our knowledge, the highest conversion of ethylene oxidation at the low temperature. However, the mechanism of support effect on oxidation of ethylene was not clear.

Bending and stretching vibration of molecules having specific functional groups that are excited by an infrared beam can be measured by infrared spectroscopy (IR) also named vibrational spectroscopy. These vibrations produce bands in well defined regions, which are characteristic of specific class of compounds.[1] Therefore, infrared spectroscopy is a powerful technique that may provide valuable information about the chemical nature, structure and chemical bond strengths of adsorbed species during catalytic reactions, which help us understand the mechanistic details of a reaction at the molecular level.[2-4] DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectroscopy can be used to find the formation of the intermediate species during reaction by its characteristic absorption bands. Compared with transmission IR spectroscopy, the advantage of this method is the short time needed for preparing the samples.

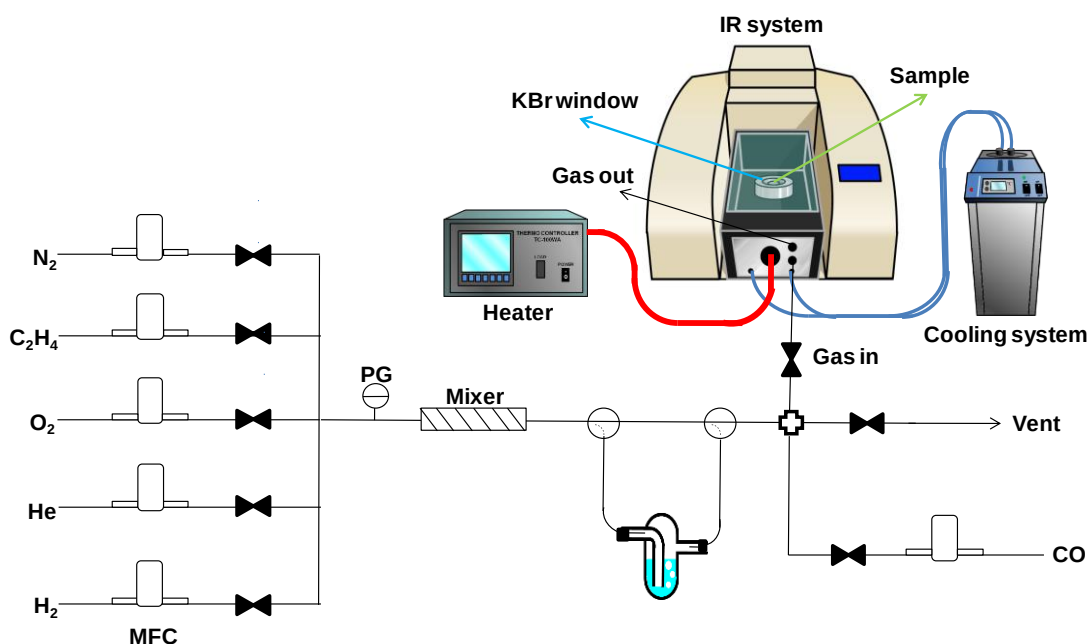
Therefore, in our present work, in order to clarify whether Pt-support interactions play a significant role on the catalytic behavior in ethylene elimination, *in situ* DRIFTS

during $\text{C}_2\text{H}_4/\text{O}_2$ reaction and probe molecular CO , HCHO , HCOOH , CH_3CHO and CH_3COOH adsorption were conducted investigation of the reaction pathway on each Pt catalysts. These investigations have been combined with catalytic studies with a laboratory-scale fixed bed reactor. Thus, a series of Pt-supported catalysts were prepared using various metal oxides including MCM-41, SiO_2 , Al_2O_3 , ZrO_2 , TiO_2 and CeO_2 .

3.2 Experimental

3.2.1 DRIFT measurements

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)



Scheme 3-1. The procedure of DRIFT measurements.

DRIFT measurements were conducted at 50°C or 150°C on a PerkinElmer Spectrum 100 (resolution 2-4 cm^{-1} , integration 64 times) equipped with an MCT detector and a S.T. Japan DRIFT heating chamber. In each experiment, sample powder

(6.0 mg) was placed in a DRIFT cell with a KBr window. Three types of DRIFT measurements were performed as follows: (1) In situ C_2H_4 oxidation: Catalyst was pretreated under H_2 atmosphere (20 mL min^{-1}) at 200°C for 1 h. After the pretreatment, the sample was cooled to 50°C or 150°C and purged under He flow (20 mL min^{-1}) for 10 min. Next, a gas mixture of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (15.8 mL min^{-1}) (total flow rate: 20 mL min^{-1}) was introduced to the catalyst. After reaching a steady state, a gas mixture of (O_2 + He) was introduced for further measurement. (2) Measurement with CO + O_2 flow: A gas mixture of 10% CO (2 mL min^{-1}) + O_2 (8 mL min^{-1}) + He (30 mL min^{-1}) (total flow rate: 40 mL min^{-1}) was used after the pretreatment described for type (1). (3) Adsorption of HCHO, HCOOH, CH_3CHO and CH_3COOH : The sample was purged under He flow (20 mL min^{-1}) for 30 min at 50°C . Then, He gas (20 mL min^{-1}) was bubbled into an aqueous solution of formaldehyde, formic acid, acetaldehyde or acetic acid. The outgas with formaldehyde, formic acid, acetaldehyde or acetic acid vapor was passed through the sample for adsorption, followed by purging with He gas (20 mL min^{-1}) for 10 min. The detailed procedure as shown in Scheme 3-1.

3.2.2 Ethylene oxidation

Catalytic activity of all catalysts for ethylene oxidation has been employed in a flow system. The detailed procedure has been introduced in Chapter 2.2.4.

3.3 Results and discussion

3.3.1 Catalyst characterization

The structure of Pt catalysts supported on various metal oxides have been characterized by using XRD, N₂ adsorption, TEM images and CO pulse in Chapter 2.3.1

3.3.2 Catalytic activity

As shown in Figure 3-1, the catalytic oxidation of ethylene over various Pt catalysts at high space velocity (9000 ml h⁻¹ g⁻¹) was investigated. At the temperature range from room temperature to 250°C, when Pt nanoparticles supported on MCM-41 and SiO₂, the ethylene conversions afford 100% at around 100°C, whereas the ethylene conversions arrive on 100% at around 200°C on Pt catalysts supported on Al₂O₃, ZrO₂, and TiO₂. The temperature for complete removal of ethylene on Pt/CeO₂ is 250°C. The big difference of catalytic oxidation of ethylene among all of catalysts can not simply explained by the difference of the particle sizes of Pt nanoparticles formed on various supports as shown in Table 2-1. However, the metal-support effect may be the main key to the different catalytic activities of ethylene oxidation. In order to obtain the detailed reaction pathway on each catalyst, *in situ* DRIFTS was employed in the next section.

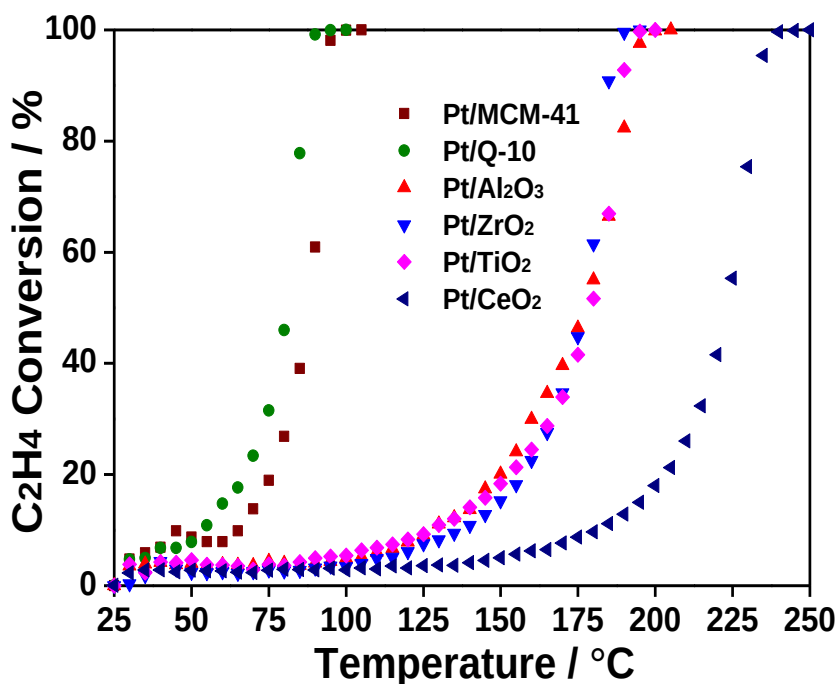


Figure 3-1. Light-off curves of catalytic oxidation of ethylene over Pt nanoparticles on various metal oxides. Pt loading: 5 wt%, space velocity (SV): 9000 ml h⁻¹ g⁻¹, catalyst: 0.2 g, C₂H₄: 1 vol%, O₂: 20 vol%, N₂: 5 vol%, He balance.

3.3.3 Mechanistic study of ethylene oxidation over Pt catalysts

3.3.3.1 Pt/MCM-41

Figure 3-2 shows the DRIFT spectra of adsorption of C₂H₄ on 5% Pt/MCM-41 catalyst. All spectra were obtained after subtraction of the background spectrum under He atmosphere. The bottom lines in Figure 3-2 display IR spectra of Pt/MCM-41 catalyst under a flow of C₂H₄ (0.2 mL min⁻¹) + O₂ (4 mL min⁻¹) + He (16 mL min⁻¹) at 50°C. No C₂H₄ peak was found in these spectra, which demonstrates the fast conversion of C₂H₄ to other species. The strong peak near 2048 cm⁻¹ is assignable to linear CO species on the Pt surface,[5-6] which is slightly shifted to lower frequency than that obtained under a flow of pure CO (2085 cm⁻¹, Figure 3-3) probably due to

lower CO coverage.[7-8] The adsorption band at 3278 cm^{-1} resulted from formation of H_2O . Moreover, bands at 2978 , 1730 and 1421 cm^{-1} can be assigned to physical adsorption of formic acid on the MCM-41 surface[9], while two other bands at 2941 and 1574 cm^{-1} are attributed to adsorption of formate species on MCM-41 (Figure 3-4c).[9-10] When the C_2H_4 flow was stopped and the $\text{O}_2 + \text{He}$ flow was continued, peak intensity of the linear CO on Pt was quickly reduced, whereas the formic acid and the formate species on MCM-41 still remained even after 35 min.

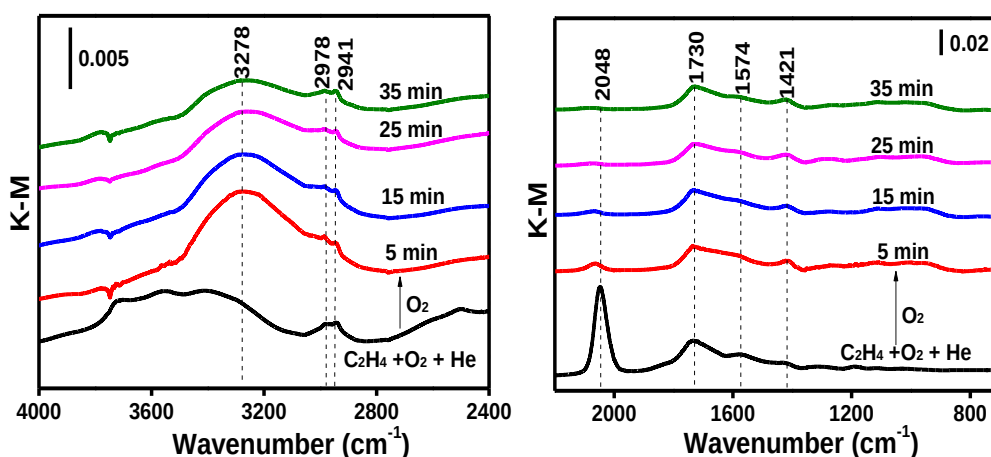


Figure 3-2. DRIFT spectra of adsorption of C_2H_4 on 5% Pt/MCM-41 catalyst. The samples were pretreated in H_2 at 200°C for 1 h. After cooling to 50°C , they were exposed to a flow of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (16 mL min^{-1}) for 30 min, then the flow of C_2H_4 was stopped while maintaining $\text{O}_2 + \text{He}$ flow for 35 min.

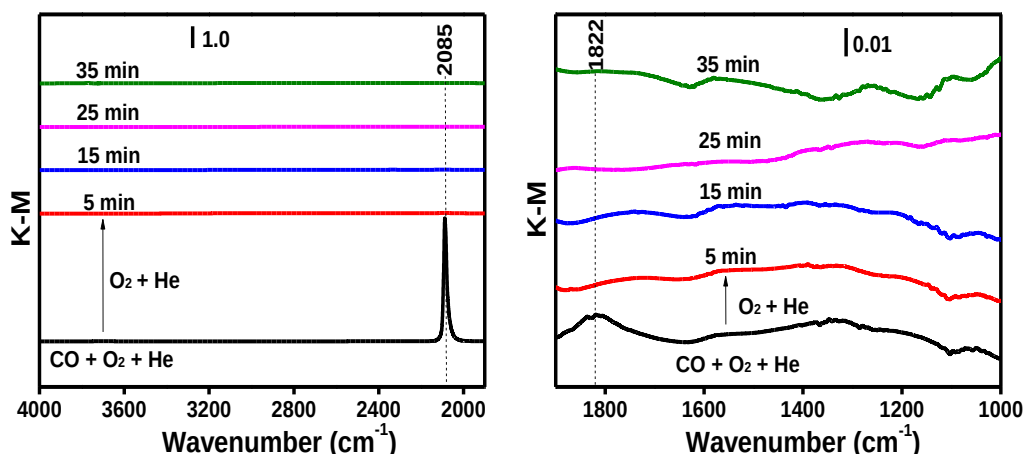


Figure 3-3. DRIFT spectra of 5% Pt/MCM-41 catalyst. After exposure to a flow of CO (2 mL min^{-1}) + O₂ (8 mL min^{-1}) + He (30 mL min^{-1}) at 50°C for 30 min, the flow of CO was stopped while keeping O₂ + He flow for 35 min.

It is notable that control DRIFT measurements by flowing vapor of HCHO and HCOOH as probe molecules into MCM-41 or Pt/MCM-41 catalyst (Figure 3-4) were employed. As shown in line a, the bands at 2840 and 1725 cm^{-1} in Figure 3-4a are assigned to the physically adsorbed HCHO on MCM-41. Other bands at 2980 , 2911 , 1480 , 1425 and 1395 cm^{-1} are due to the formation of polyoxymethylene species, which are formed by polymerization of HCHO.[10-11] All of these bands from HCHO are not observed in Figure 3-2, which proves no HCHO is adsorbed on silica surface of Pt/MCM-41 catalyst. As shown in Figure 3-4c, adsorption of formic acid on MCM-41 gives three bands at 2947 , 1727 and 1417 cm^{-1} , which are assigned to physical adsorption of formic acid on the MCM-41; other two peaks at 2904 and 1585 cm^{-1} are attributed to formate species formed on MCM-41.[9, 11] The similar bands originated from formic acid were obtained by adsorption of HCHO on Pt/MCM-41 (Figure 3-4b), except for the band at 2058 cm^{-1} of linear adsorbed CO on Pt.[8] These peaks in Figure 3-4b resemble those observed by flowing C₂H₄ and O₂ gas onto Pt/MCM-41(Figure

3-2). Therefore, these results imply that HCHO initially adsorbed on Pt is decomposed to CO, but part of HCHO is oxidized into HCOOH to be spilled over onto MCM-41 as a form of formic acid and formate species. All band assignments are listed in Table 3-1.

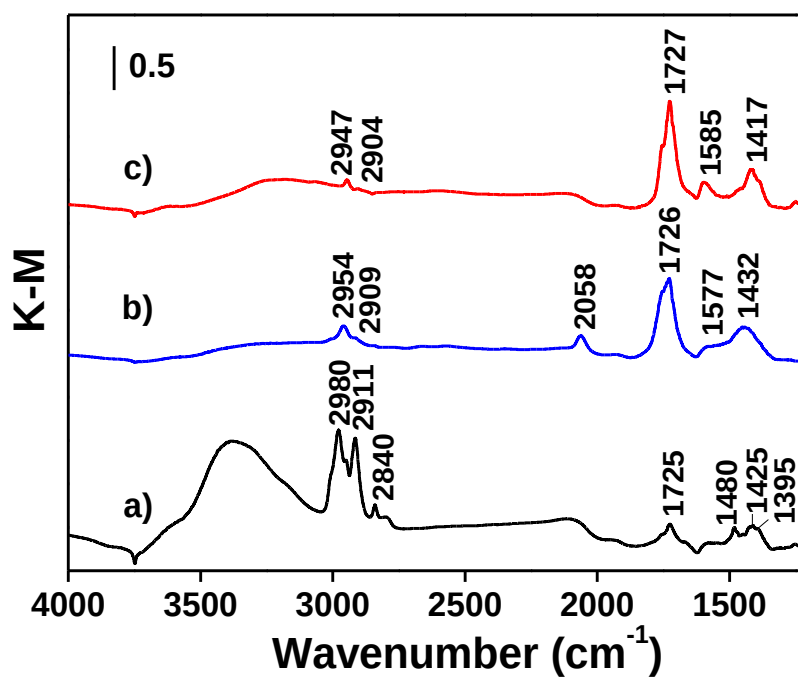
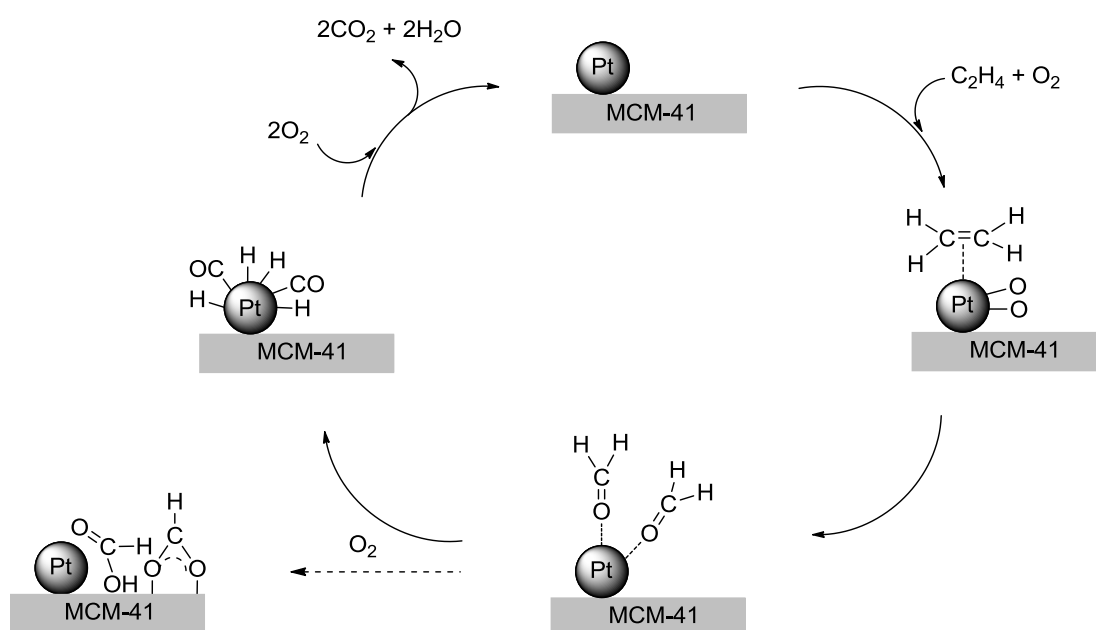


Figure 3-4. DRIFT spectra obtained by adsorption of a) HCHO vapor on MCM-41, b) HCHO vapor on 5% Pt/MCM-41 and c) HCOOH vapor on MCM-41.

Table 3-1. Peak assignment of DRIFT spectra obtained with Pt/MCM-41 and MCM-41 after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)			
	5 wt% Pt/MCM-41		MCM-41	
	C ₂ H ₄ + O ₂ + He	HCHO	HCHO	HCOOH
	Figure 3-2	Figure 3-4b	Figure 3-4a	Figure 3-4c
$\nu(\text{OH})$ H ₂ O	3278			
$\nu(\text{CH})$ Polyoxymethylene				
$\nu(\text{CH})$ Polyoxymethylene			2980	
$\nu(\text{CH})$ Formaldehyde			2911	
$\nu(\text{CH})$ Formic acid			2840	
$\nu(\text{CH})$ Formate				
$\nu_s(\text{CO})$ Pt-CO (linear)				
$\nu_s(\text{CO})$ Formaldehyde	2978	2954		2947
$\nu_s(\text{C}=\text{O})$ Formic acid	2941	2909		2904
$\nu_{as}(\text{CO})$ Formate	2048	2058		
$\delta(\text{CH}_2)$ Polyoxymethylene			1725	
$\nu(\text{C}-\text{O})$ Formic acid				
$\omega(\text{CH}_2)$ Polyoxymethylene	1730	1726		
$\omega(\text{CH}_2)$ Polyoxymethylene	1574	1577		1727
				1585
			1480	
	1421	1432		1417
			1425	
			1395	

Based on the DRIFT experiment, a reaction mechanism is tentatively proposed for the C_2H_4 oxidation on Pt/MCM-41. As depicted in Scheme 3-2, C_2H_4 and O_2 react quickly to form HCHO. HCHO adsorbed on Pt is then mainly decomposed into CO and H species, which react with O species to give CO_2 and H_2O , respectively. In this process a small amount of formic acid is generated from HCHO on Pt as a by-product and spilled over onto MCM-41.



Scheme 3-2. Proposed mechanism for ethylene oxidation on Pt/MCM-41.

3.3.3.2 Pt/SiO₂

As shown in figure 3-5, the spectrum of species obtained on Pt/SiO₂ by flowing mixture gas C₂H₄ + O₂ + He is very similar to the spectrum of those observed on Pt/MCM-41. The adsorption band at 3252 cm⁻¹ is due to the formation of water. The strong peak at 2048 cm⁻¹ shows the formation of CO species linear adsorbed on Pt, which was proved by flow probe molecule CO on Pt/SiO₂ as shown in Figure 3-6 (the band of linear adsorbed CO on Pt is 2085 cm⁻¹). The bands at 2987 and 1733 cm⁻¹ are assigned to the physical adsorption of formic acid on SiO₂ and other two bands at 2938 and 1587 cm⁻¹ may characterize the formation of formate species;[9-10] which were confirmed by flow HCHO vapor and HCOOH vapor on Pt/SiO₂ and SiO₂ as control DRIFT measurement (Figure 3-7). It is found in Figure 3-7a that when HCHO vapor was flowing on SiO₂, the bands at 2951, 2908, and 2842 cm⁻¹ show the polymerization of the HCHO on SiO₂;[10-11] which are not observed in Figure 3-5 indicating no HCHO is adsorbed on silica surface of Pt/SiO₂ catalyst. As shown in Figure 3-7c, adsorption of formic acid on SiO₂ gives two peaks at 2947 and 1727 cm⁻¹, which are assigned to physical adsorption of formic acid on the SiO₂; other two bands at 2921 and 1574 cm⁻¹ are attributed to formate species formed on SiO₂. [9-10] The similar bands originated from formic acid were obtained by adsorption of HCHO on Pt/ SiO₂ (Figure 3-7b), except for the band at 2058 cm⁻¹ of linear adsorbed CO on Pt. These peaks in Figure 3-7b resemble those observed by flowing C₂H₄ and O₂ gas onto Pt/ SiO₂ (Figure 3-5). Therefore, these results imply that HCHO initially adsorbed on Pt is decomposed to CO, but part of HCHO is oxidized into HCOOH to be spilled over onto SiO₂ as a

form of formic acid and formate species. All band assignments are listed in Table 3-2. It is also seen in figure 3-5 that when the C_2H_4 is stopped and only flow $O_2 + He$ gas on Pt/SiO₂, the CO species adsorbed on Pt is easily be removed, however, the adsorbed formic acid and formate species on SiO₂ are slightly decreased as spectator species.

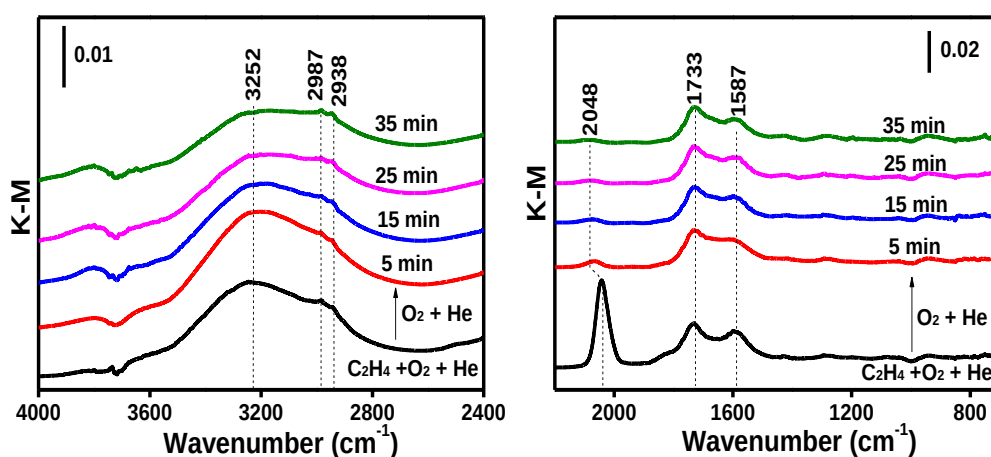


Figure 3-5. DRIFT spectra of adsorption of C_2H_4 on 5% Pt/SiO₂ catalyst. The samples were pretreated in H_2 at 200°C for 1 h. After cooling to 50°C, they were exposed to a flow of C_2H_4 (0.2 mL min⁻¹) + O_2 (4 mL min⁻¹) + He (16 mL min⁻¹) for 30 min, then the flow of C_2H_4 was stopped while maintaining $O_2 + He$ flow for 35 min.

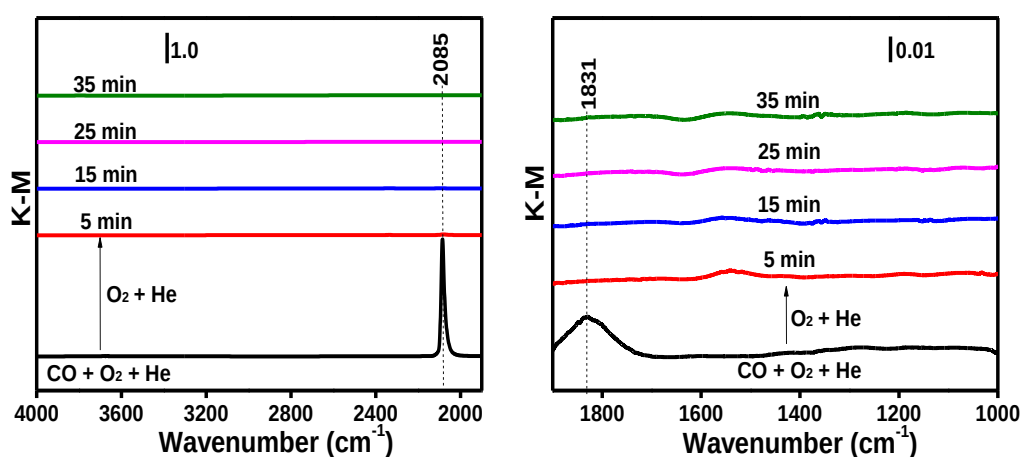


Figure 3-6. DRIFT spectra of 5% Pt/SiO₂ catalyst. After exposure to a flow of CO (2 mL min⁻¹) + O_2 (8 mL min⁻¹) + He (30 mL min⁻¹) at 50°C for 30 min, the flow of CO was stopped while keeping $O_2 + He$ flow for 35 min.

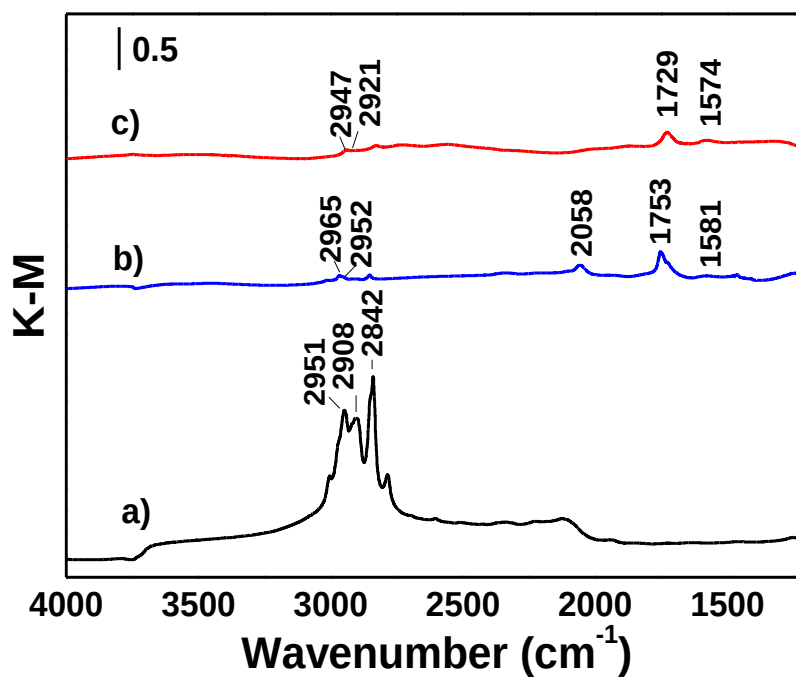
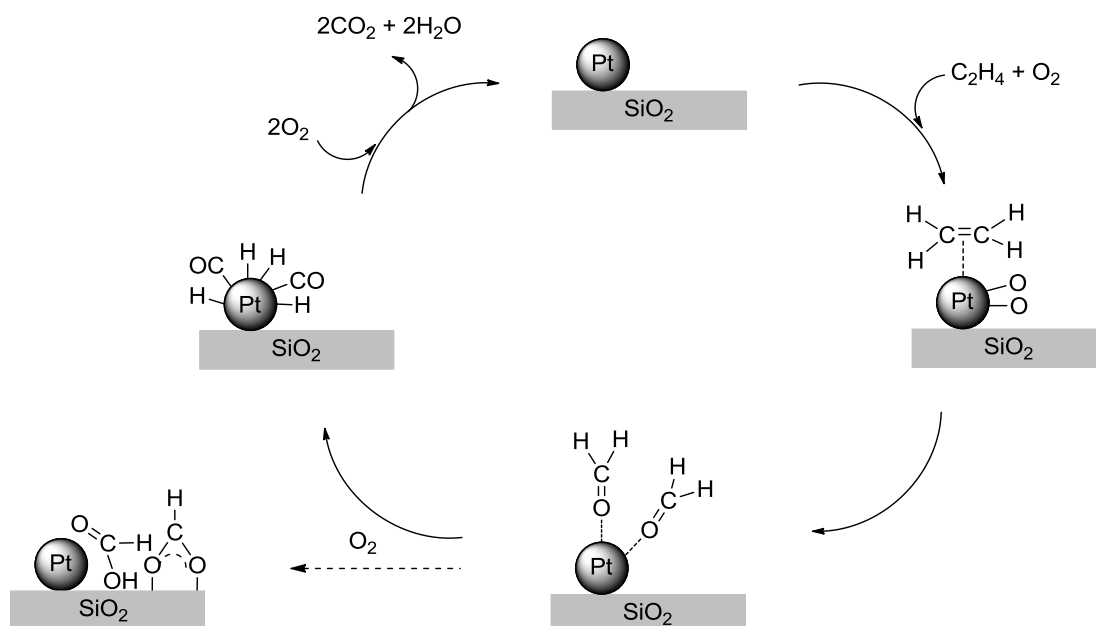


Figure 3-7. DRIFT spectra obtained by adsorption of a) HCHO vapor on SiO_2 , b) HCHO vapor on 5% Pt/ SiO_2 and c) HCOOH vapor on SiO_2 .

Table 3-2. Peak assignment of DRIFT spectra obtained with Pt/SiO₂ and SiO₂ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)			
	5 wt% Pt/SiO ₂		SiO ₂	
	C ₂ H ₄ + O ₂ + He	HCHO	HCHO	HCOOH
	Figure	Figure	Figure	Figure
	3-5	3-7b	3-7a	3-7c
$\nu(\text{OH})$ H ₂ O	3252			
$\nu(\text{CH})$ Polyoxymethylene				
$\nu(\text{CH})$ Polyoxymethylene			2951	
$\nu(\text{CH})$ Formaldehyde			2908	
$\nu(\text{CH})$ Formic acid			2842	
$\nu(\text{CH})$ Formate				
$\nu_s(\text{CO})$ Pt-CO (linear)				
$\nu_s(\text{CO})$ Formaldehyde	2987	2965		2947
$\nu_s(\text{C=O})$ Formic acid	2938	2952		2921
$\nu_{as}(\text{CO})$ Formate	2048	2058		
	1733	1753		
	1587	1581		1729
				1574



Scheme 3-3. Proposed mechanism for ethylene oxidation on Pt/SiO₂.

The possible reaction pathway was proposed according to the IR results. It is found that the reaction pathway of ethylene oxidation on Pt/SiO₂ resemble that on Pt/MCM-41. Scheme 3-3 shows that C₂H₄ and O₂ were fast converted to HCHO. Then, the adsorbed HCHO was further decomposed into CO and H species, which react with O species to give CO₂ and H₂O, respectively. In this recycling, a small amount of formic acid is generated from HCHO on Pt as a by-product and spilled over onto SiO₂.

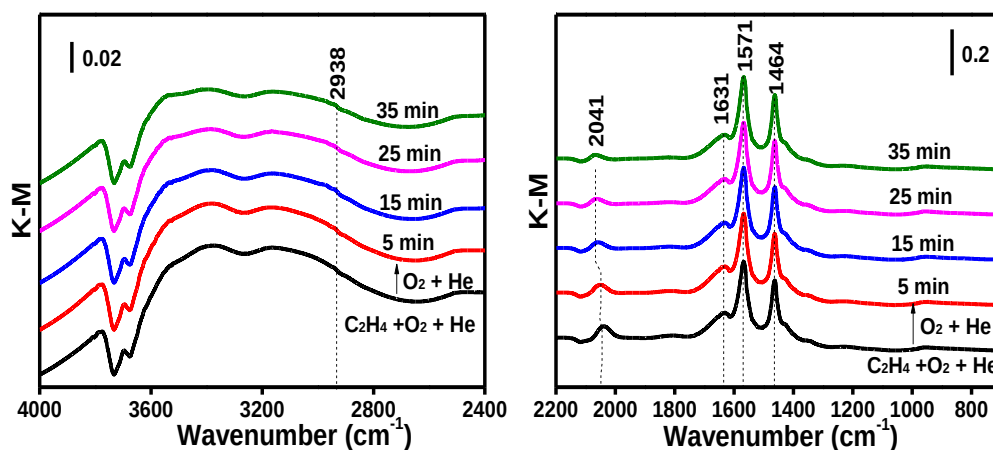
3.3.3.3 Pt/Al₂O₃

Figure 3-8. DRIFT spectra of adsorption of C₂H₄ on 5% Pt/Al₂O₃ catalyst. The samples were pretreated in H₂ at 200°C for 1 h. After cooling to 50°C, they were exposed to a flow of C₂H₄ (0.2 mL min⁻¹) + O₂ (4 mL min⁻¹) + He (16 mL min⁻¹) for 30 min, then the flow of C₂H₄ was stopped while maintaining O₂ + He flow for 35 min.

Figure 3-8 reveals the DRIFT spectra of adsorption of C₂H₄ on 5% Pt/Al₂O₃ catalyst. The signals at 2938, 1541 and 1464 cm⁻¹ originate from the formation of acetate species.[12-15] The signal at 1631 cm⁻¹ may be assigned to scissoring vibration of OH in H₂O. The band at 2041 cm⁻¹ are associated to the CO species linear adsorbed on Pt. With flowing the O₂ + He mixture gas, all of the species are almost no change except the linear adsorbed CO species is slightly deceased. In order to investigate what kind of species will be formed from CO intermediate, CO was chosen as probe molecular for *in situ* DRIFTS study. As shown in Figure 3-9, the bands peaked at 2126, 2075 and 1840 cm⁻¹ are corresponded to CO linear adsorbed on partially positively charged Pt sites (Pt^{δ+}), that adsorbed on metal Pt sites and bridged adsorbed CO on metal Pt sites, respectively.[15] With the flow of O₂ + He continuing, the linear and bridged adsorbed CO signal on metal Pt sites was decreased, however, CO signal

adsorbed on partially positively charged Pt sites is slightly increased. In addition, there is no other new peak formed indicating the decreasing of CO species may be because of its oxidation into CO_2 , which flow away with mixture gas. It is interesting that the bands at 2126 cm^{-1} is not found in Figure 3-8, which may be because the metal Pt is not easily be oxidized under this condition. Table 3-3 summarized the assignment of all of the bands in Figure 3-8 and 3-9.

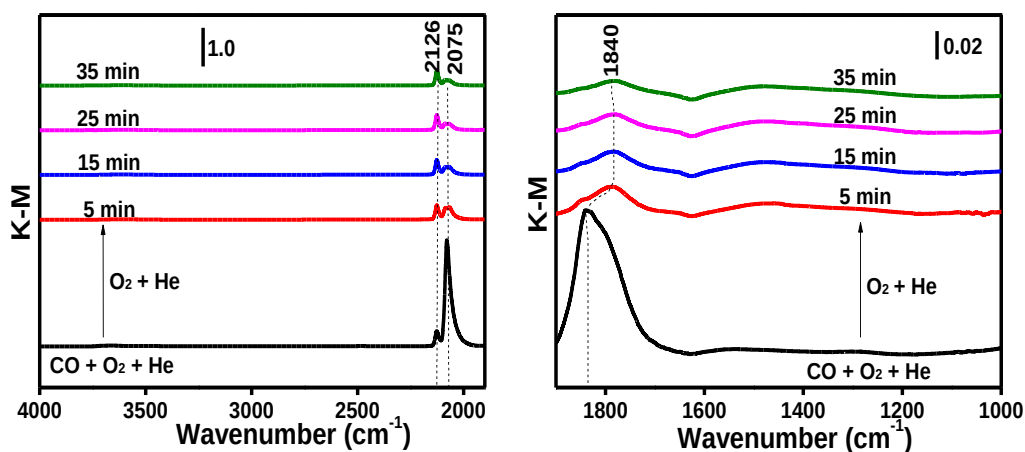


Figure 3-9. DRIFT spectra of 5% Pt/ Al_2O_3 catalyst. After exposure to a flow of CO (2 mL min^{-1}) + O_2 (8 mL min^{-1}) + He (30 mL min^{-1}) at 50°C for 30 min, the flow of CO was stopped while keeping O_2 + He flow for 35 min.

Table 3-3. Peak assignment of DRIFT spectra obtained with Pt/Al₂O₃ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)	
	5 wt% Pt/Al ₂ O ₃	
	C ₂ H ₄ + O ₂ + He	CO + O ₂ + He
	Figure 3-8	Figure 3-9
$\nu(\text{CH}_3)$ Acetate		
$\nu_s(\text{CO})$ Pt ^{δ^+} -CO	2938	
$\nu_s(\text{CO})$ Pt-CO (linear)		2126
$\nu_s(\text{CO})$ Pt-CO (bridged)		2075
$\delta(\text{OH})$ H ₂ O	2041	1840
$\nu_{as}(\text{OCO})$ Acetate		
$\nu_s(\text{OCO})$ Acetate	1631	
	1571	
	1464	

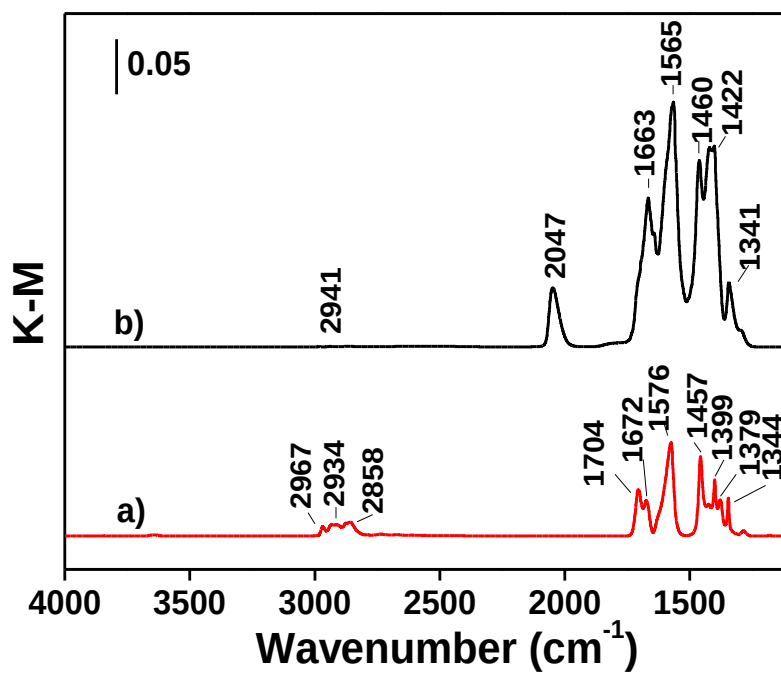


Figure 3-10. DRIFT spectra obtained by adsorption of a) CH_3CHO vapor on Al_2O_3 , b) CH_3CHO vapor on 5% Pt/ Al_2O_3 .

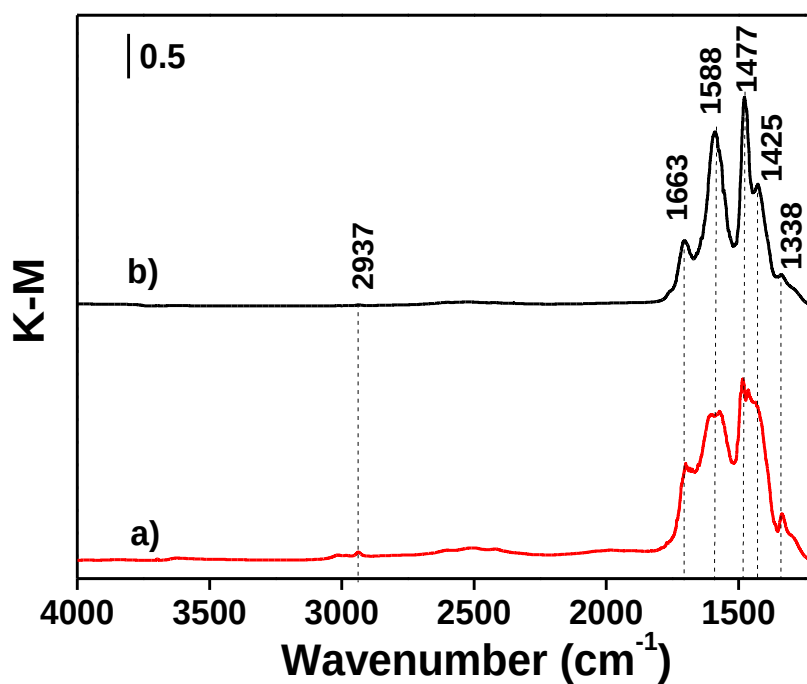


Figure 3-11. DRIFT spectra obtained by adsorption of a) CH_3COOH vapor on Al_2O_3 , b) CH_3COOH vapor on 5% Pt/ Al_2O_3 .

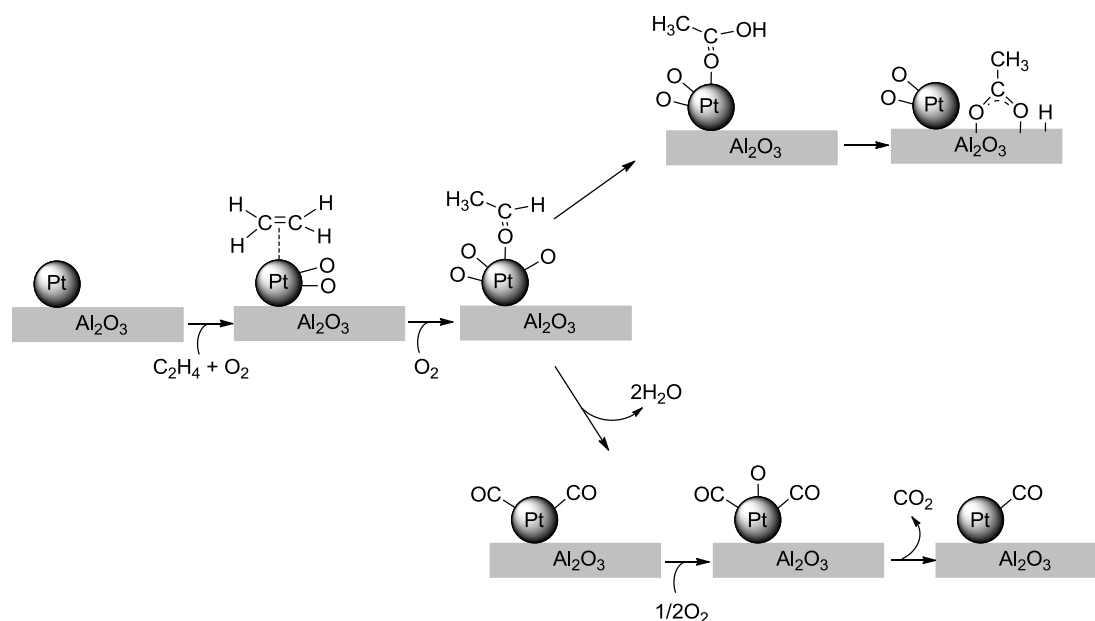
Figure 3-10 and 3-11 show the DRIFT spectra by adsorption of probe molecular

CH_3CHO and CH_3COOH on Al_2O_3 or $\text{Pt}/\text{Al}_2\text{O}_3$ for further mechanism study. It is shown in Figure 3-10a that after flowing of CH_3CHO vapor on Al_2O_3 , besides new bands at 2934, 1576, 1457, and 1344 cm^{-1} are assigned to the acetate species formed from the oxidation of acetaldehyde, lots of acetaldehyde species (the bands peaked at 2967, 2858, 1704, 1399 and 1379 cm^{-1}) still remained on Al_2O_3 . [16-17] No acetaldehyde bands obtained in Figure 3-8 reveal that there is no acetaldehyde species directly adsorbed on support of $\text{Pt}/\text{Al}_2\text{O}_3$. However, as depicted in Figure 3-10b, adsorbed acetaldehyde on $\text{Pt}/\text{Al}_2\text{O}_3$ can be oxidized into CO (the band at 2047 cm^{-1}) and acetate species (the signals at 2941, 1565, 1460, 1422 and 1341 cm^{-1}), which is similar to those observed in Figure 3-8 by flowing $\text{C}_2\text{H}_4 + \text{O}_2 + \text{He}$ mixture gas on $\text{Pt}/\text{Al}_2\text{O}_3$ indicating the acetaldehyde species firstly adsorbed on Pt, then its further oxidized into linear adsorbed CO on Pt and acetate species on Al_2O_3 . Moreover, the CH_3COOH vapor is also flowed on Al_2O_3 or $\text{Pt}/\text{Al}_2\text{O}_3$ (Figure 3-11) for proving the species centered at 2937, 1588, 1477, 1425 and 1338 cm^{-1} are acetate species formed on Al_2O_3 . All of the bands are shown in Table 3-4.

Table 3-4. Peak assignment of DRIFT spectra obtained with Pt/ Al₂O₃ and Al₂O₃ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)			
	5 wt% Pt/Al ₂ O ₃		Al ₂ O ₃	
	CH ₃ CHO	CH ₃ COOH	CH ₃ CHO	CH ₃ COOH
	Figure 3-10b	Figure 3-11b	Figure 3-10a	Figure 3-11a
$\nu(\text{CH}_3)$ Acetate	2941	2937	2934	2937
$\nu(\text{CH}_3)$ Acetaldehyde			2967	
$\nu(\text{CH}_3)$ Acetaldehyde			2858	
$\nu_s(\text{CO})$ Pt-CO (linear)				
$\nu_s(\text{CO})$ Acetaldehyde				
$\nu_s(\text{OCO})$ Acetic acid	2047		1704	
$\nu_{as}(\text{OCO})$ Acetate			1672	
$\nu_s(\text{OCO})$ Acetate			1576	
$\delta_{as}(\text{CH}_3)$ Acetate	1663	1663	1457	1663
$\delta_{as}(\text{CH})$ Acetaldehyde	1565	1588		1588
$\delta_{as}(\text{CH})$ Acetaldehyde	1460	1477		1477
$\delta_s(\text{CH}_3)$ Acetate	1422	1425	1399	1425
			1379	
			1344	
	1341	1338		1338

From all of the IR data revealed above, one probable reaction pathway on Pt/Al₂O₃ was deduced in Scheme 3-4. Firstly, C₂H₄ and O₂ were fast oxidized into CH₃CHO, then, two pathways were raised. One is that the CH₃CHO further oxidized into acetic acid, followed its spilled over onto Al₂O₃ as a form of acetate species. The other is that linear adsorbed CO species was formed from CH₃CHO, which partially oxidized into CO₂.



Scheme 3-4. Proposed mechanism for ethylene oxidation on Pt/ Al₂O₃.

3.3.3.4 Pt/ZrO₂

The DRIFTS spectrum obtained on the Pt/ZrO₂ catalyst (Figure 3-12) in the presence of C₂H₄ + O₂ + He exhibited bands at 2969, 1551, and 1461 cm⁻¹ which are related to different vibration modes of acetate species.[18-19] This bands increased with only flowing O₂ + He gas. CO linear adsorbed on metal Pt site is corresponded to the band at 2041 cm⁻¹, which is decreased when the flow of O₂ + He gas is continued, as well as, CO adsorbed on Pt²⁺ site observed at 2121 cm⁻¹ is slightly increased. In addition, weak bands at 1431, 1359 and 1377 cm⁻¹ assigned to carbonate and formate species are also obtained.[20] The strong negative peak at 3680 cm⁻¹ is attributed to the decreasing of the surface bridged OH because of its reaction with CO species to form formate species.[20]

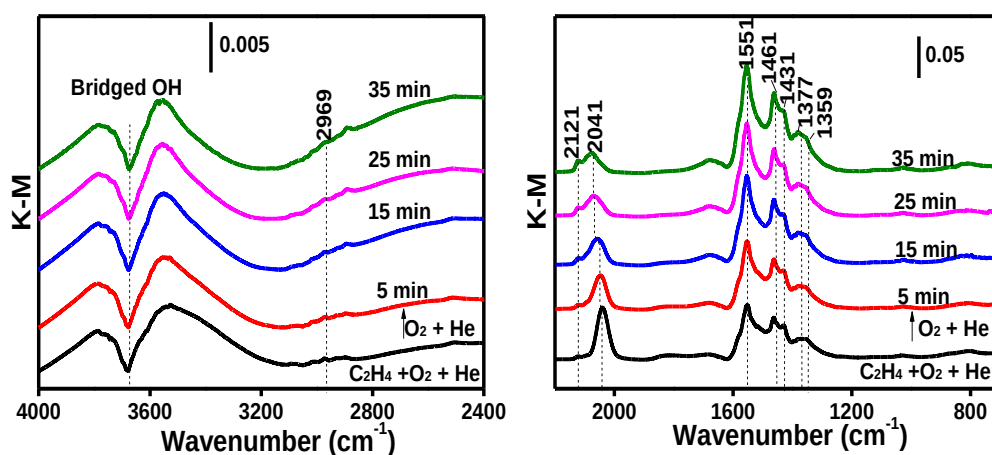


Figure 3-12. DRIFT spectra of adsorption of C₂H₄ on 5% Pt/ZrO₂ catalyst. The samples were pretreated in H₂ at 200°C for 1 h. After cooling to 50°C, they were exposed to a flow of C₂H₄ (0.2 mL min⁻¹) + O₂ (4 mL min⁻¹) + He (16 mL min⁻¹) for 30 min, then the flow of C₂H₄ was stopped while maintaining O₂ + He flow for 35 min.

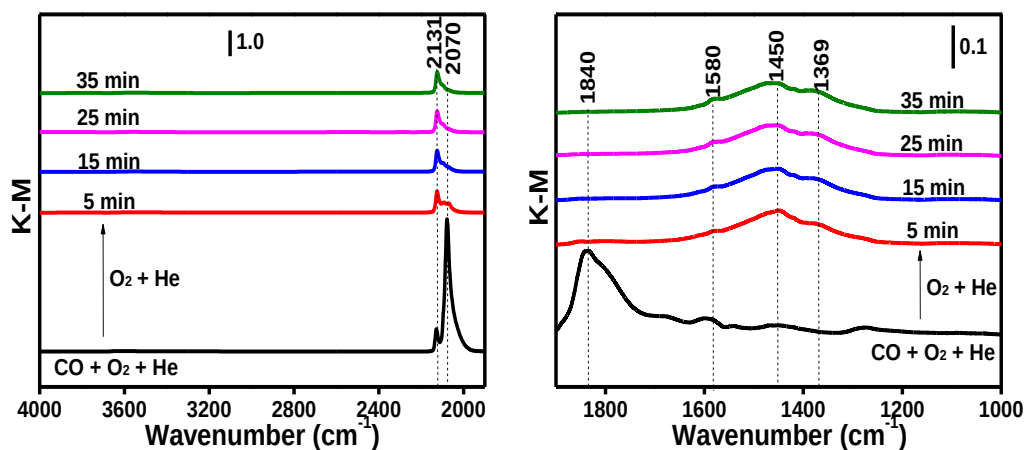


Figure 3-13. DRIFT spectra of 5% Pt/ ZrO₂ catalyst. After exposure to a flow of CO (2 mL min⁻¹) + O₂ (8 mL min⁻¹) + He (30 mL min⁻¹) at 50°C for 30 min, the flow of CO was stopped while keeping O₂ + He flow for 35 min.

Figure 3-13 demonstrates that in the presence of CO + O₂ + He, three bands at 2131, 2070, and 1840 cm⁻¹ attributed to CO adsorbed on Pt²⁺ site, CO linear and bridged adsorbed on metal Pt site, respectively were registered. The bands of CO linear and bridged adsorbed on metal Pt site were disappeared, when the CO flow was stopped in CO + O₂ + He mixture gas; however, new bands at 1580, 1369 and 1450 cm⁻¹ corresponded to formate and carbonate species were formed,[20] which indicates the conversion of CO to formate and carbonate species. All of the assignment of the bands can be seen in Table 3-5.

Table 3-5. Peak assignment of DRIFT spectra obtained with Pt/ZrO₂ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)	
	5 wt% Pt/ ZrO ₂	
	C ₂ H ₄ + O ₂ + He	CO + O ₂ + He
	Figure 3-12	Figure 3-13
$\nu(\text{CH}_3)$ Acetate	2969	
$\nu_s(\text{CO})$ Pt ²⁺ -CO	2121	
$\nu_s(\text{CO})$ Pt-CO (linear)	2041	2131
$\nu_s(\text{CO})$ Pt-CO (bridged)		2070
$\nu_{as}(\text{CO})$ Formate		1840
$\nu_{as}(\text{OCO})$ Acetate		1580
$\nu_s(\text{OCO})$ Acetate		
$\nu(\text{CO}_3)$ Carbonate	1551	
$\nu(\text{CO}_3)$ Carbonate	1461	
$\nu_s(\text{CO})$ Formate	1431	
	1359	1450
	1377	
		1369

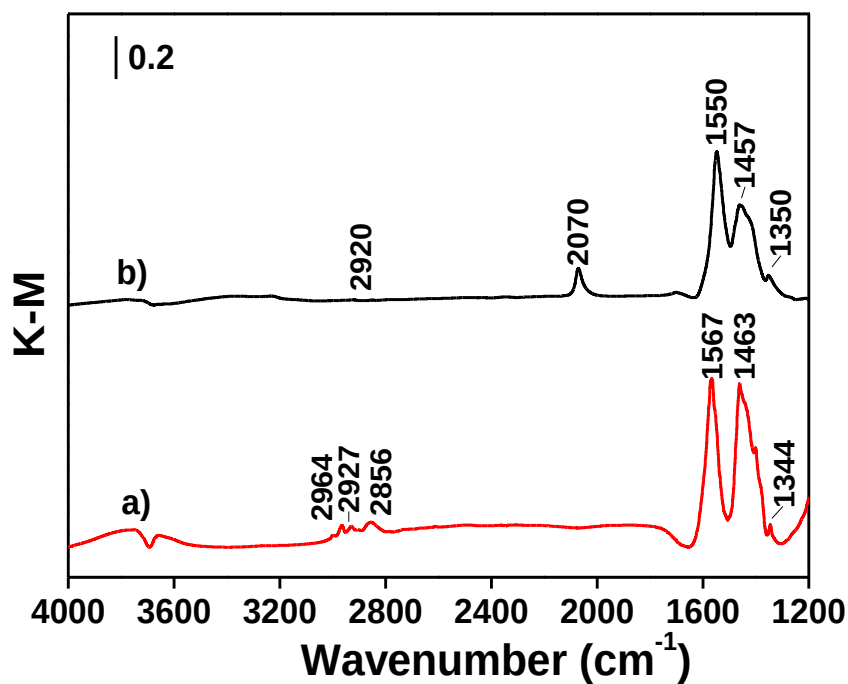


Figure 3-14. DRIFT spectra obtained by adsorption of a) CH_3CHO vapor on ZrO_2 , b) CH_3CHO vapor on 5% Pt/ ZrO_2 .

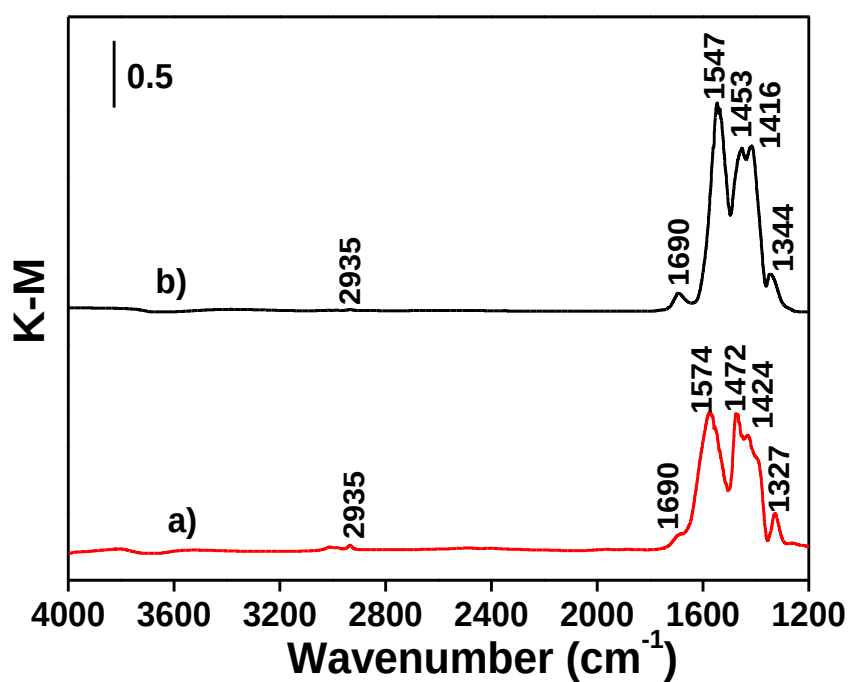


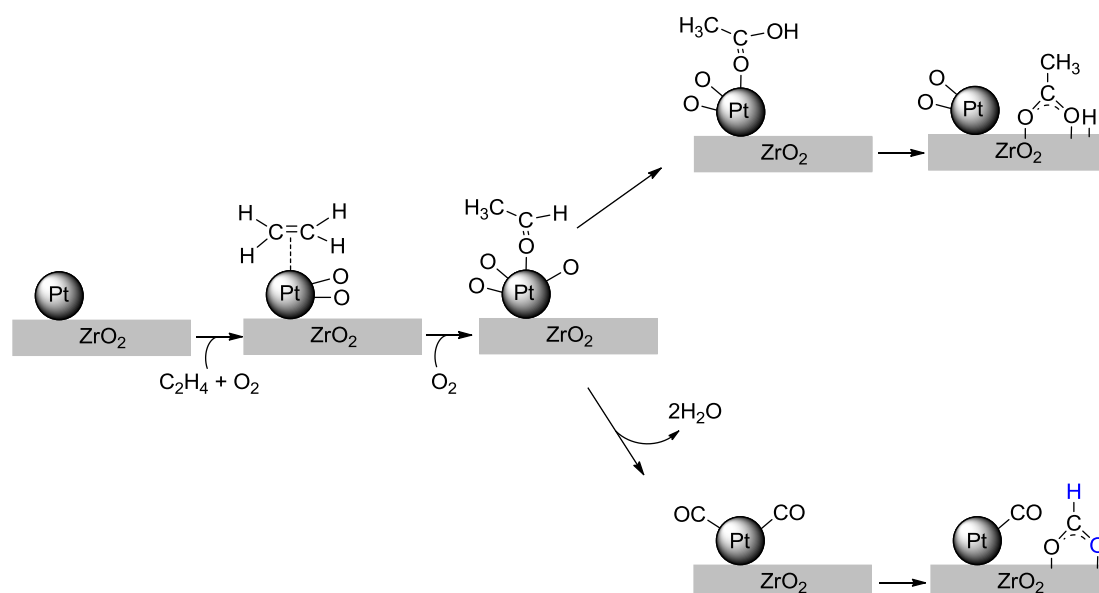
Figure 3-15. DRIFT spectra obtained by adsorption of a) CH_3COOH vapor on ZrO_2 , b) CH_3COOH vapor on 5% Pt/ ZrO_2 .

The control experiments by *in situ* DRIFTS were also applied by flow the probe molecular CH_3CHO and CH_3COOH on ZrO_2 or Pt/ZrO_2 and all of the bands were concluded in Table 3-6. Figure 3-14a exhibits the formation of acetate species by oxidation of acetaldehyde on ZrO_2 , which related to the bands at 2927, 1567, 1463, and 1344 cm^{-1} . [21] The signals at 2964 and 2856 cm^{-1} indicate the existence of acetaldehyde. All of those give evidence of no acetaldehyde species directly adsorbed on support of Pt/ZrO_2 . The bands obtained in Figure 3-14b resemble those observed in Figure 3-12. The band at 2070 cm^{-1} is assigned to the formation of CO species. Other bands at 2935, 1547, 1453, 1416 and 1344 cm^{-1} are acetate species adsorbed on ZrO_2 (Figure 3-15 gives a prove of the assignment of acetate species on ZrO_2 by directly flow CH_3COOH vapor on ZrO_2 and Pt/ZrO_2) which deduced from the oxidation of the adsorbed acetaldehyde species on Pt site.

Table 3-6. Peak assignment of DRIFT spectra obtained with Pt/ ZrO₂ and ZrO₂ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)			
	5 wt% Pt/ ZrO ₂		ZrO ₂	
	CH ₃ CHO	CH ₃ COOH	CH ₃ CHO	CH ₃ COOH
	Figure 3-14b	Figure 3-15b	Figure 3-14a	Figure 3-15a
$\nu(\text{CH}_3)$ Acetate	2920	2935	2927	2935
$\nu(\text{CH}_3)$ Acetaldehyde			2964	
$\nu(\text{CH}_3)$ Acetaldehyde			2856	
$\nu_s(\text{CO})$ Pt-CO (linear)				
$\nu(\text{CO})$ Acetyl				
$\nu_{as}(\text{OCO})$ Acetate	2070			
$\nu_s(\text{OCO})$ Acetate				
$\delta_{as}(\text{CH}_3)$ Acetate		1690	1567	1690
$\delta_s(\text{CH}_3)$ Acetate		1547	1463	1574
	1550	1453		1472
	1457	1416		1424
		1344		1327
			1344	
	1350			

Based on the DRIFTS experiment, Scheme 3-5 depicts the reaction pathway of ethylene oxidation on Pt/ZrO₂. In the first step, CH₃CHO was formed by the oxidation of C₂H₄ and O₂, then, two main directions were deduced. The first one is the formation of acetic acid on Pt sites with the further oxidation of CH₃CHO, subsequent its spilled over onto ZrO₂ as a form of acetate species. The other is that linear adsorbed CO species was formed from CH₃CHO, which partially reacts with bridged OH bond of supports to form formate species.



Scheme 3-5. Proposed mechanism for ethylene oxidation on Pt/ ZrO₂.

3.3.3.5 Pt/TiO₂

It is found that the bands formed on Pt/TiO₂ after flowing of the C₂H₄ and O₂ mixture gas shown in Figure 3-16 are similar to those formed on Pt/ZrO₂. The peaks at 2955, 1544, and 1446 cm⁻¹ show the formation of acetate species.[22] Other two peaks at 2122 and 2051 cm⁻¹ are associated with CO species adsorbed on Pt²⁺ and metal Pt sites, respectively.[23] formate (the bands at 1380 and 1361 cm⁻¹) and dioxymethylene species (the bands at 2880 and 1473 cm⁻¹) were also viewed.[24-26] The negative signal at 3676 cm⁻¹ is also found indicating the reaction between the surface OH group of support and CO species happened.[25] After the C₂H₄ flow is stopped, it is found that with the O₂ and He gas flowing, the intensities of the bands for acetate species, formate species and CO species adsorbed on Pt²⁺ site are increased, however, that for CO species adsorbed on metal Pt site is decreased.

In order to confirm what kind of species were formed from the reaction between CO species and the surface OH group of support. CO, O₂ and He mixture gas was flowed on Pt/TiO₂ catalyst. As shown in Figure 3-16 that besides the formation the CO species on Pt²⁺ (2122 cm⁻¹) and metal Pt sites (2074 cm⁻¹), formate species (the bands at 1550, 1381 and 1362 cm⁻¹) was also obtained. The increasing of the bands intensities of CO on Pt²⁺ site and formate species as well as the decreasing of that of CO on Pt⁰ site illustrating the oxidation of the Pt⁰ to Pt²⁺ and the conversion of the CO to formate species. The detailed information for each band was shown in Table 3-7

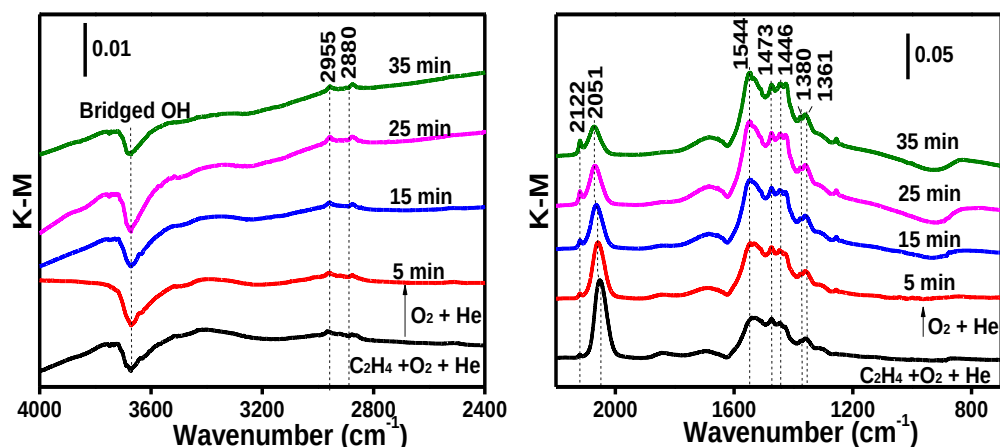


Figure 3-16. DRIFT spectra of adsorption of C_2H_4 on 5% Pt/ TiO_2 catalyst. The samples were pretreated in H_2 at 200°C for 1 h. After cooling to 50°C , they were exposed to a flow of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (16 mL min^{-1}) for 30 min, then the flow of C_2H_4 was stopped while maintaining O_2 + He flow for 35 min.

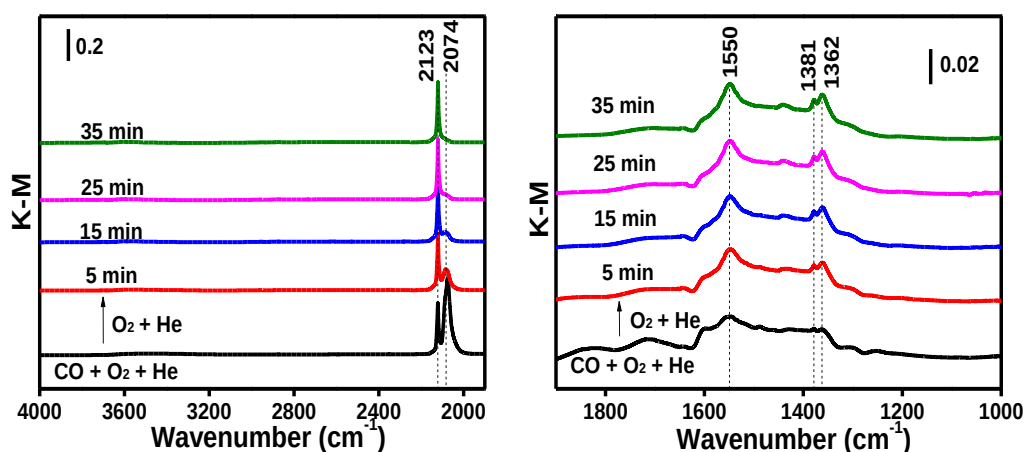


Figure 3-17. DRIFT spectra of 5% Pt/ TiO_2 catalyst. After exposure to a flow of CO (2 mL min^{-1}) + O_2 (8 mL min^{-1}) + He (30 mL min^{-1}) at 50°C for 30 min, the flow of CO was stopped while keeping O_2 + He flow for 35 min.

Table 3-7. Peak assignment of DRIFT spectra obtained with Pt/TiO₂ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)	
	5 wt% Pt/ TiO ₂	
	C ₂ H ₄ + O ₂ + He	CO + O ₂ + He
	Figure 3-16	Figure 3-17
$\nu(\text{CH}_3)$ Acetate	2955	
$\nu(\text{CH}_2)$ Dioxymethylene	2880	
$\nu_s(\text{CO})$ Pt ²⁺ -CO	2122	
$\nu_s(\text{CO})$ Pt-CO (linear)	2051	2123
$\nu_{as}(\text{CO})$ Formate		2074
$\nu_{as}(\text{OCO})$ Acetate		1550
$\delta(\text{CH}_2)$ Dioxymethylene	1544	
$\nu_s(\text{OCO})$ Acetate	1473	
$\delta(\text{CH})$ Formate	1446	
$\nu_s(\text{CO})$ Formate	1380	
	1361	
		1381
		1362

Figure 3-18 and 3-19 illustrate *in situ* DRIFTS of control experiments by flow the probe molecular CH₃CHO and CH₃COOH on TiO₂ or Pt/TiO₂. During the adsorption of CH₃CHO on TiO₂, In addition to acetaldehyde species (the bands at 2966 and 1380 cm⁻¹), the new bands of acetate species at 2932, 1549, 1438, and 1344 cm⁻¹, crotonaldehyde species at 1644, 1627, and 1598 cm⁻¹ appeared in Figure 3-18a.[21] Figure 4-18b shows the similar acetate species peaked at 2927, 1521, 1445, 1414, and

1344 cm^{-1} by adsorption of CH_3CHO on Pt/TiO_2 . The difference is the formation of CO species and no appearance of crotonaldehyde. However, there is no difference between Figure 3-16 and 3-18b, which gives evidence that CH_3CHO may be one kind of intermediates for ethylene oxidation. Finally, the acetate species formed on TiO_2 were further proved by flowing CH_3COOH vapor on TiO_2 or Pt/TiO_2 shown in Figure 3-19. The bands assignments are shown in Table 3-8.

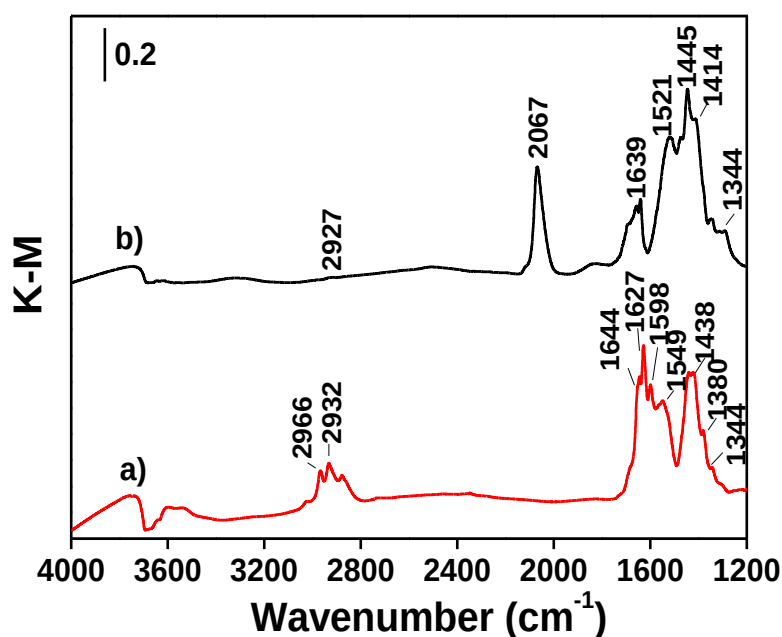


Figure 3-18. DRIFT spectra obtained by adsorption of a) CH_3CHO vapor on TiO_2 , b) CH_3CHO vapor on 5% Pt/TiO_2 .

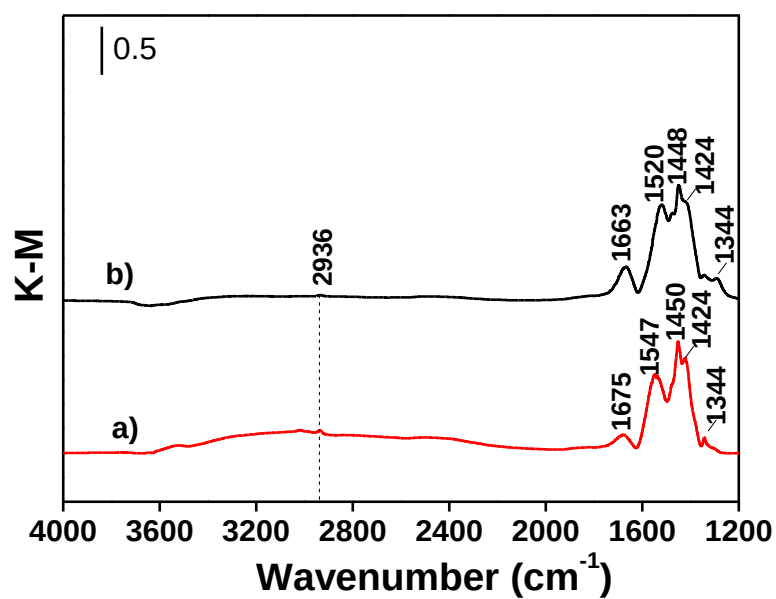
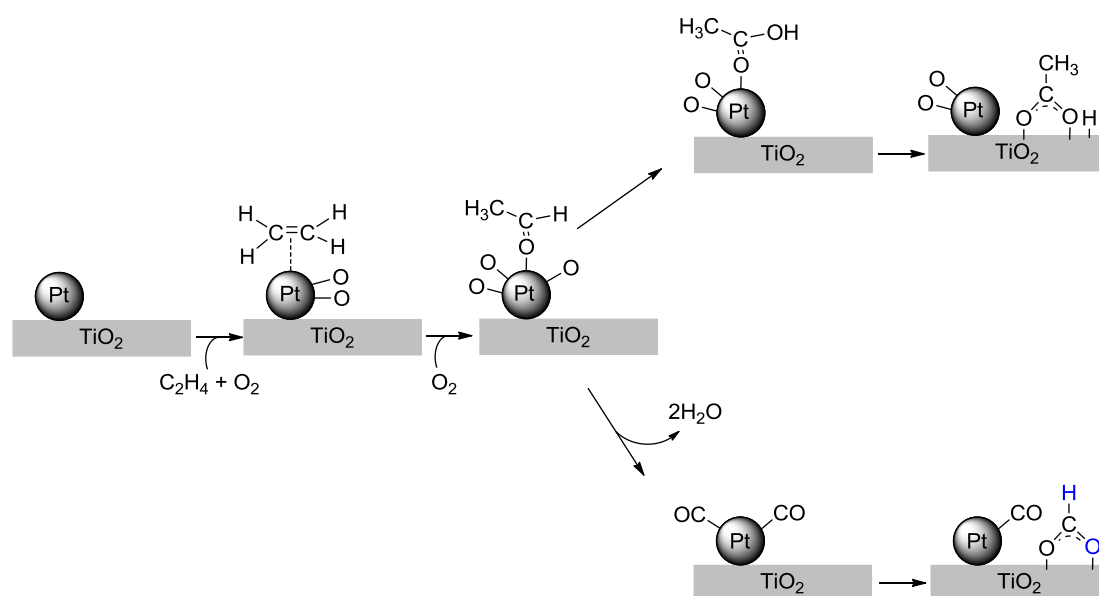


Figure 3-19. DRIFT spectra obtained by adsorption of a) CH_3COOH vapor on TiO_2 , b) CH_3COOH vapor on 5% Pt/ TiO_2 .

Table 3-8. Peak assignment of DRIFT spectra obtained with Pt/ TiO₂ and TiO₂ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)			
	5 wt% Pt/ TiO ₂		TiO ₂	
	CH ₃ CHO	CH ₃ COOH	CH ₃ CHO	CH ₃ COOH
	Figure	Figure	Figure	Figure
	3-18b	3-19b	3-18a	3-19a
$\nu(\text{CH}_3)$ Acetaldehyde			2966	
$\nu(\text{CH}_3)$ Acetate			2932	
$\nu_s(\text{CO})$ Pt-CO (linear)	2927	2936		2936
$\nu_s(\text{OCO})$ Acetic acid	2067			
$\nu(\text{CO})$ Crotonaldehyde	1639			
$\nu(\text{CO})$ Crotonaldehyde		1663		1675
$\nu(\text{C}=\text{C})$ Crotonaldehyde			1644	
$\nu_{as}(\text{OCO})$ Acetate			1627	
$\nu_s(\text{OCO})$ Acetate			1598	
$\delta_{as}(\text{CH}_3)$ Acetate			1549	
$\delta(\text{CH})$ Acetaldehyde			1438	
$\delta_s(\text{CH}_3)$ Acetate	1521			
	1445	1520		1547
	1414	1448		1450
		1424	1380	1424
			1344	
	1344			
		1344		1344

Scheme 3-6 gives a description of the mechanism of ethylene oxidation on Pt/TiO₂, which is similar to that on Pt/ZrO₂. The adsorbed C₂H₄ and O₂ are fast converted to CH₃CHO, followed its further oxidation to acetic acid to be spilled over onto TiO₂ as acetate species or its decomposition to CO species which partially reacts with bridged OH bond of supports to form formate species.



Scheme 3-6. Proposed mechanism for ethylene oxidation on Pt/ TiO₂.

3.3.3.6 Pt/CeO₂

Figure 3-20 and 3-21 exhibits the DRIFTS spectra on Pt/CeO₂ in the presence of C₂H₄ + O₂ + He or CO + O₂ + He gas. Figure 3-20 shows the appearance of the band at 3360 cm⁻¹ resulted in the ν (OH) of H₂O, the signals at 2129 and 2081 cm⁻¹ corresponded to CO adsorbed on Pt²⁺ and Pt⁰ sites, the peaks at 1613, 1441 and 1293 cm⁻¹ assigned to carbonate species.[27-29] There is no change of each species with the flow of O₂ + He gas continued. It is very interesting that the same CO (the band at 2129 and 2085 cm⁻¹) and carbonate species (the bands at 1611, 1440 and 1331 cm⁻¹) were formed on Pt/CeO₂ under the flow of CO and O₂ gas. However, it is found in Figure 3-22 that the totally different species were formed by adsorption of CH₃CHO on Pt/CeO₂. The bands at 2910, 1529, 1410, and 1358 cm⁻¹ are resulted in the formation of acetate species on CeO₂, and a weak band at 1698 cm⁻¹ is corresponded to acetyl species.[30] All of the data indicate that CH₃CHO is not one kind of intermediates for C₂H₄ oxidation on Pt/CeO₂.

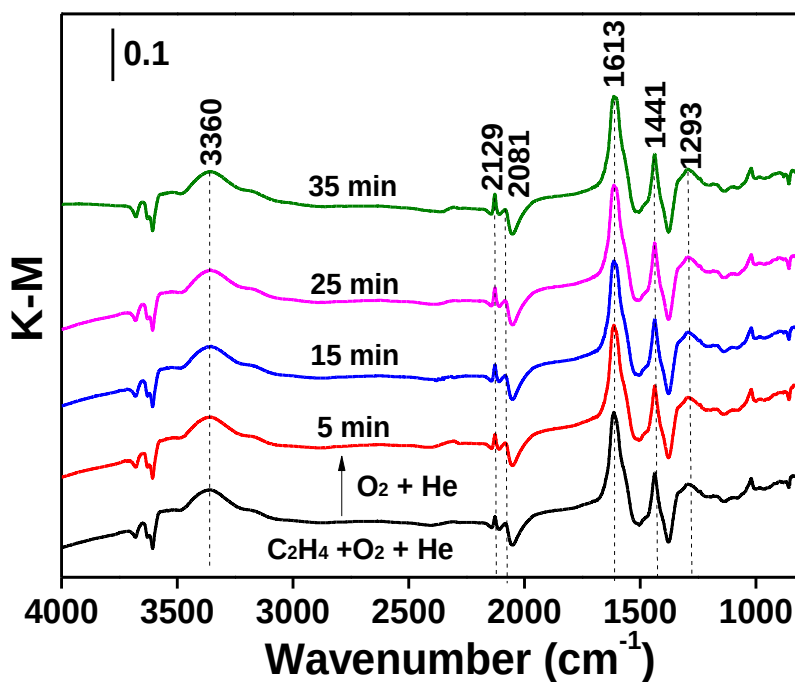


Figure 3-20. DRIFT spectra of adsorption of C_2H_4 on 5% Pt/CeO₂ catalyst. The samples were pretreated in H_2 at 200°C for 1 h. After cooling to 50°C, they were exposed to a flow of C_2H_4 (0.2 mL min⁻¹) + O_2 (4 mL min⁻¹) + He (16 mL min⁻¹) for 30 min, then the flow of C_2H_4 was stopped while maintaining O_2 + He flow for 35 min.

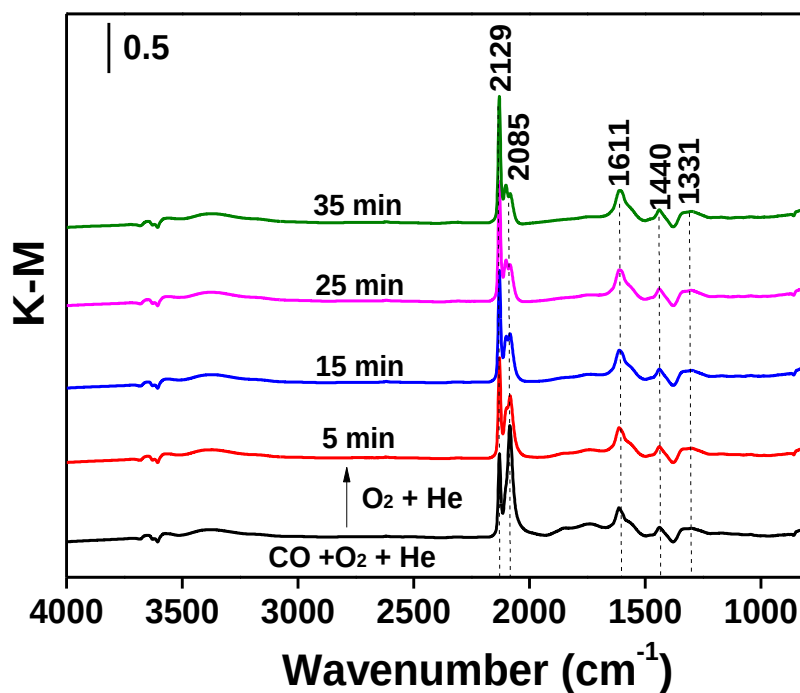


Figure 3-21. DRIFT spectra of 5% Pt/ CeO₂ catalyst. After exposure to a flow of CO (2 mL min⁻¹) + O₂ (8 mL min⁻¹) + He (30 mL min⁻¹) at 50°C for 30 min, the flow of CO was stopped while keeping O₂ + He flow for 35 min.

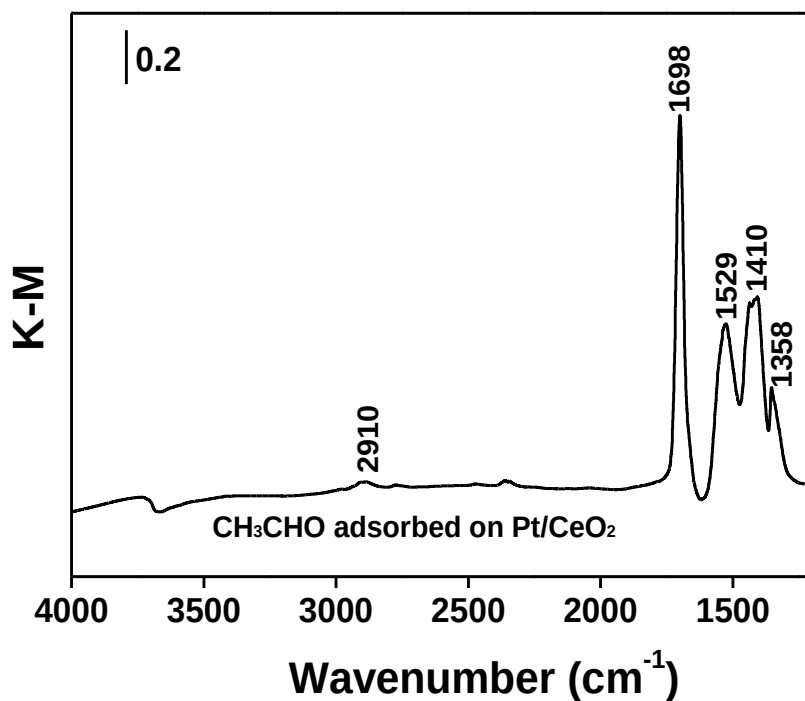
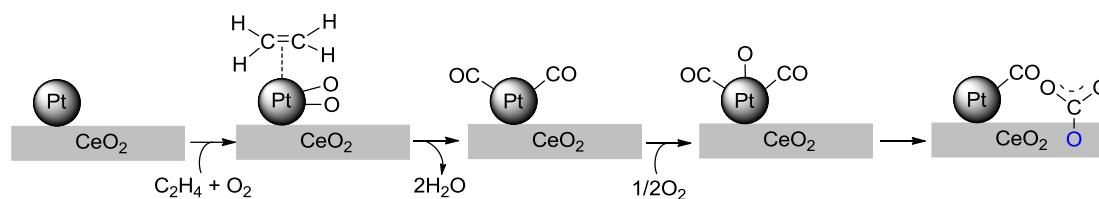


Figure 3-22. DRIFT spectra obtained by adsorption of CH₃CHO vapor on 5% Pt/CeO₂.

Table 3-9. Peak assignment of DRIFT spectra obtained with Pt/ CeO₂ after exposure to different gas flow.

Assignment	Wavenumber (cm ⁻¹)		
	5 wt% Pt/ CeO ₂		
	C ₂ H ₄ + O ₂ + He	CO + O ₂ + He	CH ₃ CHO
	Figure 3-20	Figure 3-21	Figure 3-22
$\nu(\text{OH})$ H ₂ O	3360		
$\nu(\text{CH}_3)$ Acetate			2910
$\nu_s(\text{CO})$ Pt ²⁺ -CO			
$\nu_s(\text{CO})$ Pt-CO (linear)	2129	2129	
$\nu(\text{CO}_3)$ Carbonate	2081	2085	
$\nu(\text{CO}_3)$ Carbonate	1613	1611	
$\nu(\text{CO}_3)$ Carbonate	1441	1440	
$\nu(\text{CO})$ Acetyl	1293	1331	
$\nu_{as}(\text{OCO})$ Acetate			
$\delta_{as}(\text{CH}_3)$ Acetate			
$\delta_s(\text{CH}_3)$ Acetate			
			1698
			1529
			1410
			1358

The possible mechanism of ethylene oxidation on Pt/CeO₂ is shown in Scheme 3-7; which is totally different from that on Pt catalysts supported on MCM-41, SiO₂, Al₂O₃, ZrO₂, and TiO₂. The adsorbed C₂H₄ and O₂ are fast decomposed into CO species which partially reacts with lattice oxygen of support to form carbonate species.



Scheme 3-7. Proposed mechanism for ethylene oxidation on Pt/ CeO₂.

With the combination of the catalytic activities and reaction pathways formed on Pt catalysts over different supports. It is found that supports play an important role in this reaction. *In situ* DRIFTS was explored for investigation the oxidation of ethylene on various Pt catalysts at 50°C or 150°C. As shown in Figure 3-23, when flow ethylene on Pt/MCM-41 and Pt/Q-10 at 150°C, all of the species are almost completely oxidized. However, by compared to the bands formed on 50°C, more strong bands assigned to acetate or carbonate species are formed on Pt catalysts supported on Al₂O₃, ZrO₂, TiO₂, and CeO₂, which may be due to the fast reaction rate to form those species with their no further oxidation at this temperature. Consequently, one kind of reason for higher catalytic activities obtained on Pt/MCM-41 and Pt/SiO₂ may be because of the faster removal of CO band formed on MCM-41, and SiO₂-supported Pt catalysts than that observed on Al₂O₃-, ZrO₂-, TiO₂-, and CeO₂-supported Pt catalysts; the other reason may be due to the easier formation of acetate, formate, and carbonate species on Al₂O₃-, ZrO₂-, TiO₂-, and CeO₂-supported Pt catalysts than on MCM-41, and SiO₂-supported Pt catalysts, which will be very strongly adsorbed on the surface of the catalyst and only can be completely oxidized at relative higher temperature.

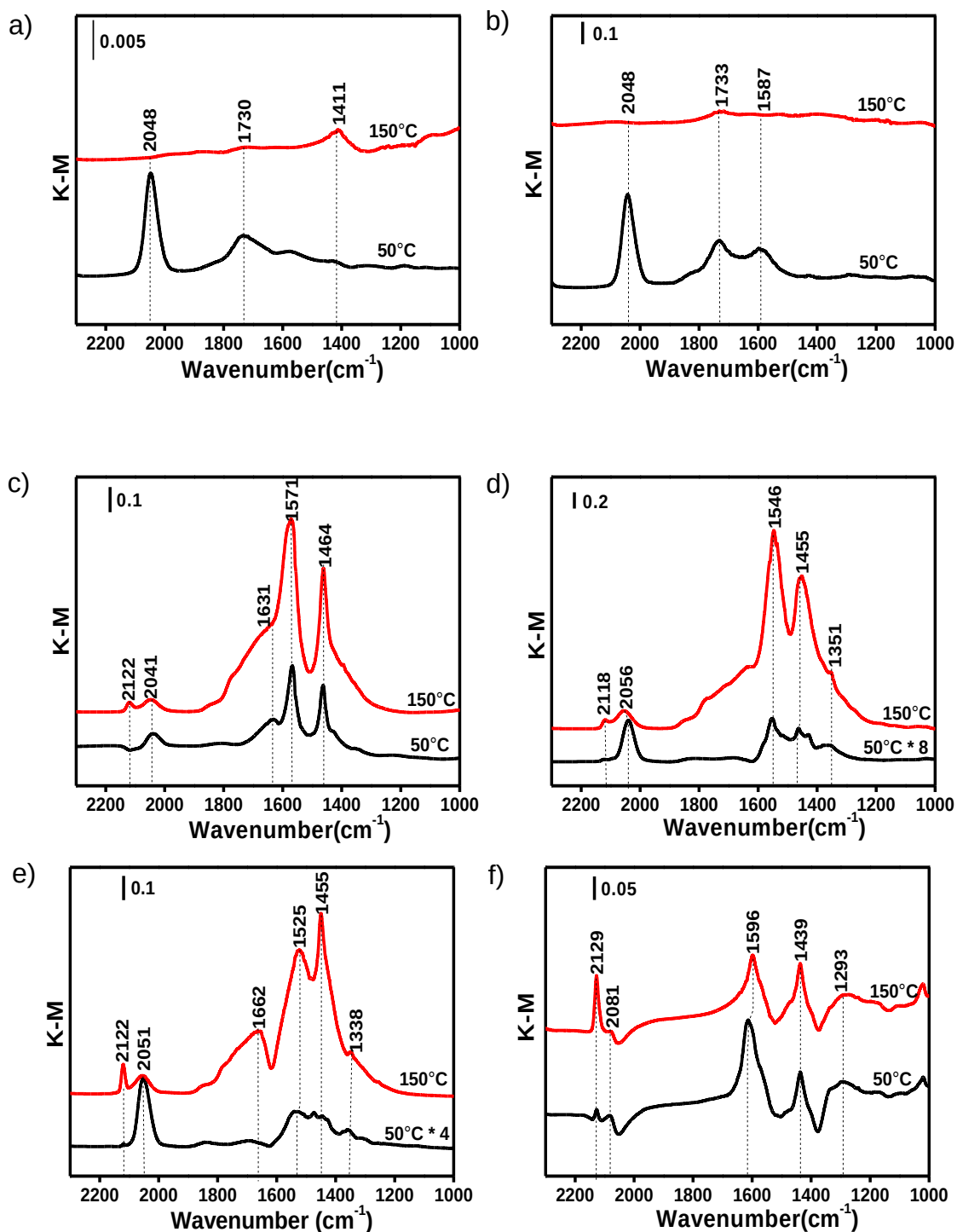


Figure 3-23. DRIFT spectra of adsorption of C_2H_4 on Pt catalysts a) Pt/MCM-41, b) Pt/Q-10, c) Pt/ Al_2O_3 , d) Pt/ ZrO_2 , e) Pt/ TiO_2 , f) Pt/ CeO_2 . The samples were pretreated in H_2 at 200°C for 1 h. After cooling to 50°C or 150°C, they were exposed to a flow of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (16 mL min^{-1}) for 30 min.

3.4 Conclusion

In conclusion, this work studied the support effect on the complete oxidation of ethylene over Pt nanoparticles supported on various metal oxides (MCM-41, SiO₂, γ -Al₂O₃, ZrO₂, TiO₂ and CeO₂). The activity order for oxidation reaction was found to be: Pt/MCM-41 $\approx$ Pt/SiO₂ > Pt/ γ -Al₂O₃ $\approx$ Pt/ZrO₂ $\approx$ Pt/TiO₂ > Pt/CeO₂. In addition, the proposed reaction pathways on various Pt catalysts were also studied by in-situ DRIFTS. We have observed that the reaction pathway was similar on Pt/MCM-41 and Pt/SiO₂, and that C₂H₄ and O₂ quickly react to form HCHO. Then HCHO adsorbed on Pt is mainly decomposed into CO and H species, which react with O species to give CO₂ and H₂O, respectively. However, different reaction pathways were found on other Pt supported metal oxides (Al₂O₃, ZrO₂, TiO₂ and CeO₂) that acetaldehyde was quickly formed and it was further oxidized into surface acetate and CO species. Then CO species was partially oxidized into CO₂ on Pt/ γ -Al₂O₃; however, it was oxidized into formate species on Pt/ZrO₂ and Pt/TiO₂. Whereas CO species was formed when C₂H₄ and O₂ adsorbed on Pt/CeO₂, and then which was further oxidized into carbonate species adsorbed on CeO₂. The IR results showed that the different reaction pathways are the key factor to obtain active ethylene elimination factors.

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Chapter 4. The Influence of Structure of Silica and the Doping of Heteroatoms on Ethylene Oxidation over Pt Catalysts

4.1 Introduction

Mesoporous inorganic or organic silicas with different porous and morphological characteristics can be prepared by using different ionic or nonionic surfactants as templates for the polycondensation of silic species, originating from different sources of silica.[1-2] Several types of mesoporous silicas such as MCM-X, SBA-X, and HMM-X have been widely used in preparation of supported metal catalysts for application in heterogeneous catalysis since their high specific surface area, high amount of hydroxyl groups or special pore structure. For example, MCM-41 and HMM-1 has been already used as supports for preparation of Pt catalysts with their application for preferential CO oxidation in hydrogen (PROX) reaction, as well as the preparation of Pd/SBA-15 for aerobic oxidation of alcohols.[3-5] However, the amorphous nature of wall structure and neutral active sites of mesoporous silica limit their application in catalytic reaction, so heteroatoms such as Al^{3+} , Ti^{4+} , or Zr^{4+} were introduced into mesoporous silica for providing redox active sites.[6]

Ethylene, as a plant hormone, prevents vegetative growth, flower and fruit development in horticultural storage facilities and accelerates normal ageing of fruit, flowers and vegetables in transportation, and refrigerator due to the endogenous production of it by the plant material. Consequently, it is necessary to removal of such

pollutant into consideration when dealing with the gaseous waste products and maintaining plant normal growth, storing and transportation.[7-10] However, before the finding of Pt/MCM-41 exhibiting good performance in oxidation of trace ethylene at low temperature in our group, there was no related report on the application of mesoporous silica in complete oxidation of ethylene. In order to further study on the effect of mesoporous silica and metal doped mesoporous silica on the oxidation of ethylene over Pt catalysts, on the one hand, various silica such as MCM-41, SiO₂, HMM-1, SBA-15, and MCM-48 have been chosen as supports for investigation of the pore structure and surface silanol group effect, on the other hand, SBA-15, Al-SBA-15, Zr-SBA-15, and Ti-SBA-15 have been prepared for study the metal doping effect.

4.2 Experimental

4.2.1 Synthesis of supports

The procedure for preparation of MCM-41 has been depicted in 2.2.1 part of Chapter 2. HMM-1 was obtained by the reported method.[11]

MCM-48 was prepared according to the reference [12]. Firstly, 35.2 g cetyltrimethylammonium bromide (CTAB) was dissolved in water, subsequently, 40 mL NaOH (2 M) and 37.0 mL Tetraethyl orthosilicate (TEOS) was added while stirring at 35°C for 0.5 h. Then, the gel was put in 100°C oven for 72 h. After filtering, washing and drying, the sample was calcined at 550°C for 12h.

The method for synthesis of SBA-15 and Al-SBA-15 (mole ratio: Si/Al=10.0) is similar to the procedure described in literature.[13] Typically, After P123 (8.0 g) was

completely dissolved in HCl solution (2.0 M, 250 mL), TEOS (17.0 g) was added to the solution while stirring at 40°C for 4 h. Then, 1.4 g $\text{Al}_2(\text{SO}_4) \cdot 18\text{H}_2\text{O}$ was added to the mixture (this procedure can be neglect for preparation of SBA-15), followed by additional stirring at 40°C for 20 h the mixture was placed under static oil bath for 24 h. After cooling to room temperature, the pH value of the solution was adjusted to 7.5 by ammonia water, followed its heating in oil bath at 100°C for another 24 h. The product was filtered and washed thoroughly with 3000 mL deionized water. The solid was dried at 100°C in an oven and calcined in air at 500°C to remove the surfactant.

Zr-SBA-15 (mole ratio: Si/Zr = 7.0) was synthesized by following the procedure in reference [14]. Firstly, 4.0 g P123 was dissolved in 110 ml HCl solution (1.1 M), followed by the addition of 8.4 g tetraethyl orthosilicate (TEOS) and stirring for 4 h at 45°C. Secondly, 1.9 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was added into the solution for stirring 0.5 h, then 9.0 g urea was introduced and the temperature was increased to 90°C. Thirdly, the mixture was stirred and refluxed at 90°C. Then, the mixture was transferred into a stainless steel autoclave and aged at 100°C for 2 days. Finally, the solid product was collected by filtration and then calcinations at 500°C for 4 h.

The synthesis of Ti-SBA-15 (mole ratio: Si/Ti = 10.0) was following the reported literature.[15] In a typical process, 12.0 g of Pluronic P123 was dissolved in 228 g of deionized water and 7.0 g of hydrochloric acid (37%) at 35°C under magnetic stirring. Then, 26.0 g of tetraethylorthosilicate (TEOS) and 3.6 g of tetrapropylorthotitanate (TPOT) were premixed and rapidly added to the initial homogeneous solution. The resulting mixture was stirred for 24 h at 35°C and subsequently hydrothermally treated

for a given time at 60°C to ensure further framework condensation. The solid products were recovered by filtration and dried in air at 100°C for 24 h. Finally, the products were calcined at 550°C for 6 h to remove the template.

4.2.2 Preparation of catalysts

A typical wet impregnation method was used for the preparation of all of the catalysts. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was used as a precursor salt, moreover, MCM-41, SiO_2 (Fuji Silysia, Cariat Q-10), HMM-1, MCM-48, and SBA-15 were used to study the pore structure and surface groups effect, while SBA-15, Al-SBA-15, Zr-SBA-15, and Ti-SBA-15 were used for investigating metal doping effect. Typically, 1.0 g support materials was impregnated with 50 ml aqueous solution containing required amount of precursor salts for corresponded metal loading. Each mixture was stirred for 18 h, evaporated to dryness and dried under vacuum overnight. The resulting solid was calcined in O_2 flow at 200°C for 2 h, and then reduced in H_2 flow at 200°C for 2 h.

4.2.3 Catalyst characterization

X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were obtained by a Rigaku diffractometer (Rigaku Miniflex) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The scanning rate of the diffractometer is 2° min^{-1} . The measurement was carried out by an X-ray generator with a voltage of 30 kV and a current of 15 mA.

Nitrogen adsorption

The nitrogen adsorption/desorption isotherms at about -196°C were obtained by a Belsorp mini II (BEL Japan) after heating the samples at 120°C under vacuum for 6 h,

the specific surface area and the pore-size distribution were calculated by Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively, where the range of a P/P° is changed from 0.05 to 0.995.

Transmission electron microscopy (TEM)

The microstructure of the metal particles was investigated by a transmission electron microscopy (TEM, JEM-2100F) with accelerating voltage of 200 kV. The samples for TEM measurements were prepared by placing a drop of dilute ethanol suspension of supported metal particles onto a copper grid and allowing ethanol to be evaporated in air.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)

DRIFT measurements were on a PerkinElmer Spectrum 100 (resolution 2-4 cm^{-1} , integration 64 times) equipped with an MCT detector and a S.T. Japan DRIFT heating chamber. In each experiment, sample powder (6.0 mg) was placed in a DRIFT cell with a KBr window. Two procedures for detecting the silanol group of Pt catalysts supported on various silica and *in situ* C_2H_4 oxidation reaction on Pt catalysts supported on different heteroatoms doped SBA-15 were shown respectively as follows: (1) Silanol group detection: In order to avoid the effect of adsorbed water, catalyst was firstly pretreated at 300°C for 30min under He flow (20 mL min^{-1}), After cooling the temperature 30°C, the measurement was started. The same procedure was employed for KBr powder as Background. (2) *In situ* C_2H_4 oxidation: Catalyst was firstly pretreated under H_2 atmosphere (20 mL min^{-1}) at 200°C for 1 h. After the pretreatment, the sample was cooled to 50°C and purged under He flow (20 mL min^{-1}) for 10 min. Next, a gas

mixture of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (15.8 mL min^{-1}) (total flow rate: 20 mL min^{-1}) was introduced to the catalyst. After reaching a steady state, a gas mixture of (O_2 + He) was introduced for further measurement.

4.2.4 Ethylene oxidation

The catalytic oxidation of C_2H_4 was performed in a stainless steel tubular fixed-bed reactor (i.d. = 4 mm) under atmospheric pressure in a flow apparatus which consists of a feed unit, the reactor and an analysis unit utilizing on-line gas chromatography. Each catalyst (0.20 g, 40-60 mesh) loaded in the reactor was pretreated under a H_2 stream (30 mL min^{-1}) at 200°C for 1 h before use. The reactant gas mixture [C_2H_4 (99.99%) 1 vol%, O_2 (99.999%) 20 vol%, N_2 (99.999%) 5 vol%, He (99.999%) balance] was fed to the reactor using mass flow controllers to achieve the desired flow rates. After reaching a steady state, typically in ca. 1 h, the reaction temperature was gradually increased from room temperature to 200°C (1°C min^{-1}), and the outlet gas was analyzed at every 5°C interval using an on-line gas chromatograph [Agilent 3000A Micro GC equipped with thermal conductivity detector (TCD) and a column of molecular sieves 5A (10 m) and Plot U (8 m)]. The detection limit of C_2H_4 was 0.1 ppm in the present analysis. The C_2H_4 conversions ($\chi_{\text{C}_2\text{H}_4}$) were calculated as follows: $\chi_{\text{C}_2\text{H}_4} = ([\text{C}_2\text{H}_4]_{\text{in}} - [\text{C}_2\text{H}_4]_{\text{out}}) / [\text{C}_2\text{H}_4]_{\text{in}} \times 100 (\%)$, where $[\text{C}_2\text{H}_4]_{\text{in}}$ and $[\text{C}_2\text{H}_4]_{\text{out}}$ is the concentration of C_2H_4 introduced to the reactor and that detected after the reactor, respectively.

4.3 Results and discussion

4.3.1 The effect of silica with different pore structure and surface silanol group

The structural parameters of supports and catalysts such as BET surface area (S_{BET}), BJH pore size, and Pt particle size calculated by the Scherrer equation (D_x) are summarized in Table 4-1.

Table 4-1. Structural parameters of supports and catalysts.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^[a]	Pore size (nm) ^[b]	D_x (nm) ^[c]
MCM-41	1006	2.9	—
SiO ₂	256	22	—
HMM-1	701	3.1	—
SBA-15	367	12	—
MCM-48	1323	2.5	—
Al-SBA-15	302	7.1	—
Zr-SBA-15	618	12	—
Ti-SBA-15	848	3.8	—
5% Pt/MCM-41	913	2.9	2.4
5% Pt/SBA-15	341	12	8.4
5% Pt/ SiO ₂	270	18	5.8
5% Pt/MCM-48	715	1.4	2.0
5% Pt/HMM-1	498	3.0	3.5
2% Pt/SBA-15	360	12	15
2% Pt/Al-SBA-15	277	7.1	11
2% Pt/Zr-SBA-15	394	9.3	14
2% Pt/Ti-SBA-15	612	3.8	16

[a] BET (Brunauer-Emmett-Teller) surface area.

[b] Pore diameter by the BJH (Barrett-Joyner-Halenda) method.

[c] Particle size calculated by the Scherrer equation.

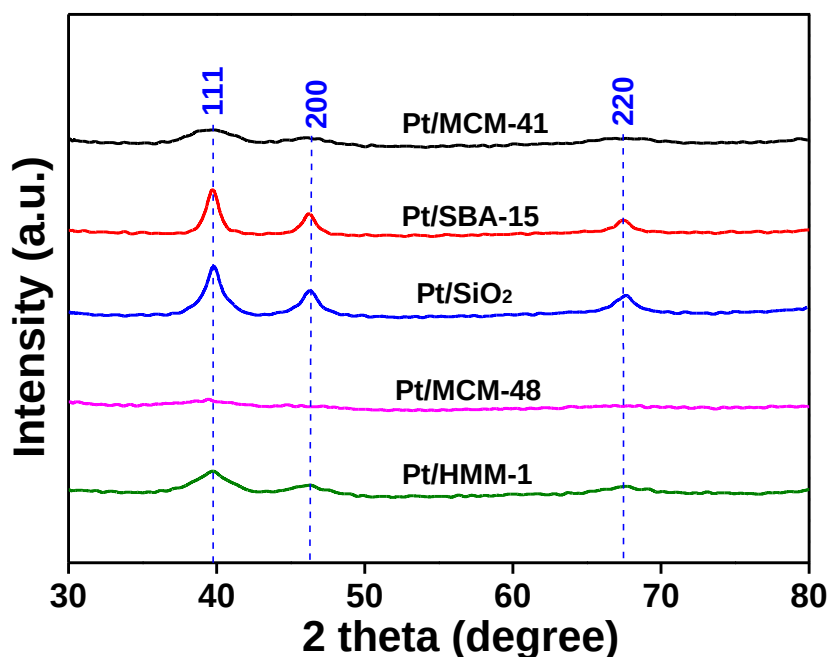


Figure 4-1. Wide angle XRD patterns of Pt catalysts supported on various SiO₂: Pt loading, 5%.

Figure 4-1 reveals the wide angle XRD patterns of Pt catalysts supported on various SiO₂. It has been characterized that three characteristic XRD peaks at 40°, 46°, and 67°, which can be assigned to (111), (200) and (220) reflections of face-centered cubic (fcc) Pt crystals, which is corresponded to the JCPDS card (No. 04-0802). The particle sizes of Pt for Pt/MCM-41, Pt/SBA-15, Pt/SiO₂, Pt/MCM-48, and Pt/HMM-1 estimated by the Scherrer equation with the (111) peaks are 2.4, 8.4, 2.0, 5.8, and 3.5 nm, respectively, which was summarized in Table 4-1.

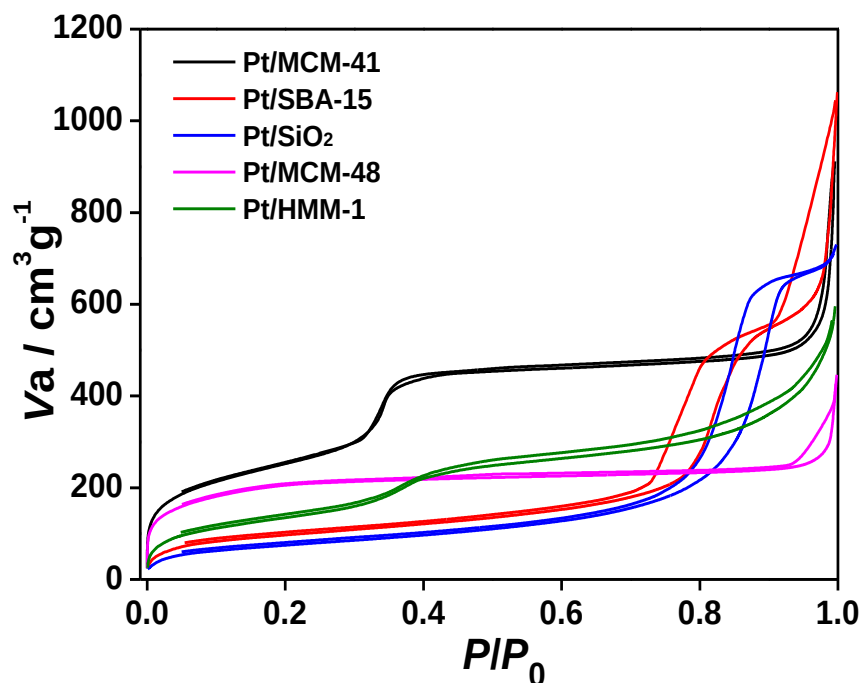


Figure 4-2. The nitrogen adsorption/desorption isotherms of Pt catalysts supported on various SiO₂. Pt loading: 5%.

The nitrogen adsorption/desorption isotherms of various Pt catalysts is shown in Figure 4-2. All of curves present type IV adsorption isotherms, which exhibit the formation of mesoporous structure of each catalyst. The different shape of the curves reveals the formation of different pore structure of each catalyst. The BET surface areas and pore sizes of the supports and Pt catalysts are also listed in Table 4-1. It is observed that the surface areas are decreased with the incorporation of Pt into supports excepting SiO₂. However, in addition to Pt/MCM-48, the pore sizes of other Pt catalysts are almost no change in comparison with those of supports, which indicating no blocking of pores by incorporation of Pt nanoparticles into supports excluding MCM-48.

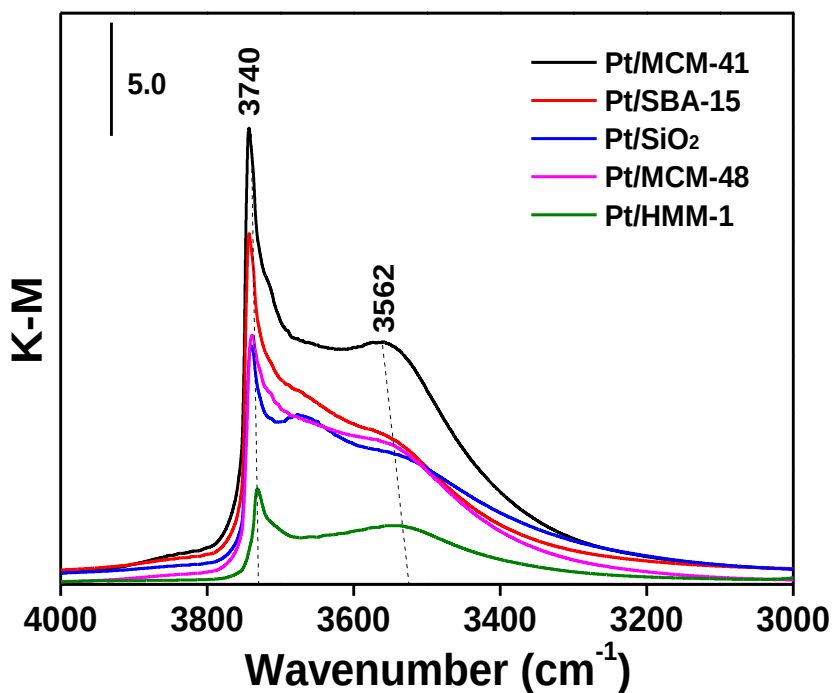


Figure 4-3. DRIFT spectra of Pt catalysts supported on various SiO₂. Pt loading: 5%.

The surface silanol groups of each catalyst were also investigated by DRIFT measurements. As shown in Figure 4-3, there are two bands formed between 3800-3700 cm⁻¹ for all catalysts. The band at around 3740 cm⁻¹ is assigned to isolated silanol groups, whereas that at around 3562 cm⁻¹ is attributed to hydrogen-bonded silanols because of the adsorption of water.[16-19] Moreover, the intensity of silanol groups are ranked as follows: Pt/MCM-41 > Pt/ SBA-15 > Pt/SiO₂, Pt/MCM-48 > Pt/HMM-1. In this respect, it is found that the big difference of the contents of silanols is obtained among all of the catalyst.

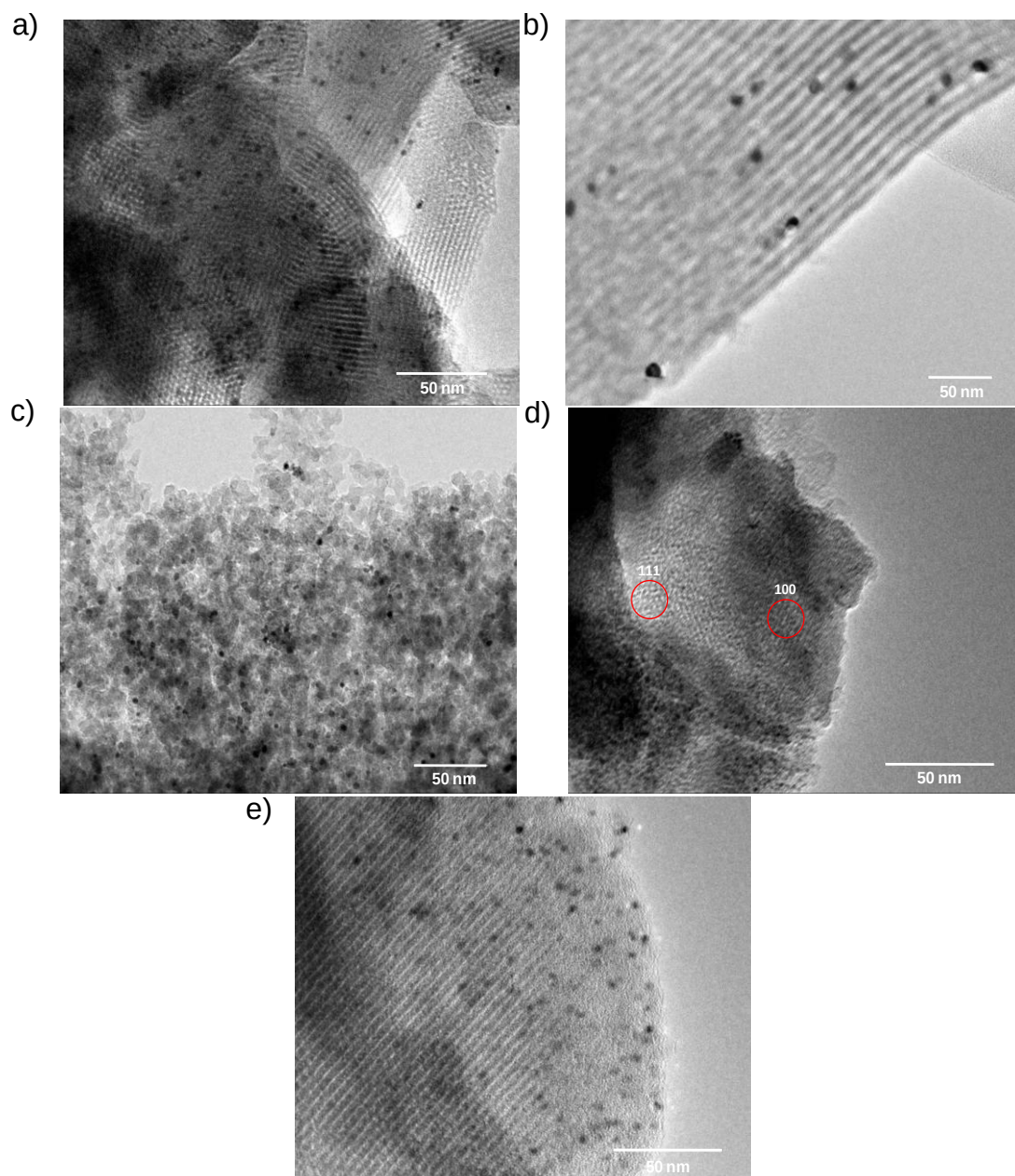


Figure 4-4. TEM images of Pt catalysts. a) Pt/MCM-41, b) Pt/SBA-15, c) Pt/SiO₂, d), Pt/MCM-48 and, e) Pt/HMM-1. Pt loading: 5%.

It is found in Figure 4-4a, c, d that Pt nanoparticles are well dispersed on MCM-41, HMM-1, and SBA-15 with ordered pores with regular size and presumably hexagonal outline as already described in the literature [11, 13, 20-21]. Figure 4-4b proves the unordered structure of SiO₂. As shown in Figure 4-4e, along the [100] indicating the uniform pore structure, while along the [111] direction showing a well-defined

hexagonal arrangement of MCM-48 with a cubic structure are formed, the Pt particles are also highly dispersed in the mesopores.[12] TEM images give an evidence of the difference of the pore structure among supports.

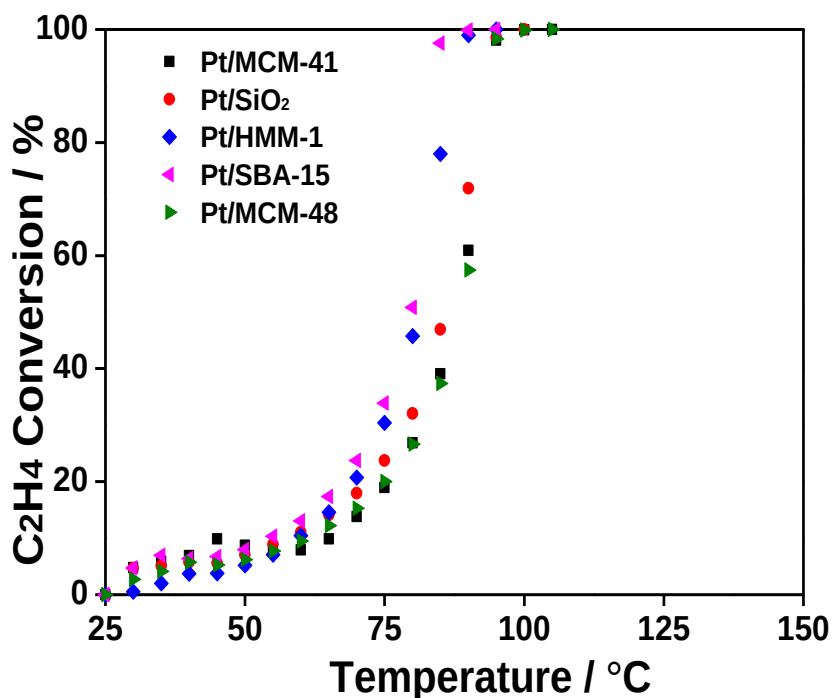


Figure 4-5. Light-off curves of catalytic ethylene conversion over Pt catalysts supported on various SiO₂. Pt loading: 5 wt%; space velocity (SV): 9000 mL h⁻¹ g⁻¹; catalyst: 0.2 g; C₂H₄: 1vol%; O₂: 20 vol%; N₂: 5 vol%; He balance.

The catalytic activities of all catalyst are evaluated. Figure 4-5 shows the results obtained. As can be observed, the trend for each catalyst is similar and all catalysts exhibit almost the same efficiency. It seems that the pore structure and surface silanol groups of supports do not have a major effect on the ethylene oxidation performance.

4.3.2 The effect of silica with different metal doping

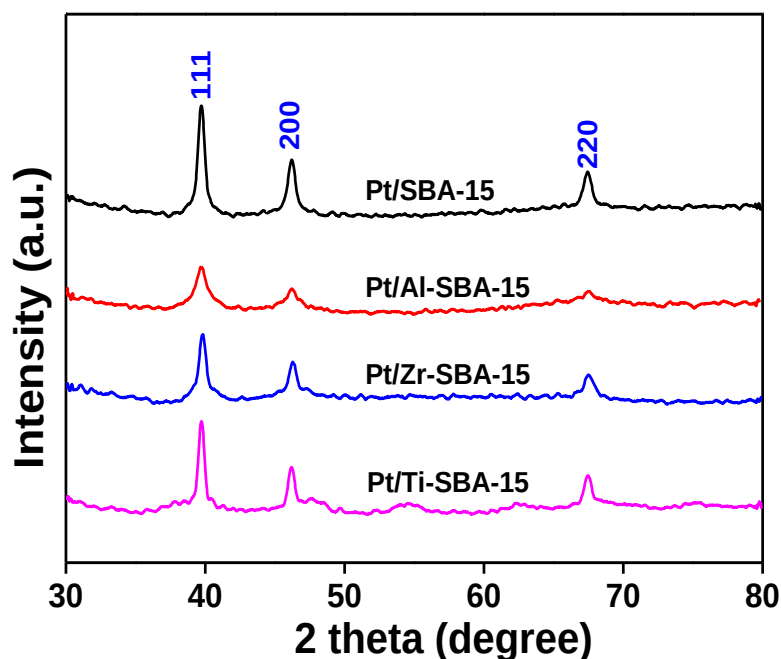


Figure 4-6. Wide angle XRD patterns of Pt catalysts supported on different metal doped SBA-15. Pt loading: 2%.

Figure 4-6 shows the wide angle XRD patterns for Pt catalysts supported on metal doped SBA-15. All positions of the diffractions lines in the XRD patterns of Pt catalysts are in good agreement with the standard pattern of face-centered cubic (fcc) Pt crystals (JCPDS card, No. 04-0802). The calculation of particle sizes of Pt from Scherrer's equation at $2\theta = 39.7$ suggest a range between 11 and 16 nm as shown in Table 4-1.

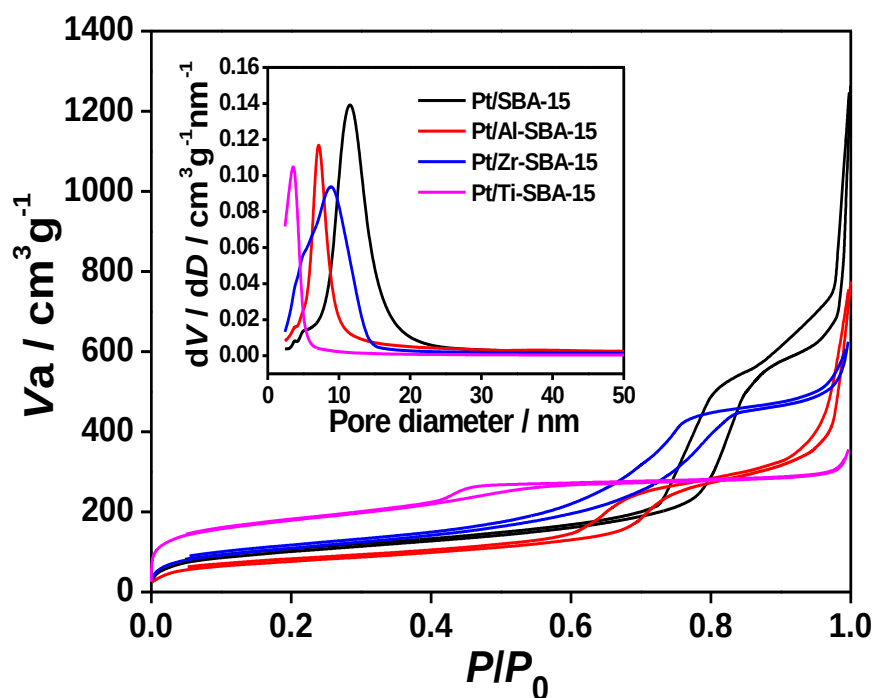


Figure 4-7. The nitrogen adsorption/desorption isotherms and the pore size distribution (the inset) of Pt catalysts supported on various metal doped SBA-15. Pt loading: 2%.

Figure 4-7 exhibits the nitrogen adsorption/desorption isotherms and the corresponded pore size distribution of various Pt catalysts supported on various metal doped SBA-15. As can be observed, typical type IV adsorption isotherms show the formation of mesoporous structures of all catalysts. The BET surface areas and pore sizes of the supports and Pt catalysts are listed in Table 4-1. The results reveal that the pore sizes of Pt catalysts are almost the same as those of supports giving evidence of no blocking of the mesopores.

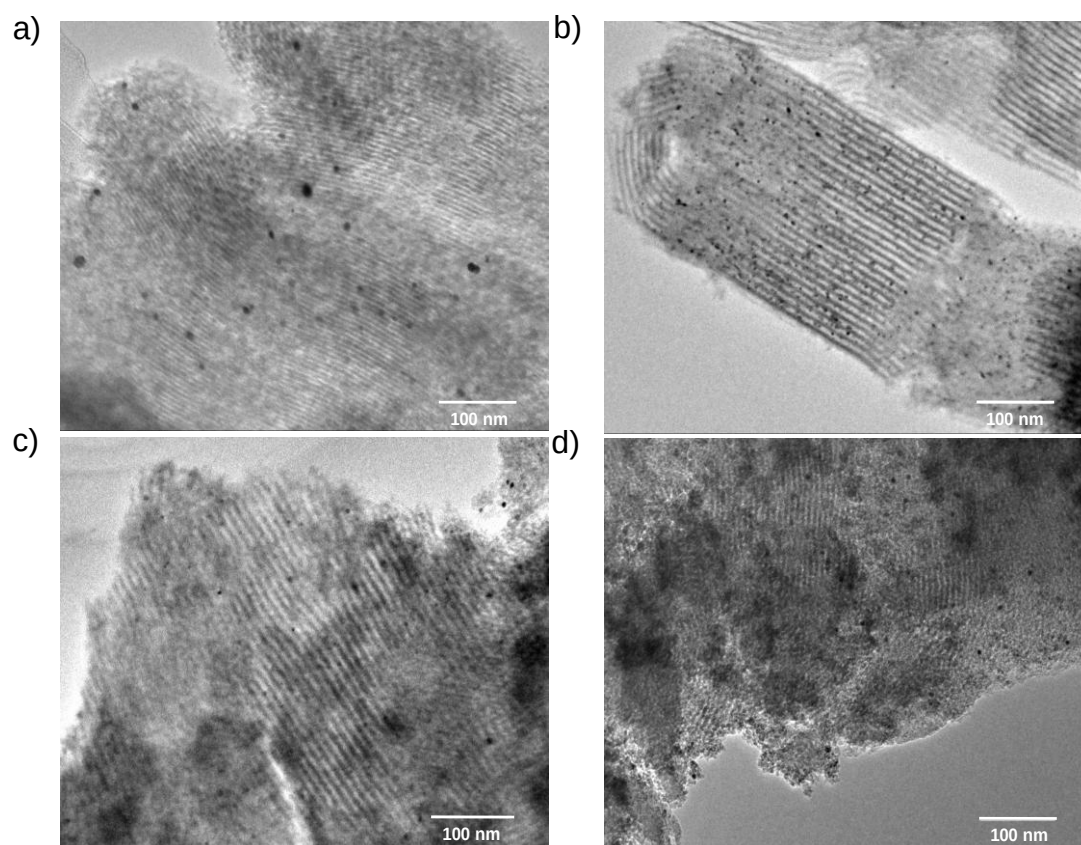


Figure 4-8. TEM images of Pt catalysts. a) Pt/SBA-15, b) Pt/Al-SBA-15, c) Pt/Zr-SBA-15, d) Pt/Ti-SBA-15. Pt loading: 5%.

As shown in Figure 4-8, all samples present high dispersed Pt nanoparticles and order mesopore with hexagonal structure, which proves no destroy of the mesopore after doping heteroatoms and incorporation of Pt nanoparticles.

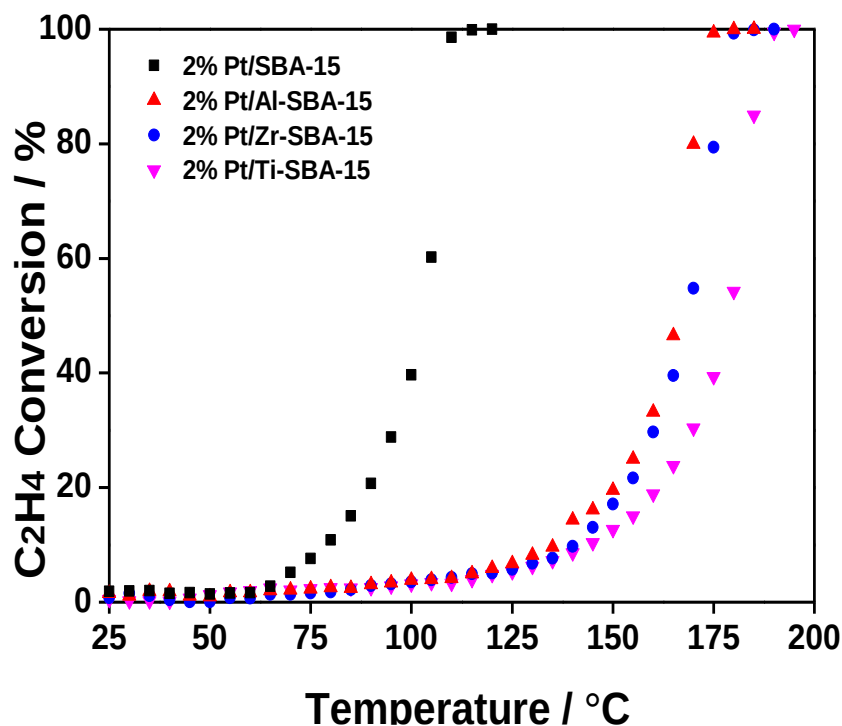


Figure 4-9. Light-off curves of catalytic ethylene conversion over Pt catalysts supported on various metal doped SBA-15: 5 wt%; space velocity (SV): 9000 mL h⁻¹ g⁻¹; catalyst: 0.2 g; C₂H₄: 1vol%; O₂: 20 vol%; N₂: 5 vol%; He balance.

The catalytic oxidation of ethylene was studied over Pt catalysts supported on various metal doped SBA-15. The ethylene conversion as a function of the reaction temperature, is shown in Figure 4-9 for all samples. Over the Pt/SBA-15 catalyst, the oxidation of ethylene starts near 65°C, reaching 100 % conversion at 120°C. With other catalysts, ethylene oxidation starts at the similar temperature of 95°C, but complete oxidation of ethylene happens at around 190°C. In summary, it can be stated that the incorporation of heteroatoms (Al, Zr, and Ti) into the tunnel structure of SBA-15 decreases the catalytic performance of this material.

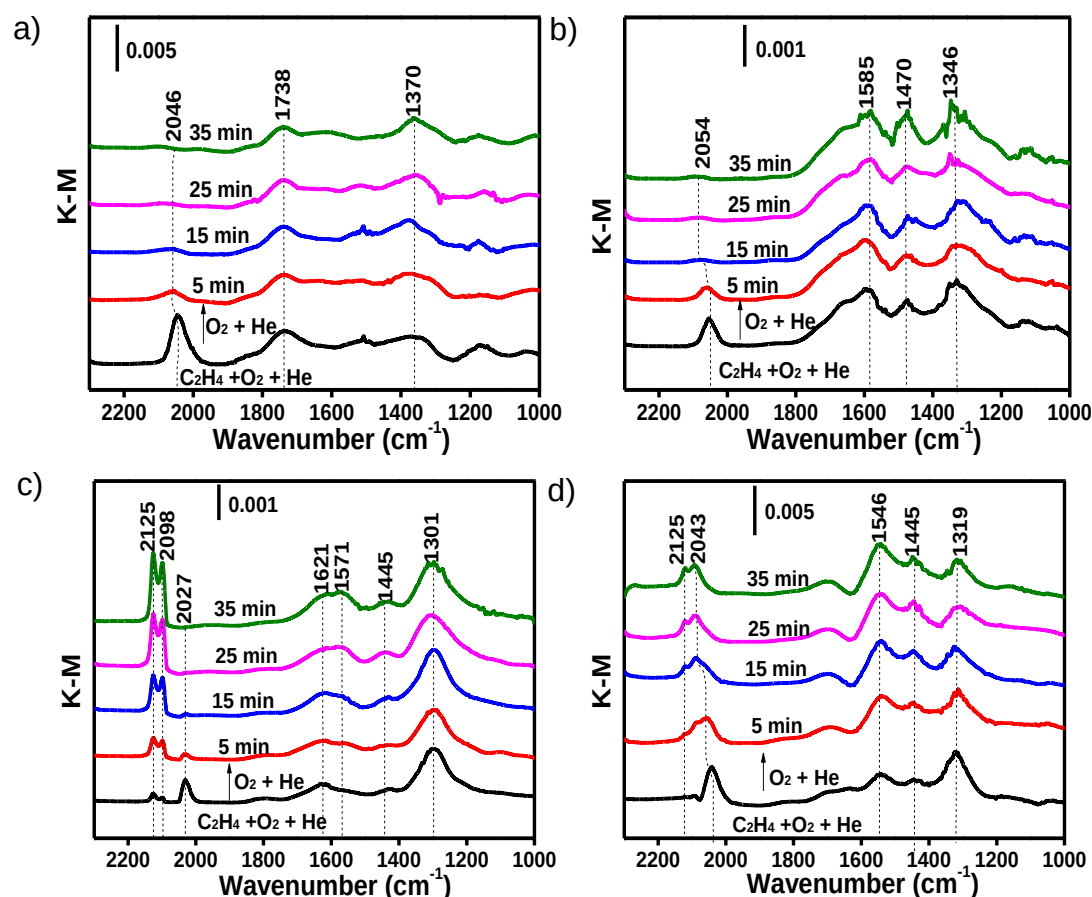


Figure 4-10. DRIFT spectra of adsorption of C_2H_4 on a) 2% Pt/SBA-15, b) 2% Pt/Al-SBA-15, c) 2% Pt/Zr-SBA-15, and d) 2% Pt/Ti-SBA-15 catalyst. The samples were pretreated in H_2 at 200°C for 1 h. After cooling to 50°C , they were exposed to a flow of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (16 mL min^{-1}) for 30 min, then the flow of C_2H_4 was stopped while maintaining O_2 + He flow for 35 min.

DRIFTS were employed for further study on the mechanism of ethylene oxidation over Pt catalysts supported on metal doped SBA-15. When C_2H_4 , O_2 and He mixture gas was flowed on Pt catalysts, various species were formed. The bands at 2046, 1738, and 1370 cm^{-1} in Figure 4-10a are assigned to linear adsorbed CO on Pt, and physical adsorbed formic acid, respectively. Figure 4-10b shown the bands at 2054, 1585, 1470, and 1346 cm^{-1} prove the formation of CO and acetate species. As shown in Figure

4-10c, three bands at 2125, 2098, 2027 cm^{-1} are related to CO adsorbed on $\text{Pt}^{\delta+}$, the dicarbonyl formed on monatomic platinum, and CO linear adsorbed on metal Pt, respectively.[22] Because of the formation of acryl species, the band at 1621 cm^{-1} is appeared. Other three bands centered at 1571, 1445, 1301 cm^{-1} are corresponded to acetate species. The similar bands of acetate species at 1546, 1445, 1319 cm^{-1} are also found in Figure 4-10d. Other two bands at 2125 and 2043 cm^{-1} are attributed to CO adsorbed on $\text{Pt}^{\delta+}$ and Pt^0 , respectively. As can be observed in Figure 4-10, with the flow of C_2H_4 stopped and the flow of O_2 and He continued, the CO species can be quickly removed on Pt/SBA-15, however, it still remained on Pt/Al-SBA-15, Pt/Zr-SBA-15, and Pt/Ti-SBA-15 even after 35 min. consequently, this may be one key reason for lower ethylene oxidation performance on heteroatom supported Pt catalysts.

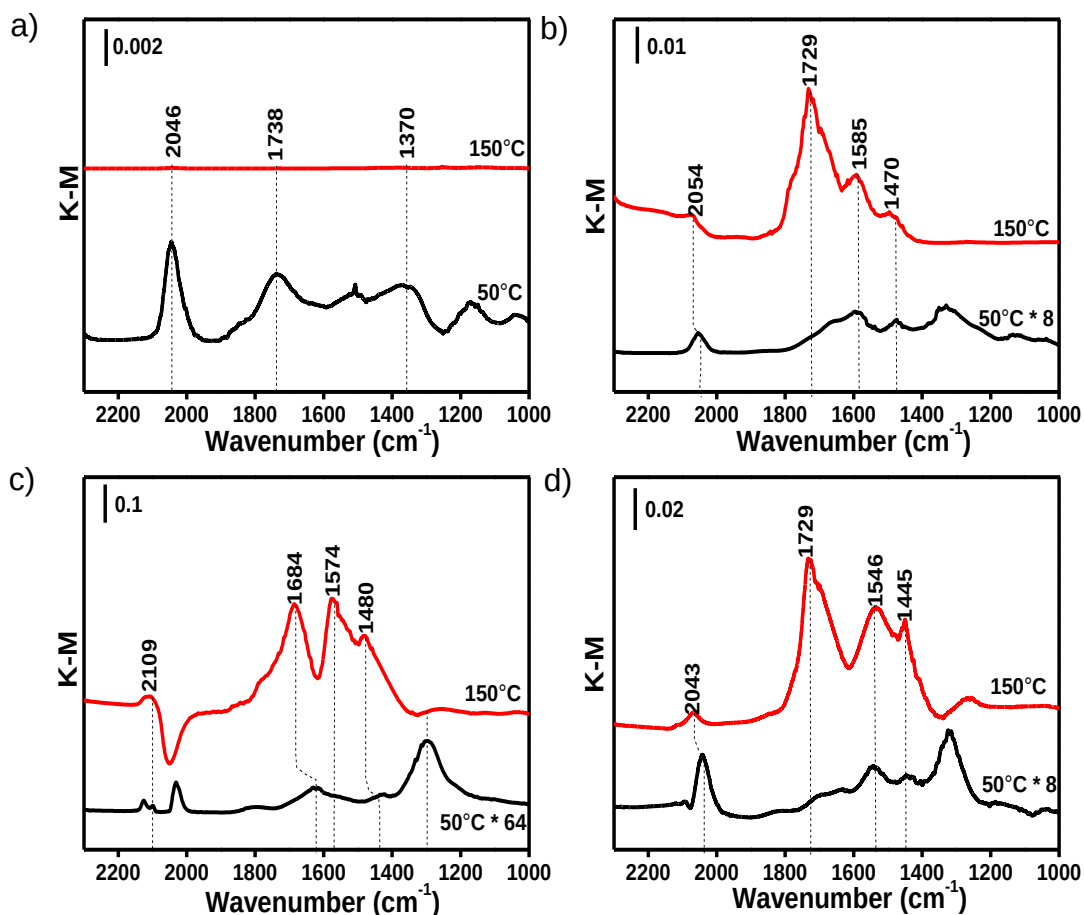


Figure 4-11. DRIFT spectra of adsorption of C_2H_4 on Pt catalysts a) Pt/SBA-15, b) Pt/Al-SBA-15, c) Pt/Zr-SBA-15, d) Pt/Ti-SBA-15. The samples were pretreated in H_2 at $200^\circ C$ for 1 h. After cooling to $50^\circ C$ or $150^\circ C$, they were exposed to a flow of C_2H_4 (0.2 mL min^{-1}) + O_2 (4 mL min^{-1}) + He (16 mL min^{-1}) for 30 min.

In situ DRIFTS study of the oxidation of ethylene on various Pt catalysts at $50^\circ C$ or $150^\circ C$ was investigated. As shown in Figure 4-11, ethylene flow on Pt/SBA-15 at $150^\circ C$, all of the species are almost completely oxidized. However, more strong bands at $150^\circ C$ assigned to acetaldehyde or acetate species are formed on Pt catalysts supported on Al-SBA-15, Zr-SBA-15, and Ti-SBA-15 than those are formed at $50^\circ C$. It is interesting that these results are similar to those happened on Pt catalysts supported on MCM-41, Al_2O_3 , ZrO_2 , and TiO_2 . Therefore, two similar proposed explanations for

higher catalytic activities obtained on Pt/SBA-15 are that CO species formed on SBA-15-supported Pt catalyst can be removed faster than that observed on heteroatoms doped SBA-15-supported Pt catalysts and acetaldehyde or acetate species form easier on heteroatoms doped SBA-15-supported Pt catalysts than on SBA-15-supported Pt catalyst which can only be removed at higher temperature.

4.4 Conclusion

In summary, we have investigated the influence of silica with different pore structure and surface silanol groups and SBA-15 with doping of different heteroatoms on the complete oxidation of ethylene over Pt nanoparticles supported on MCM-41, SiO₂, HMM-1, SBA-15, MCM-48, Al-SBA-15, Zr-SBA-15, and Ti-SBA-15.

Characterization results by XRD, N₂ adsorption method, TEM and DRIFTS show that the pore structure and surface silanol groups present no effect on the ethylene conversion efficiency, however with the doping of heteroatoms into SBA-15, great decreasing of ethylene performance is happened. The probable reason may be because of the change of the reaction pathways after doping heteroatoms into SBA-15 analyzed by DRIFTS.

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Chapter 5. Selective Hydrogenation of Phenylacetylene by Pt Catalyst Supported on Zeolite-Templated Carbon

5.1 Introduction

In heterogeneous metal-catalyzed reaction, support materials play a key role in modifying catalytic activity and selectivity. Various metal nanoparticles have been prepared on numbers of metal oxides and carbons for a wide variety of catalytic application. Novel catalytic performance can be expected with a catalyst prepared from a new type of support material. Zeolite-templated carbon (ZTC) [1-4] is a potentially promising support, because ZTC is a carbon replica obtained from a zeolite as a template, giving ordered three-dimensional micropores consisting of nano-sized graphene units. Although ZTC has been extensively studied as attractive materials for storage of hydrogen,[5-13] electrochemical capacitors [13] and lithiumion batteries,[13] its application in catalysis has been limited to the studies related with fuel cell.[14-15] We have envisioned further utilization of ZTC as a support for metal catalysts. Herein we report the preparation of Pt nanoparticles on ZTC and their catalytic performance in hydrogenation of phenylacetylene.

Selective hydrogenation of phenylacetylene to styrene is an important industrial process, because phenylacetylene contaminated in styrene deactivates styrene polymerization catalysts.[16] Many inorganic and organic materials such as SiO₂,[17-18] γ -Al₂O₃,[19] pumice,[20-21] zeolites,[22] polymers,[23] organic matrices,[24] pillared clays,[25-26] mesostructured silica[27-28] and TiO₂[29] have

been already employed as supports for Pt, Pd, Ni and Cu catalysts in the hydrogenation of phenylacetylene. As recent examples of supported metal catalysts on carbon materials, Pd, Pt, Ru and Pt-Ru on carbon nanotube were used for this reaction,[30-33] whereas metal catalysts supported on ZTC have not been applied.

5.2 Experimental

5.2.1 Catalysts preparation

ZTC was obtained by the reported method.[4] The Pt catalyst supported on ZTC (Pt/ZTC) was prepared by a typical wet impregnation method. ZTC (0.2 g) was mixed with an aqueous solution (50 mL) of diamminedinitrito-platinum(II) ($\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$) with a Pt loading of 2 wt%. The mixture was stirred for 18 h, evaporated to dryness and dried under vacuum for overnight. The resulting solid was reduced in H_2 flow at 400°C for 2 h. For comparison, commercially available carbon materials such as Norit SX ultra (denoted as AC) and Ketjen Black EC-600JD (KB) were used as supports to prepare Pt/AC and Pt/KB, respectively. As another Pt precursor, hydrochloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was used to prepare a Pt catalyst on ZTC (Pt/ZTC-Cl). The four Pt catalysts used in this study are summarized in Table 1.

5.2.2 Phenylacetylene hydrogenation

Selective Hydrogenation of phenylacetylene was carried out with 0.50 mL of phenylacetylene, 5.0 mg of the catalyst and 4.5 mL of ethanol in a 50 mL autoclave under controlled H_2 pressures and temperatures. The molar ratio of

phenylacetylene/Pt(bulk) was 8900. The products were analyzed by a Shimadzu GC-14B gas chromatograph using an FID detector with a capillary column (HR-1, 0.25 mm $\times$ 50 m). A known amount of dodecane was added to the reaction mixture as internal standard.

5.3 Results and discussion

Figure 5-1 shows XRD patterns of the Pt catalysts and the carbon supports. No obvious Pt peaks were obtained for Pt/ZTC and Pt/KB, giving weak and broad peaks at 40°. In contrast, three intense peaks were found with Pt/AC and Pt/ZTC-Cl at 40, 46 and 67°, which was assigned to (111), (200) and (220) reflections of face-centered cubic (fcc) Pt crystalline (JCPDS card, No. 04-0802), indicating the formation of large Pt nanoparticles. The Pt particle sizes of Pt/ZTC, Pt/KB, Pt/AC and Pt/ZTC-Cl were estimated by the Scherrer equation with the (111) peaks to be 1.7, 2.5, 4.4 and 17 nm, respectively (Table 5-1).

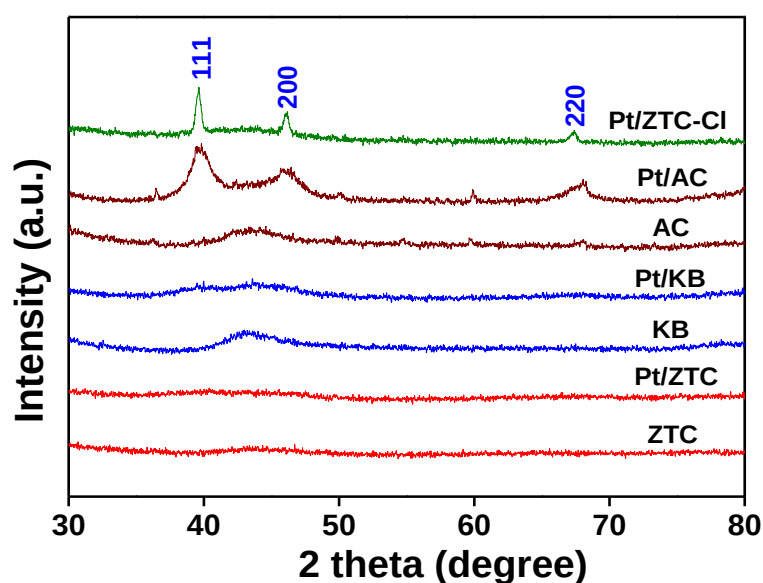


Figure 5-1. XRD patterns of carbon supports and supported Pt catalysts.

In the TEM observation (Figure 5-2), the Pt particles on Pt/ZTC were highly and uniformly dispersed on ZTC with a mean diameter of 2.2 ± 0.8 nm based on 100 particles in random regions (Figure 5-2a). Larger Pt particles were observed in Pt/KB and Pt/AC with mean sizes of 3.5 ± 1.2 nm and 4.4 ± 1.1 nm, respectively, as shown in Figure 5-2b and c. In contrast, Pt/ZTC-Cl catalyst had a relatively larger size and broader distribution with 15 ± 11 nm (Figure 5-2d). The Pt particle sizes analyzed by TEM were in good accordance with the results estimated by XRD (Table 5-1).

Table 5-1. Preparation of Pt catalysts and their particle sizes.

Sample	Precursor	D _{XRD} (nm)	D _{TEM} (nm)
Pt/ZTC	Pt(NH ₃) ₂ (NO ₂) ₂	1.7	2.2 ± 0.8
Pt/ZTC	H ₂ PtCl ₆ ·6H ₂ O	2.5	3.5 ± 1.2
Pt/KB	Pt(NH ₃) ₂ (NO ₂) ₂	4.4	4.4 ± 1.1
Pt/AC	Pt(NH ₃) ₂ (NO ₂) ₂	17	15 ± 11

The uniformly dispersed smaller Pt particles observed in Pt/ZTC can be attributed to the presence of higher amount of surface functional groups on ZTC surface compared to KB and AC.[4] More specifically, the cationic Pt precursor, Pt(NH₃)₂²⁺, possibly has a strong attractive interaction with the high density of oxygen-containing functional groups on ZTC. In contrast, the anionic Pt precursor, PtCl₆²⁻, can have a repulsive interaction with the surface functional groups [34] on ZTC, which may enhance the aggregation of the Pt nanoparticles in Pt/ZTC-Cl.

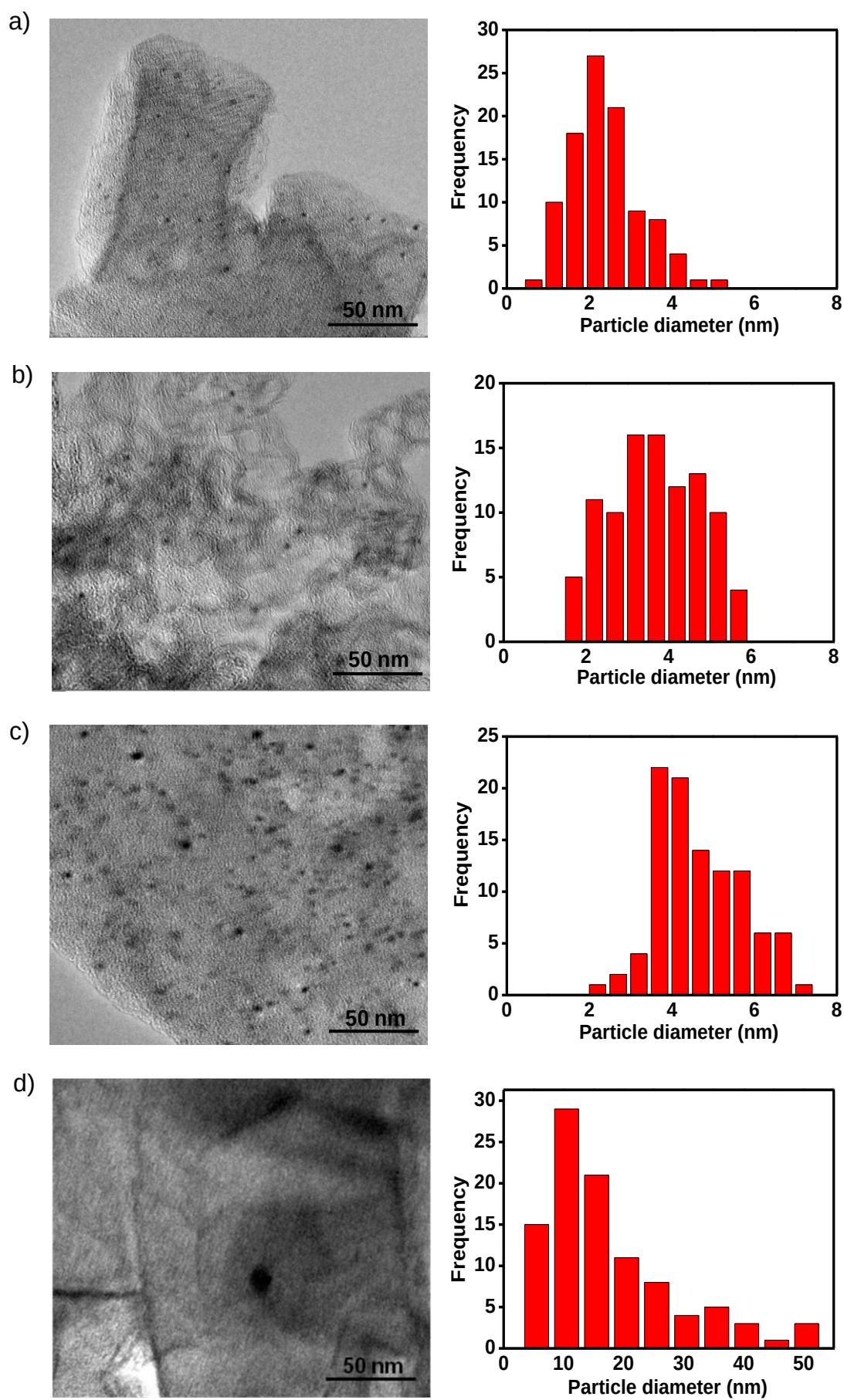


Figure 5-2. TEM images (left) and particle size distributions (right) of the a) Pt/ZTC, b) Pt/KB, c) Pt/AC and d) Pt/ZTC-Cl.

Figure 5-3 compares the conversion and selectivity for styrene by the Pt catalysts under the conditions of 0.40 MPa H₂ at 50°C for 1 h. Pt/ZTC catalyst afforded 63% conversion, which was apparently the best among the tested catalysts. Pt/KB and Pt/AC gave conversions of 53 and 25%, respectively. Pt/ZTC-Cl resulted only in 3% conversion. The striking difference in conversion among the tested catalysts can be attributed to the difference in Pt particle size. The catalysts with smaller Pt nanoparticles gave the higher conversions due to the higher Pt surface area available for the reaction. The selectivity for styrene over the tested catalysts was relatively comparable, giving 85-90%. Thus, the yield of styrene over Pt/ZTC was 54%, which was higher than those over other catalysts. The remaining product was only ethylbenzene with the all Pt catalysts examined in this study.

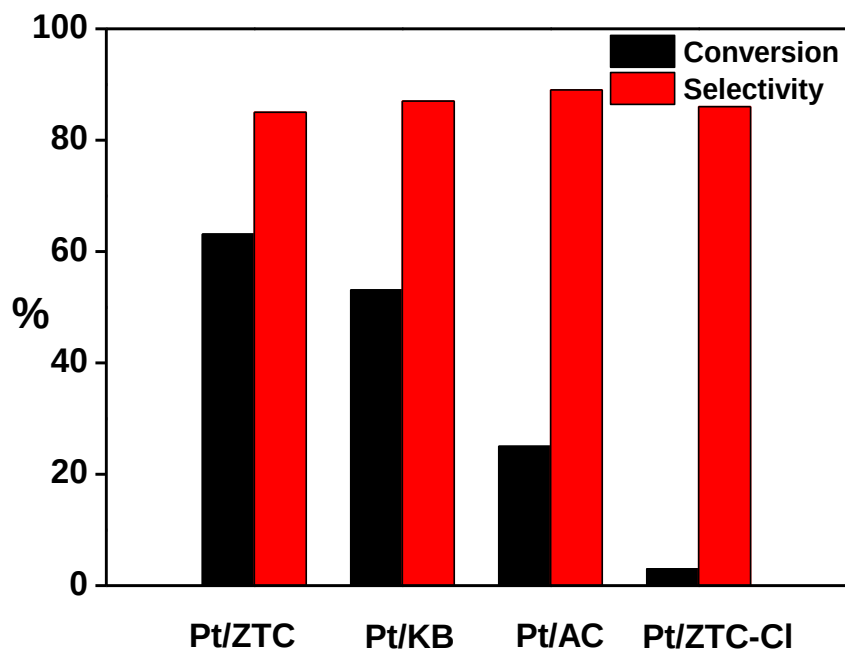


Figure 5-3. Hydrogenation of phenylacetylene over the different Pt catalysts supported on carbon. Reaction conditions: 0.4 MPa H₂, 50°C, 1 h.

Pt/ZTC catalyst was further utilized to investigate the influence of H₂ pressure (Figure 5-4) and reaction temperature (Figure 5-5) on hydrogenation of phenylacetylene. As shown in Figure 5-4, the higher H₂ pressure afforded the higher conversion of phenylacetylene, but the selectivity to styrene dramatically dropped under 0.70 MPa H₂. Figure 5-5 indicates that elevated reaction temperature increases the phenylacetylene conversion while the styrene selectivity gradually decreases. The optimized conditions are 0.4-0.5 MPa and 60-80°C, giving 75-78% yields of styrene in 1 h.

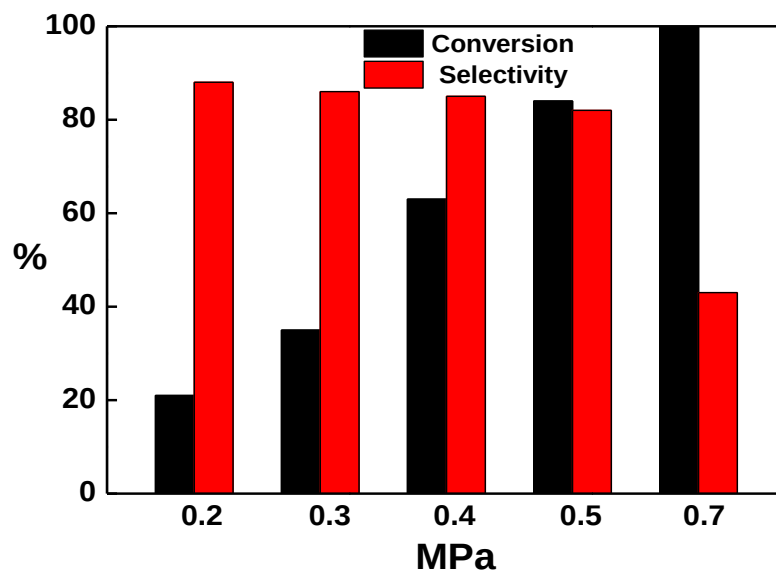


Figure 5-4. H₂ pressure effect on hydrogenation of phenylacetylene over the Pt/ZTC catalyst. Reaction conditions: 0.2-0.7 MPa H₂, 50°C, 1 h.

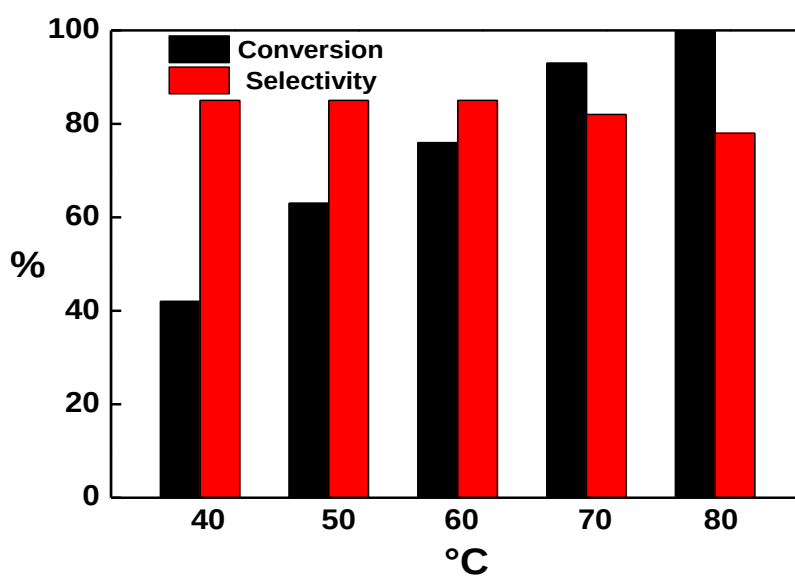


Figure 5-5. Reaction temperature effect on hydrogenation of phenylacetylene over the Pt/ZTC catalyst. Reaction conditions: 0.4 MPa H₂, 40-80°C, 1 h.

5.4 Conclusion

In summary, Pt catalysts supported on zeolite-templated carbon (ZTC) were

prepared and applied to selective hydrogenation of phenylacetylene to styrene. The catalyst prepared on ZTC with a cationic Pt precursor gave highly and uniformly dispersed Pt nanoparticles and exhibited the highest conversion in hydrogenation of phenylacetylene among the Pt catalysts used in this study.

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Chapter 6 General Conclusion

Plant fresh keeping and polystyrene industrialization are very important in today's society. However, the decay of the plant by ethylene released from plant and the poisoning of phenylacetylene are the major problems in these processes. The removal of ethylene and phenylacetylene is not so easy. In this thesis, the author has developed novel catalytic systems for complete oxidation of ethylene and selective hydrogenation of phenylacetylene so as to solve these problems.

Chapter 2 has focused on the screening of the metal and supports effects. Pt nanoparticles supported on mesoporous silica MCM-4 showed high activity and durability for complete oxidation of ethylene. With its application under practical conditions, the conversion of ethylene at 0°C was >99.8%, which is higher than any previously reported results.

A detailed study of reaction mechanism is reported in Chapter 3. The author investigated the probable reaction pathways of ethylene oxidation on various metal oxides supported Pt catalysts by *in situ* DRIFTS. Resembling reaction pathways were observed on Pt/MCM-41 and Pt/SiO₂. In both cases HCHO and CO species were formed as intermediates during C₂H₄ complete oxidation into CO₂ and H₂O. Moreover formic acid and formate species were also formed as spectators. However, totally different reaction pathways were occurred on Pt catalyst prepared using metal oxide supports other than mesoporous silica. In this case, intermediates of acetaldehyde, and CO species and spectators of acetate, formate or carbonate species were formed, which

can only be completely removed at higher temperature. The IR analysis exhibited that use of diverse supports results in different reaction pathways, which is the determining factor for ethylene oxidation reaction.

As depicted in Chapter 3, Pt nanoparticles supported on two kinds of SiO₂ (MCM-41 and Q-10) demonstrated similar catalytic activities and reaction pathways for ethylene oxidation. In order to further study the effect of mesoporous silica on ethylene oxidation, Chapter 4 described the influence of pore structures, surface silanol groups and the doping of heteroatoms in mesoporous silica. The results showed that the pore structure and surface silanol groups had no effect on the ethylene oxidation efficiency. However, the doping of heteroatoms caused a decrease in catalytic performance.

In Chapter 5, Pt catalyst supported on a novel zeolite-templated carbon (ZTC) was prepared for the purpose of selective hydrogenation of phenylacetylene to styrene. Pt nanoparticles were highly dispersed on ZTC by means of a cationic Pt precursor. The catalyst exhibited the high conversion in hydrogenation of phenylacetylene into styrene.

In the light of above studies, the author concluded that Pt catalysts supported on silica presented high catalytic activities of ethylene oxidation. The catalytic performance towards ethylene oxidation was not affected by pore structure or surface silanol groups but by the doping of heteroatoms in mesoporous silica structure. Pt catalyst supported on ZTC with smaller particle size allowed highly selective hydrogenation of phenylacetylene to styrene. The author hope that this work will contribute towards development of new methods for solving the problems related to

plant fresh keeping and styrene polymerization.

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Publications in International Journals:

1. **Chuanxia Jiang**, Kenji Hara, and Atsushi Fukuoka. Low-Temperature Oxidation of Ethylene over Platinum Nanoparticles Supported on Mesoporous Silica. *Angew. Chem. Int. Ed.* 2013, 52, 6265-6268 (DOI: 10.1002/ange.201300496).
2. **Chuanxia Jiang**, Kenji Hara, Kotaro Namba, Hirokazu Kobayashi, Somlak Ittisanronnachai, Hirotomo Nishihara, Takashi Kyotani, and Atsushi Fukuoka. Selective Hydrogenation of Phenylacetylene by Pt Catalyst Supported on Zeolite-templated Carbon. *Chem. Lett.* Submitted.

Conference:

1. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Oxidation of Ethylene over Pt Nanoparticles Supported on Mesoporous Silica”, CRC International Symposium, P8, Hokkaido, Japan 1/26-27/2012 [1/27].
2. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Ethylene Elimination over Pt Nanoparticles Supported on Ordered Mesoporous Silica”, The 5th GCOE International Symposium, PMo17, Hokkaido, Japan 2/21-22/2012 [2/22].

3. **Jiang Chuanxia**, Hara Kenji, Fukuoka Atsushi, “Complete Oxidation of Ethylene over Supported Pt Nanoparticles at Low-Temperature”, 109th CATSJ meeting, 1P36, Tokyo, Japan 3/28-29/2012 [3/28].
4. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Complete Oxidation of Ethylene over Pt Nanoparticles Supported on Mesoporous Silica”, International Association of Colloid and Interface Scientists Conference (IACIS2012), S4P16-09, Sendai, Japan 5/13-18/2012 [5/16].
5. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Oxidation of Ethylene over Pt Nanoparticles Supported on Mesoporous Silica”, International Symposium on Zeolites and Microporous Crystals (ZMPC2012), OA32, Hiroshima, Japan 7/28-8/1/2012 [8/1].
6. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Low-Temperature Elimination of Ethylene over Pt Nanoparticles Supported on Mesoporous Silica”, CRC International Symposium New Challenges on the Bio-interfaces: Structures and Dynamics, P4, Hokkaido, Japan 2/5-6/2013 [2/5].
7. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Elimination of Ethylene at Low-Temperature over Supported Pt Nanoparticles”, The 4th Joint symposium, Hokkaido, Japan 5/9/2013.
8. **Chuanxia Jiang**, Kenji Hara, Atsushi Fukuoka, “Oxidation of Ethylene over Pt Nanoparticles Supported on Mesoporous Silica”, International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (ISHHC-16), 2P-24, Hokkaido, Japan 8/4-9/2013 [8/6].

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