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STOICHIOMETRIC MODIFICATIONS OF ZnO-Cr₂O₃ CATALYST SYSTEM IN OXIDIZING AND REDUCING ATMOSPHERES

By

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Abstract

The stoichiometry and phase compositions during the thermal decomposition of ZnO-CrO₃ system were studied under oxidising and reducing atmospheres by the DTA, TGA and thermomagnetic techniques. It was found that the end products obtained at 500°C in air (I) and in hydrogen (II) atmosphere have compositions corresponding to (ZnO, Cr₂O_{2.46}) and (ZnO, Cr₂O₃) respectively. These specimens showed magnetic moments of 2.7 and 2.86 B.M. respectively and account for only two unpaired electrons. A third sample (III) obtained by heating sample I in a hydrogen stream and having the composition (ZnO, Cr₂O_{2.96}) showed very low reducibility, exhibited an unusually low magnetic moment of 1.8 B.M. The spin loss in this case is attributed to the dissociative chemisorption of hydrogen on chromium ions. The decomposition of methanol on the catalysts was studied in the pulse regime.

The reaction was found to obey the first order kinetics. Samples I and III, although somewhat different in their magnetic properties showed similar catalytic activity with an activation energy of 8~12 Kcal/mole. Catalyst II showed low specific reaction rates and an activation energy of 16~19 Kcal/mole. Role of the chromium oxide as a promoter has been discussed and a tentative mechanism for methanol decomposition is suggested.

Introduction

Many unpromoted oxides as those of Zn, Cu, Mn, U, Be and Zr act as catalysts for the synthesis of methanol¹⁾. STORCH²⁾ had found that ZnO promoted with Cr₂O₃ possesses improved catalytic activity for the synthesis reaction and also has a better sulphur tolerance. Since then, the binary systems of zinc oxide-chromium oxide catalysts have been widely used^{3,4)} in the synthesis and decomposition of methanol. Although the thermal

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and magnetic studies on ZnO-CrO₃ have been reported in literature⁵⁻¹⁰, the stoichiometry and the structure of the catalyst species are still elusive.

The present work is an attempt to follow up the constitutional changes in the ZnO-CrO₃ system during the catalyst formation upto 600°C. in both oxidizing and reducing atmospheres. Anomalies observed in the chemical constitution, from the thermal and magnetic studies have been explained. Results of the catalytic decomposition of methanol have been discussed and a tentative mechanism for the reaction suggested.

Experimental

1. Preparation of the samples

- (a) Weighed amount of ZnO was kneaded with the required quantity of chromic anhydride dissolved in distilled water, to give a Cr/Zn ratio of 0.7. The kneading was carried out for about 1 hr. The material was then dried at 100°C for 12 hours in an air oven. The dried mass on chemical analysis was found to contain 52.69% CrO₃ and 47.31% ZnO.
- (b) One part of the above material was calcined at 500°C in air for 5 hours (Sample-I).
- (c) Part of the original oven dried mass was cured in a stream of purified H₂ at 500°C for 5 hours (Sample-II).
- (d) Part of sample-I was heated in a stream of H₂ at 500°C for 5 hours (Sample-III).

2. Thermal Studies

- (a) For the TGA measurements a helical quartz spring balance was used which had a sensitivity of 0.01 mg. The sample was heated at the rate of 5°C/min. The all glass housing of the balance had a provision for introducing H₂ or any other gas into the sample chamber.
- (b) The DTA experiments were carried out in a specially designed all glass dual cell assembly which could be used in conjunction with the DTA apparatus described earlier¹¹.

3. Thermomagnetic studies

The magnetic measurements were carried out using a Faraday type balance constructed around a helical quartz spring as the weight sensing element. Data on the samples were obtained between 77° and 873°K under a running vacuum of 10⁻⁵ torr. The sample size in each case was about 30 mg.

4. Catalytic Activity

Methanol decomposition activities of the samples were measured in the

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pulse regime using a micro reactor similar to the one described by KOKES *et al.*¹²⁾. The reactor was connected in series with a 2 meter long "Carbowax -1500 on Celite" column fitted in a Griffin and George D6 gas chromatograph. The column temperature was 120°C. The carrier gas, argon had a flow rate of 30 ml/min. 0.3 cc of the Catalyst samples (50~60 mesh) were used for the activity measurements. Pulses of 2-microlitre size of methanol (*BDH, AR grade*) were introduced at the top of the catalyst bed. Preliminary scouting experiments with all the three samples showed that the gaseous products were CO and H₂. The degree of conversion for samples I and III were measured from the decrease in the methanol peak areas. The product

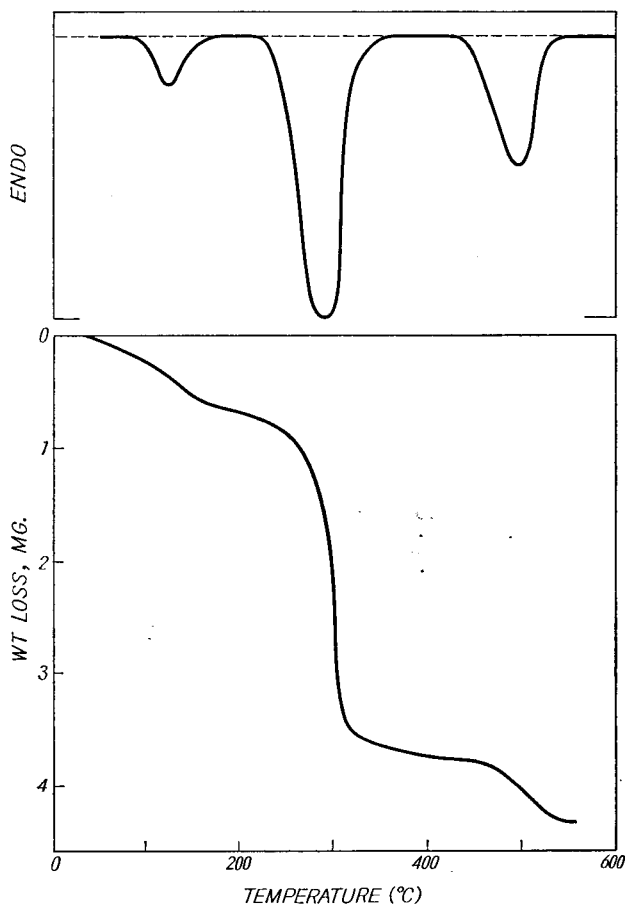


Fig. 1. Above: DTA thermogram of the dried mass in air.
Below: TGA curve of 24.5 mg dried mass in air.

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gases eluted in a single peak with a heavy tailing. However, the tailing effect was not so pronounced for sample II therefore it was possible to determine the degree of conversion by measuring the gas peak area assuming a 100 percent conversion at 400°C. The material balance between the input pulses and the effluents did not show any loss.

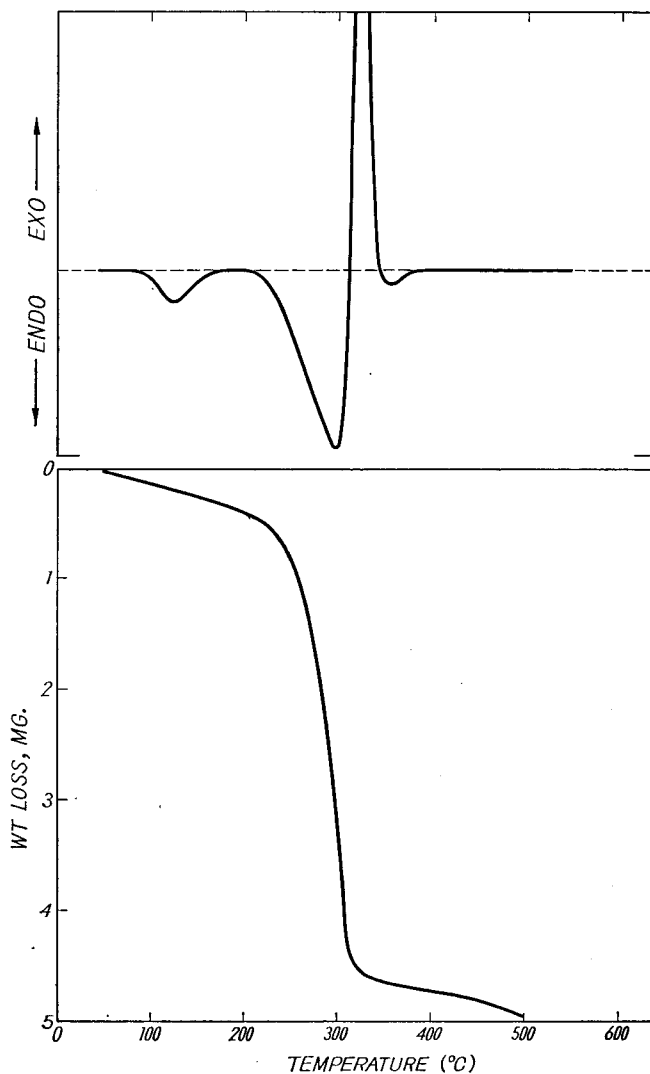


Fig. 2. Above: DTA thermogram of the dried mass in flowing hydrogen. Below: TGA curve of 33.6 mg dried mass in flowing hydrogen.

Results

The DTA and TGA curves in air for the dried mass are shown in Fig. 1. Three definite steps of weight loss were observed in the TGA curve upto 600°C. The DTA trace also showed three endothermic peaks corresponding to the weight losses.

The DTA and TGA curves for the dried mass in a stream of H₂ are given in Fig. 2, the temperature scanning limits being the same as for the runs in air.

The TGA curve for the air calcined sample in H₂ is shown in Fig. 3. The rate of reduction was found to be insignificant even at 500°C. The final loss did not correspond to a bulk phase reduction. For these reasons no DTA curve could be obtained for this process.

Fig. 4 shows the thermomagnetic behaviours of the samples. Curve I was obtained for the air calcined sample; curve II for the sample prepared by the reduction of the dried mass in H₂ and curve-III is for the air calcined sample heated in H₂.

Discussion

The chemical analysis showed that the original dried mass had the empirical formula of ZnO·CrO₃ containing 5% excess ZnO and the material was found to be diamagnetic at room temperature and feebly paramagnetic at 77°K. X-ray phase analysis of the uncured mass showed the composition to be (ZnO·CrO₃)₂H₂O, ZnO. The theoretical water content of the sample must therefore be about 5%. Decomposition of this mass in air takes place in three steps (Fig. 1). The loss of water extends upto 250°C. The DTA curve shows the first endothermic peak for the loss of water. The total loss of water corresponds to about 4%, which is close to the expected value. The compound formed at 250°C is therefore a mixture of ZnO and CrO₃.

Second decomposition occurs at 300°C accompanied by a loss of oxygen to form a lower oxide of chromium. Its formula, on the basis of the TGA data (Table 1) can be assigned as ZnO·Cr₂O_{2.96}. Further decomposition takes place at 500°C, yielding a specimen with the formula: ZnO·Cr₂O_{2.46}.

The stoichiometry is obviously disturbed due to the highly oxygen deficient character of ZnO lattice. The above reactions are clearly illustrated in the DTA thermogram in the same figure by the three strong endothermic peaks at the corresponding temperatures. YAKERSON *et al.*¹³⁾ also observed a similar scheme of decomposition of the zinc chromate type catalysts leading

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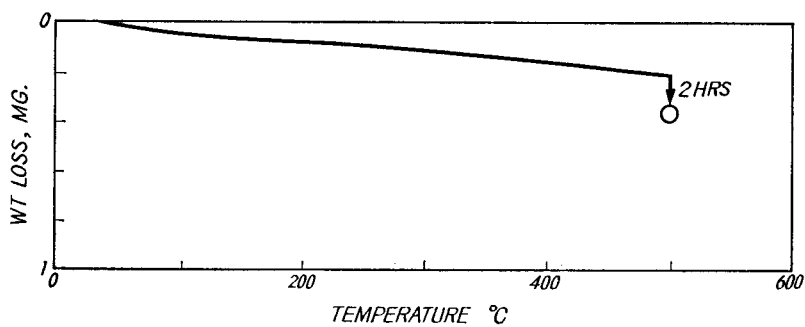


Fig. 3. TGA curve of 30 mg air calcined sample in flowing hydrogen.

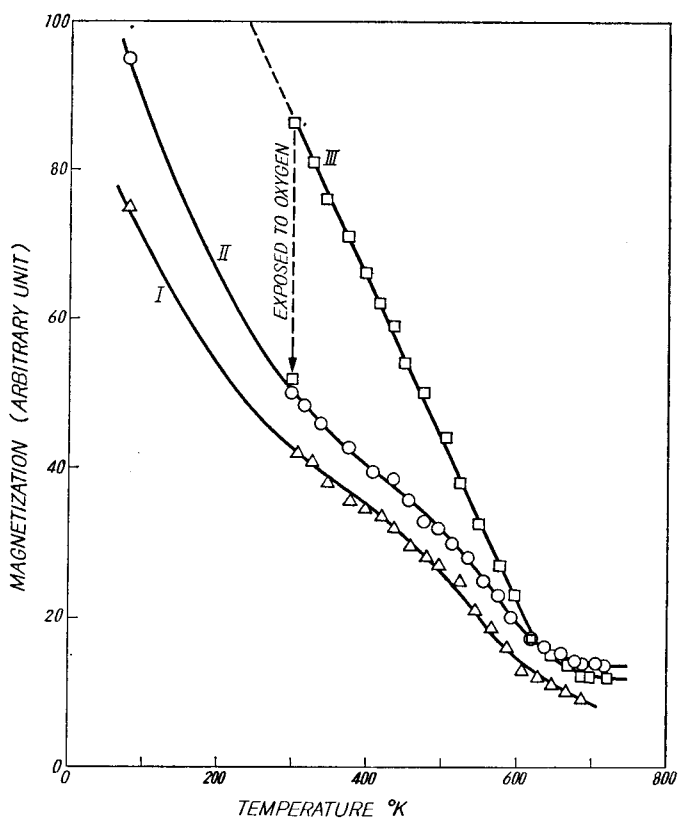


Fig. 4. Thermomagnetic behaviours of the air cured (I), hydrogen cured (II) and air cured then heated in hydrogen (III) samples.

to the formation of zinc chromite. The second and the third endothermic peaks in the present case are associated with the stepwise loss of oxygen at 300° and 500°C. It is also clear from the DTA curves that no spinel structure is formed below 600°C.

It is reported in literature¹⁴⁾ that CrO_3 decomposed at 300°C. in air to form Cr_6O_{15} and Cr_5O_9 at 420°C. and Cr_2O_3 at about 450°C. In the present case the composition (Table 1) of the oxide at 300°C. corresponds to $\text{Cr}_2\text{O}_{2.96}$ and to $\text{Cr}_2\text{O}_{2.46}$ at 500°C. These obviously do not match with any of the above oxides obtained when CrO_3 is heated alone. The presence of ZnO therefore modifies the reactions leading to the formation of oxides of a much lower state of oxidation than when CrO_3 is heated alone.

The DTA and TGA thermograms of the dried mass in H_2 are shown in Fig. 2. The thermal behaviour of $2\text{ZnO}\cdot\text{CrO}_3\cdot\text{H}_2\text{O}$ was found to be similar, upto 300°C to its behaviour in air. Around 300°C the chromium oxide, probably of the type formed in air at 300°, is reduced sharply and no significant weight change or phase transformation appeared further in the H_2 atmosphere upto 600°C.

The reaction is better illustrated in the DTA curve (Fig. 2). The water of crystallisation is expelled at 150°C as shown by the endothermic peak. The composite peak around 300°C shows that initially, the reaction was endothermic in nature as observed in air. But it is dominated by a strong exothermic change as the reaction progresses. The X-ray diffraction studies of the end product obtained 600°C showed that it contained ZnO and Cr_2O_3 as distinct phases. The colour of the residue was green. Thus around 300°C in the H_2 atmosphere the chromic anhydride is reduced to give Cr_2O_3 .

The basic difference between the reactions in air and in H_2 atmospheres lies in the fact that the decomposition in air is associated with the liberation of oxygen, while in the H_2 atmosphere CrO_3 is reduced to Cr_2O_3 , the oxygen is expelled in the latter case as H_2O leaving ZnO and Cr_2O_3 in the residue.

The reduction is drastic and the ZnO matrix has no influence on the reaction. KAWAMURA and IRIE¹⁵⁾ studied the reduction kinetics of the ZnO– CrO_3 type synthesis catalyst in various reducing atmospheres. But they have not reported the stoichiometries of the intermediate or the end products obtained. IRIE and SHIRAIISHI¹⁶⁾ also studied the effect of high temperature treatment of ZnO– CrO_3 catalyst and reported a spinel formation only at 700°C. However in the present case the formation of a spinel structure could not be confirmed from the X-ray diffraction studies. The colour of the end product obtained at 600° was green which showed that

TABLE 1. Thermal Decomposition Data And Magnetic Properties

Sample	Temp. °C	% Loss in weight.	Chemical compo- sion on dry basis.	X_M 77°K	Weiss constant °K	μ obs, B.M	Number of unpaired electrons	Colour of the specimen.
Uncured dried mass.	150	—	ZnO·CrO ₃	Feedly paramagnetic.	—	—	—	yellow
I Air Calcined	150	2.45	ZnO·CrO ₃	—	—	—	—	—
	300	12.49	ZnO·Cr ₂ O _{2.96}	—	—	—	—	—
	500	2.04	ZnO·Cr ₂ O _{2.46}	3.46×10^{-3}	-184	2.70	2	Pink
II Calcined in H ₂	150	2.05	ZnO·CrO ₃	—	—	—	—	—
	300	12.13	ZnO·Cr ₂ O ₃	4.60×10^{-3}	-144	2.86	2	Green
III Air Calcined heated in H ₂	500	—	ZnO·Cr ₂ O _{2.96}	5.24×10^{-3}	0	1.80	1	Grey

Cr_2O_3 existed as a distinct phase in the residue.

The intermediate oxide formed by the air-calcination of the oven dried mass is not easily reducible in the presence of H_2 as shown by the TGA curve (Fig. 3). This was further confirmed from the DTA run of the sample in H_2 atmosphere which gave a steady base line from $150\sim 600^\circ\text{C}$. No DTA trace has therefore been included.

The thermomagnetic curves of the specimens are shown in Fig. 4. The intensity of magnetization in all the cases was calculated on the basis of chromium content per gram of the catalyst. In contrast to sample I and II, the sample III prepared by heating the air calcined sample in H_2 showed a steep magnetization *vs.* temperature relationship in the lower temperature region. MASSOTH and SCARPIELLO¹⁷⁾ have shown that no significant reduction of ZnCr_2O_4 or Cr_2O_3 takes place below 540°C . It is also known from the thermodynamic considerations^{18,19)} that a bulk phase reduction of these compounds is not favoured at 500°C . However, these considerations are applicable to the bulk phase reductions. But the situation at the surface layer may be entirely different. The slight reduction observed (Fig. 3) therefore suggests the possibility of a surface film reduction in the case of sample III. After obtaining the magnetization-temperature data for this sample, it was cooled down to room temperature and then the sample was exposed to oxygen atmosphere. Magnetization intensity dropped after the oxygen exposure (Fig. 4). This experiment supports the possibility of the surface film reduction when the air-calcined sample is heated in a stream of H_2 . A similar oxidation of the hydrogen treated zinc chromite was observed by TAYLOR and LIANG²⁰⁾ even at liquid air temperature.

The thermomagnetic curves for the three samples show a magnetic phase-transition in the temperature range of $600\sim 650^\circ\text{K}$ (Fig. 4). It was therefore considered necessary to further investigate the electronic and magnetic characteristics of the specimens.

All the three samples were found to obey the Curie-Weiss law over a very short temperature region. Plots of T *vs.* $1/x_g$ for the three catalyst samples have been shown in Fig. 5. Samples I and II have negative Weiss constants in the low temperature region showing that these specimens are antiferromagnetic. On the other hand the straight line for sample III passes through the origin indicating this catalyst to be paramagnetic in the low temperature region. The magnetic moments for the samples were calculated from the experimental data using the formula :

$$\mu_{\text{obs}} = 2.84\sqrt{X_M(T - \mathcal{A})} \quad (1)$$

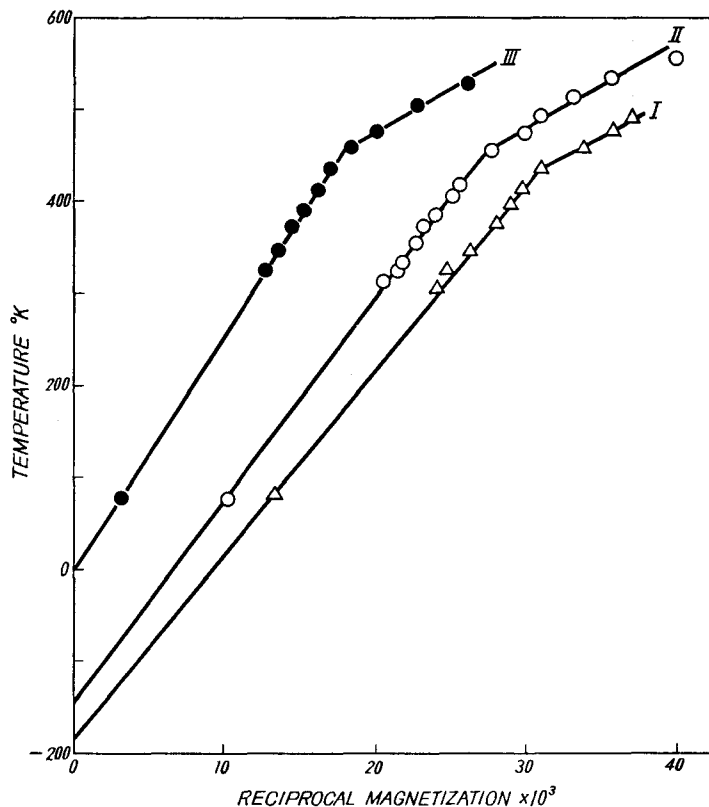
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Fig. 5. Temperature vs. reciprocal magnetic susceptibility relationship for the catalysts.

The values of μ_{obs} at 77°K are given in Table 1. From the theoretical considerations, the Cr³⁺ ion will have a spin only value of 3.87 B.M. corresponding to three unpaired electrons. Although the observed magnetic moments in this case correspond to two unpaired electrons in samples I and II, from the chemical stoichiometry, the Cr-ion appears to be in Cr³⁺ state. This anomaly in the spin values can be attributed to the intercationic interaction of the neighbouring Cr-ions in the intermediate oxide and Cr₂O₃ lattices. Moreover, the negative Weiss constants found for these samples also suggest a spin compensation due to the antiferromagnetism.

In the case of sample III, the observed magnetic moment corresponds to 1.8 B.M. with a zero Weiss constant. This shows the specimen to be paramagnetic below 180°C. The observed magnetic moment corresponds to one unpaired electron, which would predict the Cr-ion to be in the penta-

valent state. This however seems to be improbable, since it is not possible to convert Cr^{3+} to Cr^{5+} ions by reduction with H_2 . The apparent spin loss in this sample therefore may be due to a strong dissociative adsorption of hydrogen during the hydrogen treatment.

Catalytic Activity

The catalytic behaviour of methanol decomposition over the specimens was studied in the pulse regime. The gaseous products obtained during the reaction eluted as a single peak of the gaschromatograph. It was observed that these peaks for samples I and III exhibited a heavy tailing effect throughout the temperature range studied. It was also noticed that the retention times for the gas peaks were independent of the temperature of the catalyst bed. The tailing effect in the case of sample II was not so pronounced. The stationary phase (carbowax -1500) used for the separation of methanol and the gaseous products is polar and does not show any preference for the adsorption of CO_2 or H_2 . The tailing nature of the gas peak therefore indicates that either the liberation or desorption of one of the gases from the catalyst surface could be the rate controlling step of the over all reaction.

The decomposition of methanol is considered to be a zero order reaction²¹⁾, the rate of which obeys the following equation,

$$r = k \quad (2)$$

where k is the rate constant. The equation holds good when the catalyst surface is fully covered by the reactant or reaction intermediates. However, deviation from linearity is observed²²⁾ at lower partial pressures of methanol. Some workers²³⁾ have also shown the reaction to be not exactly of zero order. TAMURA and SHIBA²⁴⁾ found that for low methanol partial pressures the reaction is a consecutive first order type. The order of this reaction has not thus been fully established in the low pressure region.

The pulse chromatographic technique provides scope for investigating the kinetics of this reaction at reactant pressures approaching zero. The conversion data obtained from this technique fitted well in to the following first order rate equation used for evaluating the kinetics in the pulse regime :

$$k = 2.303 \frac{F}{W} \log \frac{1}{1-x} \quad (3)$$

where, x is the degree of conversion, F the flow rate and W the weight of the catalyst. The specific rate constants obtained for the catalysts on the basis of equation (3) have been shown in Fig. 6 plotted against the reaction temperatures.

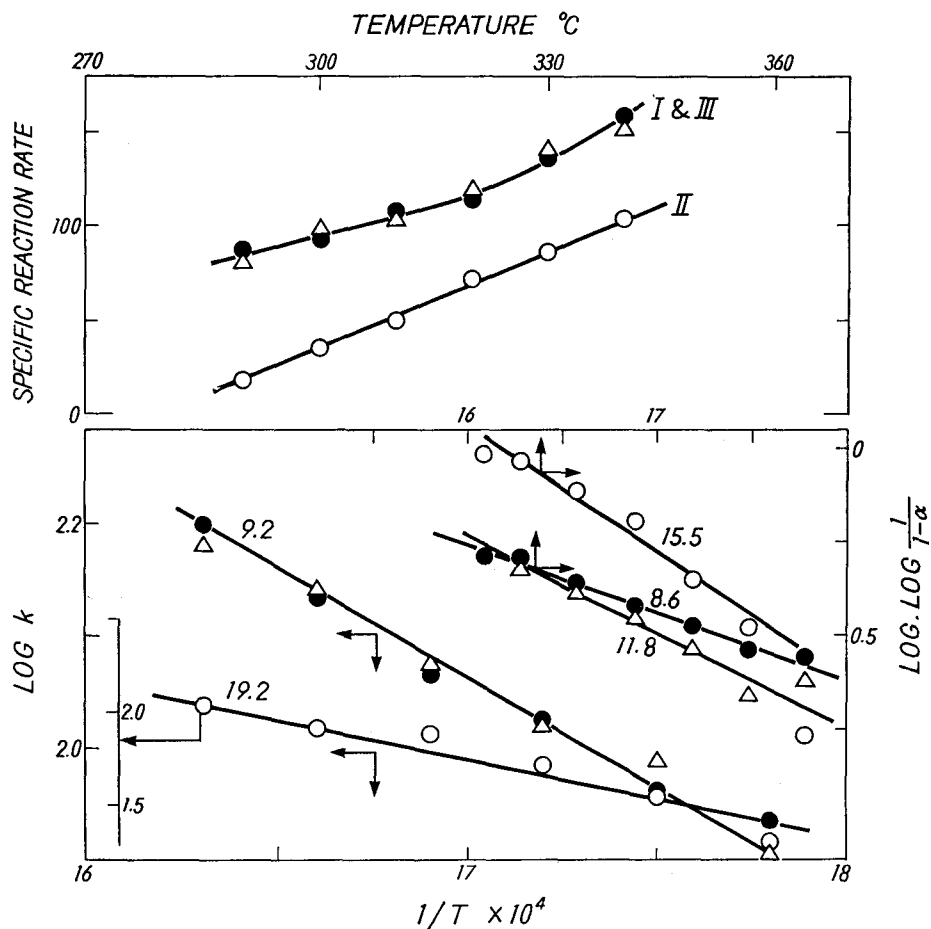
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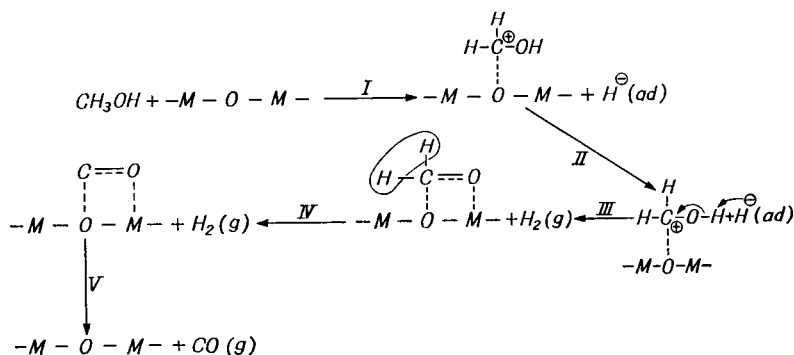
Fig. 6. Above: The specific reaction rates ($\text{ml}\cdot\text{min}^{-1}\cdot\text{g}^{-1}\text{Cat}$) for methanol decomposition by the Catalysts. Below: Arrhenius plots for the first order rate equations and the apparent activation energies (Kcal/mole).

SCHWAB and WATSON²⁵⁾ proposed an equation for the determination of the energy of activation of methanol decomposition from pulse data assuming the reaction to be of the first order. The equation is:

$$\log \log \frac{1}{(1-x)} = C - \frac{E}{2.303RT} \quad (4)$$

where x is the degree of methanol decomposition and C a constant. Arrhenius plots for the catalysts based on Eqs. (3) and (4) have been shown in Fig. 6. From the perfect fit of the experimental data in to both the

equations, it can be said that the reaction is of first order in the pulse regime. The energies of activation obtained by using both the equations were found to be of the same order of magnitude. Samples I and III exhibited similar activity pattern with an energy of activation 8~12 Kcal/mole between 290~350°C. This confirms the structural identity of these two samples. Sample II, which contained a mixture of ZnO and Cr₂O₃ phases showed an activation energy of 16~19 Kcal/mole. The specific reaction rates were also lower in this case than the other two catalysts. The average value of the activation energy is of the same order as that reported by MUKHLENOV *et al.*²³⁾. It was shown by DANCHEVSKAYA *et al.*²⁶⁾ that an increase in the surface Zn concentration in ZnO, increases the activity of the methanol decomposition. The phenomenon was attributed to the super-stoichiometric effect of Zn. A 50% increase in the Zn concentration in the octahedral sites of ZnO gave rise to a sharp increase in the catalytic activity. On the other hand the electron clouds of the promoter chromium oxide in ZnO provide the necessary donar levels to facilitate the complex adsorption processes involved in the decomposition of methanol over the zinc oxide-chromium oxide system. The proposed mechanism for the decomposition of methanol over the catalyst surface is illustrated as follows :



As suggested by KRYLOV²⁷⁾ it is assumed that the adsorption of methanol leading to the dehydrogenation occurs at the anionic vacancies of the catalyst surface. This results in the release of a hydride ion on the catalyst surface leaving the carbonium ion (step I). It is shown in step II that the adsorbed hydride ion attacks the proton of the OH group of the carbonium ion. The proton and the hydride ions combine to give a molecule of hydrogen (step III). Step IV shows the cleavage of the two remaining carbon-hydrogen bonds to give another molecule of hydrogen leaving an adsorbed CO molecule.

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Step V shows the desorption of CO from the catalyst surface and the regeneration of the surface. It should be noted that the sites for the adsorption of the hydride ions must be adjacent to and selectively different from those sites responsible for the adsorption of methanol. In the pulse regime none of the adsorbed species are in equilibrium with any of the components in the gas phase. The formation of the adsorbed complexes is an instantaneous process since no evidence of formaldehyde formation is observed in the product analysis. Hydrogen liberation is also a non-adsorptive process. The desorption of the carbon monoxide from the catalyst surface must therefore be the rate controlling step of the overall reaction. Low activation energies observed for the reaction in the present case as compared to those reported over ZnO alone²¹⁾, or other catalysts²⁵⁾ suggest the role of the chromium as one of either providing additional adsorption sites for the reaction or stabilizing the sites already existing on the ZnO surface. The stabilizing action of the chromium ions can be visualized as the localization of the free electrons of the super stoichiometric zinc in ZnO by overlapping them with their own electron clouds. One of the reasons for the observed loss of spin and less than the expected magnetic moment in all the samples speaks in favour of this hypothesis. The apparent loss of spin can not be attributed to any other possibility such as the spinel formation except that a part of the lost component might be used up in the chromium oxide crystallite growth as suggested earlier. Although the lower activity and higher energy of activation observed in sample II suggest a greater extent of spin compensation in forming Cr₂O₃ lattice and poisoning²⁸⁾ of the active sites through hydrogen chemisorption²⁸⁾ it is evidently not possible to directly correlate the catalytic activity with the observed magnetic moments of the catalysts.

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