Sodium Hydroxide Doped Magnesium Oxide for the Catalytic Decomposition of Methyl Formate to Methanol and Carbon Monoxide

FU-QIN MA,[1] DA-SHUN LU,[2] AND ZHI-YING GUO

Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi, 030001, People's Republic of China

Sodium hydroxide doped MgO samples were characterized and examined for their performance as catalysts for methyl formate (MF) selective decomposition to CO and CH_3OH. The BET area and the chemisorption of CO_2 increase rapidly with increasing Na^+ content, reaching a maximum, and then decrease sharply to a low value. The basicity seems to be closely related to BET area rather than to Na^+ content. Fresh samples showed only the XRD pattern of MgO, but used samples gave diffraction peaks of an unidentified new crystalline phase. XPS studies gave also a new Na 1s peak with lower BE for used samples. Surface elemental analysis and sputtering indicate the confining of Na^+ to the surface, and the loss of Na^+ and the increase of surface oxygen on use. Infrared examination established the formation of HCOONa during reaction. Plots of Ln X (X is % conversion of MF) against time on stream give broken lines indicating rapid and slow deactivation stages. The rapid stage is supposed to be related to formate formation and the slow stage to Na^+ loss, surface area decrease, and other causes, such as poisoning. TPSR and FTPSR (frontal temperature programmed surface reaction) studies reveal the delay of CO evolution compared to methanol in the decomposition of dissociatively adsorbed MF, the start of substantial conversion of MF at around 483 K, and the appearance of H_2 above 600 K. Two mechanisms might have been involved in the decomposition of MF, one is dissociative and the other non-dissociative. Strong basic centers of Na_2O are believed to be the active sties, and MgO serves mainly as a carrier. © 1992 Academic Press, Inc.

INTRODUCTION

Methyl formate as a chemical of potential importance has been noticed recently because of its versatility in undergoing chemical transformations leading to a wide variety of important chemicals (*1*). Mitsubishi Gas Chemical Co. developed a method of producing high purity CO from methanol via MF (*2*). A process for obtaining H_2 and CO separately based on that process has been patented (*3*).

Basic catalysts were used for the selective decomposition of MF to CH_3OH and CO (*3–9*). But most of the results appeared in the patent literature, and academic studies were rare (*4, 9*). Though high activity and selectivity were obtained for many of the catalysts tested, the stability and other features of these catalysts have not been properly characterized.

The present paper presents results of sodium doped MgO, which has been tested as a possible promising catalyst for the selective decomposition of MF by Ushikubo *et al*. (*4*). Our results reveal some aspects not observed previously.

EXPERIMENTAL

Catalyst Preparation

Chemically pure MgO powder, provided by Shenyang Chemical Factory, was pelletized and crushed to 60 ~ 80 mesh. It was then placed in a quartz tube, evacuated to about 2 Torr and heated to 873 K in 1 h and kept at this temperature under continuous

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[1] Present address: Test Center for Zhengzhou University, Zhengzhou, Henan, 450052, PRC.
[2] To whom correspondence should be addressed.

evacuation for 3 h. The heat treated sample was stored in a dessicator right after cooling.

For NaOH doping, given amounts of NaOH were dissolved in distilled water and loaded by incipient wetness impregnation onto the MgO samples prepared as above. After drying in a rotary evaporator, the samples were again heat treated as described above under vacuum. The exact Na content of the catalyst samples were determined by atomic absorption spectroscopy using a Per-kin–Elmer 3030 spectrometer. Sodium contents of used samples were also analyzed on this apparatus.

Adsorption Measurements

The BET surface area of the samples were measured on a Micromeritics Digisorb 2500 instrument by low temperature nitrogen adsorption.

Carbon dioxide adsorption was used to estimate the amount of basic centers on the catalyst surface. Before adsorption, the samples were subjected to programmed heating in a stream of argon carrier gas up to 873 K, in order to desorb previous adsorbates. After cooling to room temperature in an Ar stream, calibrated amounts of CO_2 were dosed onto the samples by successive injections, until the effluent CO_2 gave constant peaks on the recorder of the detecting catharometer. The amount of CO_2 adsorbed was evaluated from the peak areas of the pulses.

Test of Catalysts

The activity and selectivity of the catalyst samples for MF decomposition were tested in a flow system, consisting of a glass reactor of 6 mm i. d. and facilities for temperature and flow control and monitoring. The reactor wall and glass wool used for supporting the catalyst proved to be inert to the reaction studied. Methyl formate was charged into a thermostated saturator and carried by a stream of argon through the catalyst bed, at a concentration corresponding to saturation of the carrier gas by MF at 273 K (partial pressure of MF was 195 Torr). The amount of catalyst used was 200 mg, and the reac-

tion was carried out at 523 K under atmospheric pressure. The volume rate of carrier gas was 30 ml/min, corresponding to a GHSV of about 8000 h^{-1}. Products were analyzed by an on-line GC-9A chromatograph with data processor, at intervals of 40 min. Two columns connected by a switching valve were used: a Carbosiev 601 column for H_2, N_2, CO, CH_4 and CO_2, and a Porapak-T column for H_2O, CH_3OH, and MF. The conditions for analysis were: carrier gas Ar 34 ml/min, column temperature 413 K, detector TCD. A single run usually lasted no less than 10 h.

From product analysis throughout the whole work, only CO, methanol, and unreacted MF were detected by GC under the above reaction conditions. Small amounts of hydrogen and carbon dioxide were detected at higher temperatures, while water was detected only by MS in TPD experiments (see below).

Spectral Studies

X-ray diffraction studies were carried out on a Rigaku Dmax-rA diffractometer, operating at 40 kV, 40 mA, using a Cu target and a graphite monochromator. The range of scanning was $2\theta = 5°$ to $50°$ (or $80°$).

XPS studies were carried out on a VG ESCALAB-5 spectrometer, operating at 10 kV and 20 mA, with AlK_α as the X-ray source, and with pass energy 50 eV. The analyzer was operated in CAE mode. The energy scale was calibrated by Au $4f_{7/2}$ and the resolution was about 0.2 eV.

Infrared studies were carried out on a Digilab FTS-15-90-E infrared spectrometer.

Temperature Programmed Desorption and Decomposition Studies

The TPD of CO and methanol, and the TPSR (decomposition) of MF were performed on a flow system similar to that described above for catalyst testing, connected to the MS part of a JMS-D300 GC-MS instrument. The sample studied was subjected to a blank TPD treatment up to 873 K before adsorption, to remove previ-

TABLE 1

NaOH Doped MgO Samples

	Catalyst code					
	A	B	C	C'[a]	D	D'[a]
Na weight%	0	0.95	3.07	2.54	6.13	4.69
mmol Na/g MgO	0	0.42	1.38	1.13	2.84	2.14
BET surface area (m^2/g)	23.9	55.0	7.8		6.9	6.0
CO_2 chemisorbed (mmol/g)	0.039	0.080	0.022		0.015	

[a] Used samples.

ous adsorbates, and cooled to 298 ~ 333 K in the helium carrier gas stream (30 ml/min). Adsorbates were then added by injection or frontal feeding up to saturation. The system was then flushed with the same He stream to attain a stable background. Heating was started at a rate of 15 K/min up to 873 K, and desorption profiles were followed by the MS at the same time.

For frontal temperature programmed surface reaction (FTPSR) of MF, the adsorption step was omitted and a stream of He saturated with MF at 273 K was switched on, replacing the pure He carrier gas stream, after the blank TPD treatment and before the start of heating. The sample weight for CO and methanol TPD was 100 mg, and those for MF TPSR and FTPSR were 50 and 20 mg, respectively.

RESULTS AND DISCUSSION

Relationship between Surface Area, Basicity, and Sodium Content

Four samples of NaOH doped MgO were prepared with different Na contents as listed in Table 1, together with their BET surface areas and CO_2 chemisorption data. Perrichon and Durupty (10) reported that "in all instances, the initial impregnated support has a lower BET surface than the support alone," but our result shows a rapid increase in BET surface area at first with increasing Na content, reaching a maximum at around 0.4 mmol Na/g MgO, and then the

area decreases abruptly to a low value. This does not mean simple conflict, because at the loading used by Perrichon and Durupty (2.5 mmol Na/g MgO), our result also gave a depressed surface area. The area maximum occurs only at very low loading. The chemisorption of CO_2 by the samples follows the same trend, and the two plots nearly coincide if proper scales for the ordinates are chosen, as illustrated in Fig. 1. This implies that the chemisorption of CO_2 or the number of surface basic sites actually varies with the surface area. Or more expressively, the density of basic centers on the surface is scarcely dependent on the amount of NaOH doped onto the MgO.
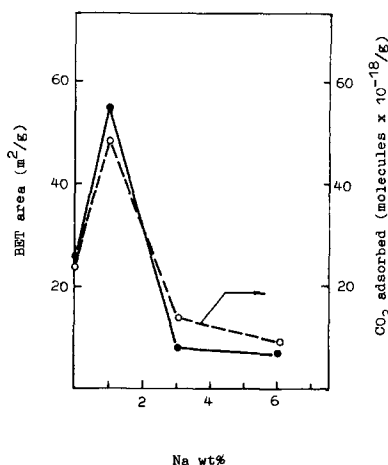

FIG. 1. BET area and CO_2 adsorption versus Na content.

If the amount of CO_2 adsorbed is expressed in 10^{18} molecules/m^2, the values for CO_2 chemisorption on samples A, B, C, and D are 0.97, 0.87, 1.17, and 1.32, respectively. A factor of less than 2 was found in the variation of CO_2 surface density from sample B to sample D, compared to a factor of 7 for difference in Na content. Sample A, which is pure MgO, has a surface basic center density nearly equal to that of sample B, which contains 0.4 mmol of NaOH per gram of MgO. This suggests that the basic centers of Na_2O largely covered the originally present MgO basic centers, instead of providing additional centers.

The possible maximum monolayer coverage of MgO by Na_2O, proposed by the model of Xie et al. (11, 12), is about 2.95×10^{19} Na$^+$/m^2 (0.049 mmol/m^2). If the stoichiometry of CO_2 adsorption is 1, i.e., $CO_2/Na_2O = 1$, the maximum CO_2 adsorption will be 1.48×10^{19} CO_2/m^2, which is about one order of magnitude higher than the values attained for all the samples studied as mentioned above. Either the prediction based on the above model is too high or the stoichiometry is incorrect, or both.

On the other hand, the number of Na$^+$ ions doped onto 1 m^2 of MgO was 4.53×10^{18} (0.0075 mmol), 1.03×10^{20} (0.17 mmol), and 2.33×10^{20} (0.39 mmol) for samples B, C, and D, respectively. The coverage of MgO by Na_2O for sample B based on the above model was only about 15%, while those for samples C and D were about 350 and 800%, respectively. Obviously, for samples C and D, multilayers or aggregates of the dopant were present.

Finally, the occurrence of a maximum in basicity on NaOH doped MgO with respect to NaOH content has also been observed by some other authors (13). The maximum occurred at 0.35 mmol NaOH/g, very close to our result of 0.4 mmol/g.

Results of X-ray Diffraction

XRD studies of NaOH doped MgO gave quite distinct patterns. An example is given in Fig. 2 for sample C. Only diffraction peaks of MgO and graphite (used as lubricant in pelletizing) are observed, implying that no Na_2O crystallites or crystalline phases involving Na$^+$ have been formed. However, new diffraction peaks appear between $2\theta = 13°$ to $32°$, for the same sample after use (Fig. 3). The new crystalline phase has not been identified yet.

X-ray Photoelectron Spectroscopy

Results of XPS studies of the samples are shown in Table 2. The binding energies of Mg $2p$ and Na $1s$ electrons are fairly constant for all the fresh catalyst samples. This means that the addition of NaOH caused no appreciable change in the chemical environment of the Mg^{2+} ions, or no chemical reaction took place with increasing NaOH dosage and calcination at an elevated temperature. But for a used sample (C′), the BE of Mg $2p$ was slightly lowered, and a shoulder at 1070.2 eV appeared in the spectrum for Na $1s$ (Table 2). A new surface species might have been formed in the course of MF decomposition reaction. This is discussed below.

The variation of O $1s$ BE with NaOH dosage is not in agreement with basic strength. According to Vinek et al. (14), higher EPD (electron pair donor) strength of surface sites corresponds to lower BE of the sites (O^{2-}). The increase in NaOH dosage should increase the alkalinity or EPD strength of the surface. But actually, the BE increased slightly. Probably, more OH groups might be responsible for this.

The atomic ratio of Na/Mg increases with increasing NaOH dosage as expected, so does the O/Mg ratio. The relatively high Na/Mg ratio indicates effective surface coverage of MgO by Na_2O. Comparison of the Na/Mg ratios of samples C and C′ indicates a loss of surface Na$^+$ during reaction. In Table 1, which gives the total analysis of Na content, the loss of Na is also observed for sample pairs C, C′ and D, D′. Thus, such a loss is real and not caused by the diffusion of Na$^+$ into the bulk of MgO. Perrichon and Durupty have also reported the loss of alkali metals
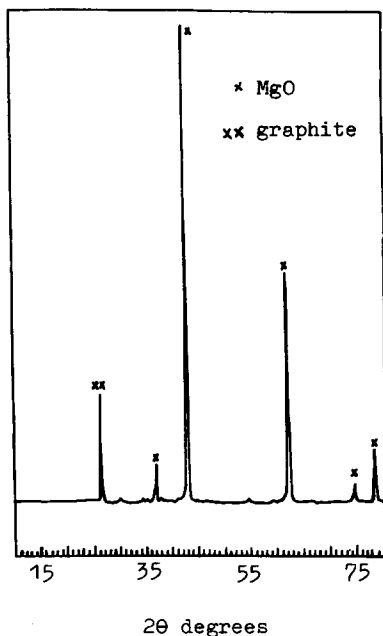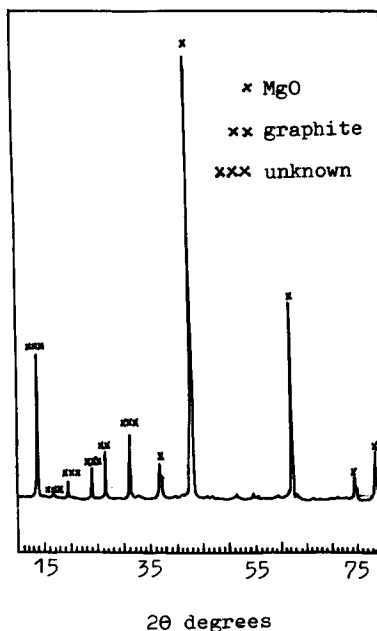
FIG. 2. XRD pattern of catalyst sample C.

FIG. 3. XRD pattern of catalyst sample C'.

from supports at high temperatures (>773 K) (10) and have attributed it to reaction with the vessel wall. We are not in a position to postulate a more convincing explanation. But, the above mentioned loss occurred at a much lower temperature (523 K) under our reaction conditions, and surface oxygen increased considerably at the same time, suggesting the formation of oxygen-rich species.

Depth profiling has been performed on samples C and C', and the results show that

Na^+ is present only on the surface of MgO, both for the fresh and used samples (Table 2). The argon ion beam used can only strip off a layer of about 30 Å from the surface, yet it caused a reduction in Na/Mg ratio by a factor of 30 to 40.

Catalyst Performance

For all the samples which showed detectable activity, only CO, methanol, and unreacted MF were found in the product, as

TABLE 2

Results of XPS Studies

Sample	Binding energy (eV)			Surface atomic ratio	
	Mg 2p	O 1s	Na 1s	Na/Mg	O/Mg
A	50.4	531.6			8.6
B	50.4	531.7	1073.2	1.1	8.3
C	50.4	532.1	1073.1	3.5 (0.12)[a]	9.6
C'	50.2	532.0	1072.5	2.9 (0.07)[a]	11.5
			1070.2		
C	50.4	532.3	1073.2	12.2	12.6

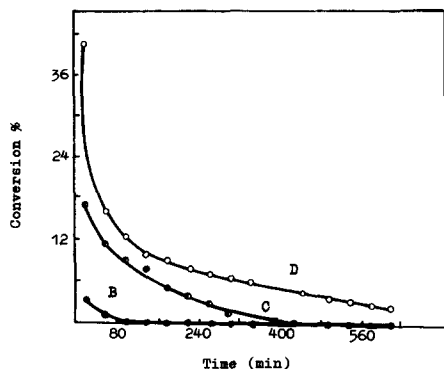[a] Etched by Ar^+ for 90 sec at 2 kV and 6 μA.

FIG. 4. Operating curves of catalyst samples B, C, and D.

mentioned above. The selectivity of MF decomposition to methanol and CO is therefore practically 100%, for all the samples tested under the conditions employed in this work.

Pure MgO (sample A) gave no appreciable conversion of MF, at variance with the literature result (4). The purity of the MgO sample and the adequacy of the pretreating temperature were doubted. So, a sample of 99.9% purity provided by the Beijing Chemical Factory was pretreated under vacuum at 1273 K and tested for activity. The result was only the confirmation of that obtained with our CP MgO sample pretreated at 873 K.

The NaOH doped samples are all active, and their operating curves are given in Fig. 4. The activity depends on Na content and decays with time on stream. The rate of decay is high at first and slows down quickly. If a first order law is assumed for the decay, and Ln X (X is conversion of MF in %) is plotted against time, the decay lines are broken, as shown in Fig. 5, suggesting the presence of different processes and stages of deactivation. Second-order decay plots are curvilinear. From Fig. 5, a rapid stage followed by a slow stage of deactivation is observed for samples B and D. With sample C, three stages seem to exist.

Several processes may be enumerated as the possible causes of deactivation, includ-

ing the loss of Na$^+$, decrease in surface area, poisoning, and the formation of new less-active phases. The first two have been mentioned above and given in Table 1 for samples C and D. These are slow processes. Poisoning by H$_2$O, CO$_2$, and CH$_3$OH has been tested for a NaOH doped zeolite catalyst, which showed that water is a strong poison. The same might be true in the case of NaOH/MgO. But this topic forms a part of another paper and shall be reported later. The formation of a new phase is indicated both in the XRD and XPS studies, but not identified. Maybe the rapid process is related to this process. The deactivation is not reversible under reaction conditions. Flushing of the catalyst bed right after 10 h of operation with Ar for 8 h at reaction temperature did not restore the activity to an appreciable degree.

Infrared studies of the fresh (C) and used (C') catalyst samples gave the IR absorption spectra shown in Figs. 6 and 7. The spectrum for the used sample differs greatly from that of the fresh sample. Comparison with standard profiles established the identity of Fig. 7 with the profile for HCOONa (15). Therefore, the unidentified new phase appearing in XRD and XPS studies is probably HCOONa, which is formed from the disso-
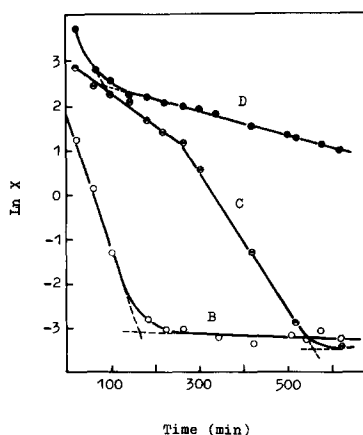

FIG. 5. Plot of Ln X against reaction time for catalyst samples B, C, and D, X being the conversion of MF in %.
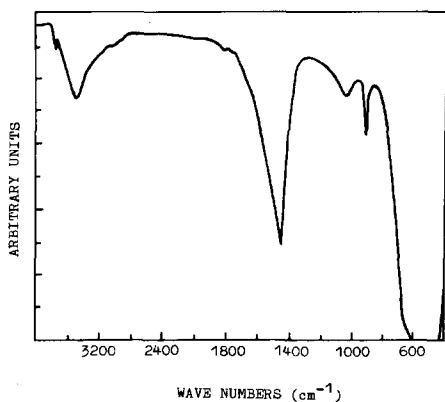
FIG. 6. IR spectrum of fresh NaOH/MgO catalyst (sample C).

ciative adsorption or the saponification of MF. The Na $1s$ peak of lower BE for sample C′ (Table 2) might be attributed to Na $1s$ in HCOONa, which should have a lower BE than that in Na oxide (*16*). The increase in surface O/Mg ratio in sample C′ vs sample C is also in accord with the existence of this species. The formation of HCOONa on the catalyst should be relatively rapid and its catalytic activity low compared to NaOH on the surface. The comparison of NaOH and HCOONa as dopant on MgO is difficult owing to the decomposition of HCOONa on calcination.
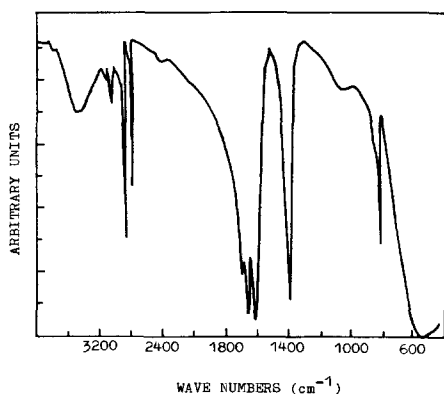
The hypothesis that the rapid deactivation

of the catalyst is caused by the formation of some new surface Na species is further supported by examining the relationship between activity and Na content. Figure 8 gives a plot of it, in which curve (a) is for initial activity, obtained by extrapolating the curves in Fig. 5 to zero time, and curves (b) and (c) are for activities at 20 and 620 min on stream, respectively. It can be seen that at the same level of operation time, the activity is approximately (not exactly) proportional to Na content, but for the same Na content, the activity decays with operation time. The extent of decay cannot be accounted for by the decrease in surface area, and the only possible explanation is the change in chemical state of the Na^+, i.e., from NaOH (or Na_2O) to HCOONa.

Sodium formate is formed by the reaction of MF with NaOH. If this reaction is rapid enough, no high activity stage of alkali doped catalyst would be observed. This is not the case. Therefore, either NaOH in dry state reacts relatively slowly with MF, or the alkali exists mainly as Na_2O, with the number of OH groups far less than stoichiometric, limiting the rate of saponification, and allowing the alkali to act as a catalyst before turning into Na formate, probably in the presence of an incident OH group or water molecule. But, HCOONa is not a permanent trap for the active species. It decomposes at high temperature conditions, as revealed by

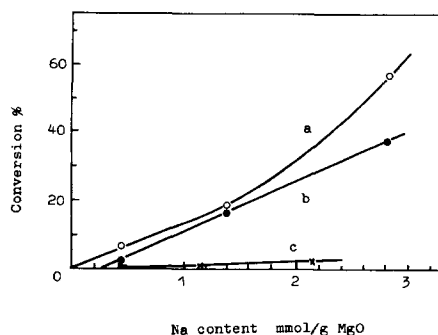FIG. 7. IR spectrum of used NaOH/MgO catalyst (sample C′).

FIG. 8. Correlation of activity to Na content at different operating times: curve (a) zero time, curve (b) 20 min, and curve (c) 620 min.

FTPSR experiments (*vide infra*). Under a reaction temperature of 523 K employed here, HCOONa does not decompose at an appreciable rate, since the deactivated catalysts were not regenerated by flushing with the carrier gas at reaction temperature for 8 h.

The possible formation of HCOONa from MF is also supported by the monitoring of material balance throughout the reaction course. For sample B, the least heavily doped, the balance at 20 min reaction was already 97%, and reached 99–100% soon (with individual data being 101 or even 103% due to analysis error by GC, which is usually 2 to 5% relative). For sample D, the most heavily doped, the balance was only 89% at 20 min and gradually increased to 97% at 180 min, reaching 99% at 300 min. Sample C is in between and somewhat more resembles sample B in this respect. But the conversion and selectivity of MF to methanol and CO reported in this paper are not affected by this extra consumption of MF to form HCOONa, since they were calculated from the amount of CO and hydrogen (actually none) found in the product, instead of from the MF consumed. Our method of calculation is more reliable, because the amount of MF consumed has to be calculated from the difference of two large numbers.

If the above description is used to explain the broken lines in Fig. 5, the steep stage for curve B might be attributed to the formation of HCOONa and the sloping tail to the slow decrease in Na content and surface area. The steep and sloping parts of curve C can be explained in the same way, but the initial sloping stage is additional, which might correspond to surface coverage by HCOONa with underlying NaOH (or Na_2O). The sloping part of curve D should correspond to the initial sloping stage of curve C, while the corresponding steep stage has not yet attained, owing to its high Na content. The initial steep stage of curve D cannot be explained by this reasoning and might probably be associated with the disappearance of extremely active free NaOH.
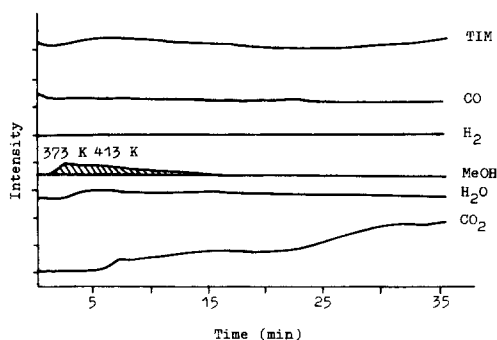
The above picture is of course still specu-

FIG. 9. TPD profile of methanol from catalyst sample C, 100 mg, 15 K/min, 333–873 K.

lative. However, the existence of rapid and slow stages in the deactivation of NaOH doped MgO for MF decomposition and the formation of HCOONa during the reaction are reasonably established.

Temperature Programmed Desorption and Temperature Programmed Surface Reaction Studies

Carbon monoxide was not appreciably adsorbed by NaOH doped MgO. Methanol was adsorbed at 333 K and desorbed without decomposition over a relatively wide range of temperature with peaks at 373 and 413 K, as shown in Fig. 9. An ever increasing desorption of CO_2 was observed in all the cases, including a blank TPD run for NaOH/MgO (not given here). Therefore, it might be attributed to CO_2 absorbed by the alkaline catalyst from the atmosphere, during storage and manipulation, probably in some form of surface carbonates. The blank TPD treatment before each TPD operation seems to be insufficient for removing all chemically bound carbon dioxide, and it persists in the later TPD runs, as shown in Figs. 9 and 10. It is improbable that the carbon dioxide was produced by the action of the catalyst on the adsorbed methanol or MF or was carried in by the feed or carrier gas as an impurity. In the former case, other products (at least water) should be produced and observed; in the latter case, only the
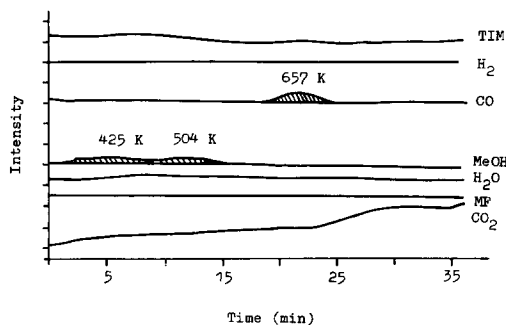
FIG. 10. TPSR profile of MF on catalyst sample C, 50 mg, 15 K/min, 333–873 K.

background or baseline would be affected, if CO_2 were present in the carrier gas (which had been passed through several purification columns). The methanol and MF used were all analytical reagents, and no CO_2 was found in using them as reference samples for quantitative calibration. The desorption of water is very little and is also considered as being originated from atmospheric moisture adsorption or a trace amount of it present in the feed, since no methane or dimethyl ether has been detected, whose formation would give water as a byproduct. These same considerations apply also to the carbon dioxide and water desorptions in the following TPSR and FTPSR experiments with MF.

The TPSR of MF is shown in Fig. 10. In addition to a broad desorption peak of methanol similar to that in Fig. 9, a desorption peak at 657 K for CO was observed. No H_2 or MF was desorbed, indicating that the adsorbed MF is wholly and selectively decomposed. It has been mentioned above that CO is not adsorbed on NaOH/MgO, so this CO is newly formed from the decomposition of MF. As another decomposition product, CH_3OH, evolves much earlier, there should be an intermediate containing CO which evolves CO at a higher temperature. This intermediate is very likely the formate. Since it generates CO at a temperature higher than the reaction temperature (523 K) used in this work, it will inhibit the

reaction if a basic site is used to form it, as already discussed above.

Further informations were obtained from the FTPSR of MF, as shown in Fig. 11. In this figure, the tracings $m/e = 31$ and 60 (methanol and MF) become negative after about 10 min of heating (corresponding to about 483 K). This is a sign of substantial conversion of MF. From this moment on, the signal of CH_3OH evolution, $m/e = 31$, is completely masked. A second important point is the evolution of $H_2(m/e = 2)$ above about 600 K, which is a sign of complete decomposition of MF to $H_2 + CO$, a reaction not desired. The reaction temperature chosen in this work is 523 K, which is higher than 483 K and well below 600 K. Therefore, significant conversion of MF and nearly 100% selectivity to $CO + CH_3OH$ are easily attained, by careful selection of reaction conditions.

The evolution of CO is somewhat earlier compared to Fig. 10. In fact, CO is produced freely at 523 K during the test runs. So, the decomposition of MF through the intermediate formation of a formate is not the only or even not the main mechanism of the reaction. When MF is continuously provided in the gas phase, the involvement of weak or non-dissociative adsorption sites is possible. Methyl formate adsorbed on these sites would be flushed away before programmed heating, in the TPSR experiments. A mecha-
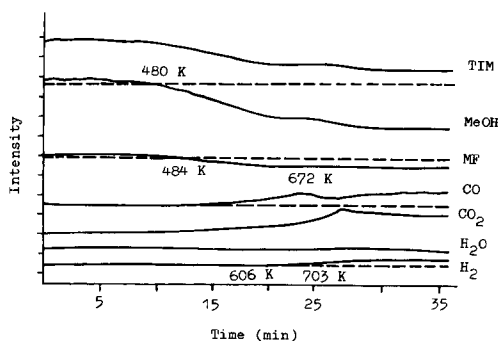

FIG. 11. FTPSR profile of MF on catalyst sample C, 20 mg, 16 K/min, 333–873 K.

nism producing CO and CH_3OH simultaneously should be predominant or at least present under ordinary continuous flow reaction conditions. Further discussion will be made in connection with investigations on other catalyst systems, which provide more data and permit proposals on a more sound basis.

At the present stage, it can only be proposed that there might be two mechanisms in the selective decomposition of MF over alkali doped MgO catalysts. One involves a dissociative adsorption of MF and gives off methanol and CO separately from CH_3O-s1 and HCO-s2 respectively, where s1 and s2 denote adsorption sites. The other involves a non-dissociative mechanism and gives off methanol and CO simultaneously, probably through a certain transition state. These are inferred from the TPSR and FTPSR results. As to the nature of the active sites, strong basic centers provided by NaOH or more probably by Na_2O are proposed, which deteriorate rapidly through the formation of HCOONa which is quite inactive and accumulates on the catalyst surface under the reaction conditions employed. Magnesia seems to be acting merely as a carrier.

ACKNOWLEDGMENTS

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