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Thermal Decomposition of Methanol Adsorbed on Magnesia[1]

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The thermal desorption of methanol and its decompostion products from magnesium oxide powder was recorded over the temperature range 300–1123 K. The formation of formaldehyde was observed in small quantities above 438 K. Large quantities of CO and H_2 were evolved at 723–900 K, accompanied by smaller amounts of CH_4. No ether formation was detected. Methanol desorption was observed below 773 K, with structure in the spectrum revealing at least two different phases of the desorption process. The variation of this structure with initial coverage serves to confirm and clarify previous models for methoxyl on MgO, based on infrared absorption studies. The ease of adsorption, desorption, and migration of methanol species on MgO are also studied, and these features are compared with the corresponding properties of the methanol/Al_2O_3 system. The differences between them are correlated with the differences in proposed models for surface species in the two cases.

I. INTRODUCTION

The decomposition of methanol on magnesia at relatively high pressures has been studied by Kagel and Greenler (*1*) employing infrared spectroscopy to monitor the nature and relative concentration of adsorbed species. Surface methoxide forms at 300 K and above, and begins to be converted to surface formate at 438 K. The formate is converted to surface carbonate above 703 K, and methyl carbonate may also be formed if methanol is present in the gas phase. More recent ir studies, carried out in the absence of gas phase methanol and with carefully dried reagents, indicate that the formation of long-lived surface formate and carbonate also require the presence of methanol vapor (*2*). The low resolution (nitrogen stream) thermal desorption spectrum of ethanol from MgO (*3*) confirms that magnesia, unlike alumina, selectively promotes the dehydrogenation, rather than the dehydration, of alcohols.

In this study, we report thermal decomposition studies of methanol on magnesia for low pressure (10^{-5} Torr) (1 Torr = 1.3 × 10^2 Pa) exposures. Previous work of this kind for the methanol/alumina system (*4*) has demonstrated the usefulness of the technique for elucidating details of the reaction mechanism, and the results of the present study make possible a systematic comparison of the properties of the alumina and magnesia substrates with respect to methanol adsorption, desorption, and decomposition.

II. EXPERIMENTAL METHODS

1. *Apparatus*

The experiments were conducted in a bakeable ultrahigh vacuum system having a background pressure of 5×10^{-9} Torr. Adsorbate vapor was admitted through a continuously variable leak valve, and the

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system was continuously pumped by an ion pump during substrate cleaning, exposure, and desorption. The total pressure was monitored via the ion pump current while partial pressures were monitored mass spectrometrically. The mass spectrometer filament was turned off during methanol exposure to avoid partial decomposition of the vapor. The magnesia sample was supported and heated by a V-shaped stainless steel boat lined with fine stainless steel net, as previously described for alumina (*4*). The temperature was monitored by an iron–constantan thermocouple spot-welded to the boat.

2. Magnesia Substrate

The sample consisted of about 1.5 mg of powdered magnesia, prepared by precipitation of the carbonate from Mg $(NO_3)_2$ solution, followed by heating in air at 1100 K for 4 hr 40 min (*5*). The initial active surface area of the sample was 32.4 m^2/g (*6*), although further dehydration was routinely carried out by heating to 1173 K prior to each experiment until a pressure less than 5×10^{-8} Torr was achieved. Following this pretreatment, the sample was allowed to cool for 30 min, then exposed to methanol vapor at constant pressure, typically 1×10^{-5} Torr. Unless otherwise noted, exposure was for 15 min, and the system was then evacuated for 30 min prior to desorption. The desorption was carried out by heating at 100 K/min and monitoring the desorbed products with the mass spectrometer. Typically, the ambient pressure at the beginning of a desorption cycle was 5×10^{-8} Torr.

III. RESULTS AND DISCUSSION

1. Desorbed Species

The principal desorbed species, as revealed by the mass spectrometer, were H_2, CH_4, H_2O, CO, H_2CO, CH_2OH, and CO_2. Typical curves for the relevant m/e values are shown in Figs. 1 and 2. Mass 44 (CO_2) is not shown because it can be accounted for entirely by methanol fragmentation on the ion gauge filament. Methanol begins to desorb almost immediately as the temperature is raised, reaches a maximum near 473 K, and declines sharply above 723 K. Beginning near this temperature, the remaining surface species are desorbed primarily as CO and H_2, with small amounts of CH_4. We note that the desorption of these species begins just above the temperature at which Kagel and Greenler (*1*) first reported the formation of surface carbonate, indicating that surface carbonate or its surface precursor is the probable source of desorbed CO and H_2. The onset and peak temperatures for methanol desorption were independent of coverage over the range of coverages considered ($\theta = 0.2$ to 1.0 relative to the limiting coverage for long exposures at 1×10^{-5} Torr).

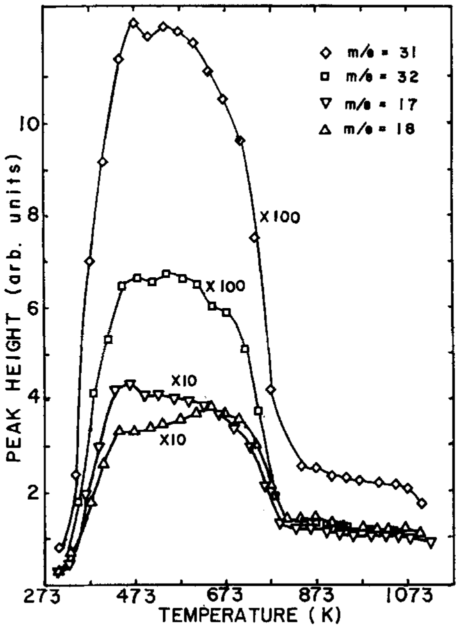

FIG. 1. Typical desorption curves for CH_3OH and H_2O.

The curves for $m/e = 17$ and 18 (Fig. 1) are due primarily to H_2O, but $m/e = 17$ also contains some contribution from OH

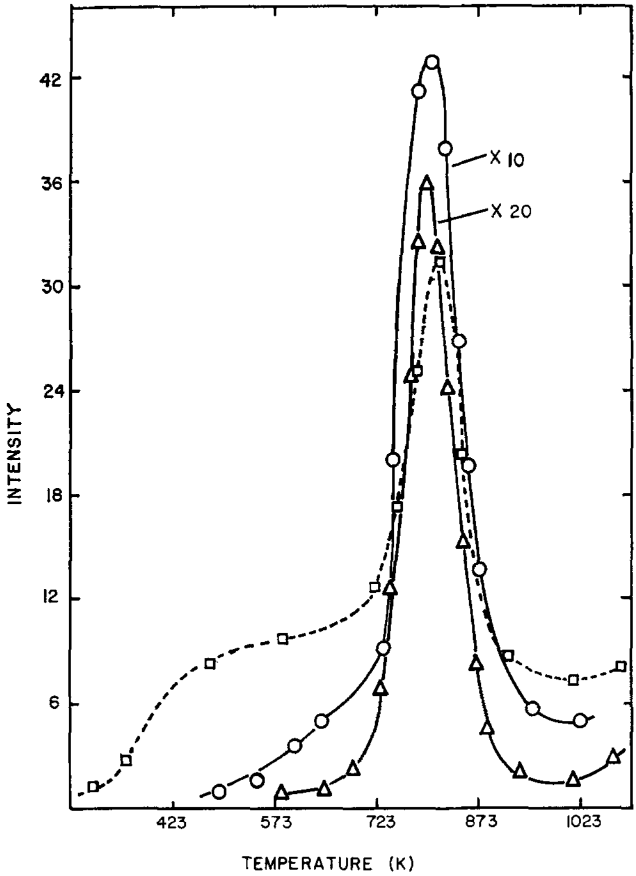

FIG. 2. Desorption curves of H_2 (○), CO (△), and CH_4 (□) from MgO after adsorption of CH_3OH.

produced by methanol fragmentation at the filament. The increase of $m/e = 18$ in the 373–673 region is attributable to the additional desorption of surface hydroxyl pairs as H_2O, presumably promoted by surface migration of hydroxyl groups at higher temperatures (see Sect. III.3 below). No attempt has been made to correct these two curves for contributions from methanol fragmentation, since the methanol used was already contaminated with a trace of H_2O.

Masses 29 and 30, corrected for methanol contributions and taken to represent formaldehyde production, are shown in Fig. 3. The onset of the formaldehyde peak occurs just above 438 K, at which temperature surface formate is first observed in ir studies (*1*). The quenching of the formaldehyde peak above 723 K also correlates with the beginning of CO desorption and the end of methanol desorption. Since surface formate is not observed in the absence of gas phase methanol (*2*), we suppose either that formaldehyde is de-

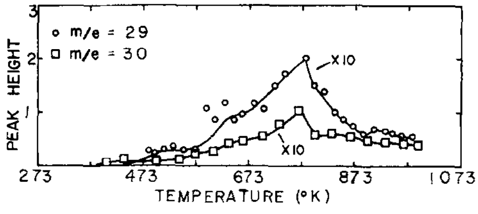

FIG. 3. Desorption curves for *m/e* 29 and 30 (formaldehyde), corrected for methanol contributions.

sorbed immediately upon formation, or else that the gas phase methanol being desorbed is involved in the formation of the oxidizing agent responsible for formaldehyde production. The relatively large scatter in the data of Fig. 3 is due to the fact that the methanol correction being subtracted is 4–5 times larger than the remaining signal attributed to formaldehyde.

Masses 45 and 46 were monitored during desorption from 300 to 1123 K and no measurable production of methyl ether was observed. This confirms the general notion that MgO is a highly selective dehydrogenation catalyst, and does not typically promote dehydration (*2*).

2. Adsorption and Desorption Rates of Methanol

Figure 4a shows the relative coverage of methanol as a function of methanol exposure at 300 K and 1×10^{-5} Torr. The coverage was estimated from the thermal desorption curve for mass 31, assuming the relative production of methanol, formaldehyde and CO to be independent of coverage. The time required for apparent saturation is 2–3 times larger than that required in the case of Al_2O_3 (*4*).

The apparent limiting coverage of Fig. 4a is not independent of exposure pressure; exposure for 120 min at 1×10^{-4} Torr gave a coverage of 1.4 times greater than the maximum shown in Fig. 4a. This result may be due in part to the increased exposure (Langmuirs) but may also be related to the relative inaccessibility, because of packing, of certain parts of the powdered MgO surface to gas phase methanol.

Figure 4b shows the relative coverage as a function of evacuation time, normalized to the saturated exposure of Fig. 4a. The decline of the coverage is much more rapid for MgO than for Al_2O_3 (*4*). These differences in room temperature adsorption and desorption rates for the two substrates indicate that the heat of chemisorption is higher for Al_2O_3 than for MgO. Further confirmation of this is given by the fact that the peak maximum for methanol desorption from AlO_3 occurs at a temperature ~25 K higher than that for desorption from MgO.

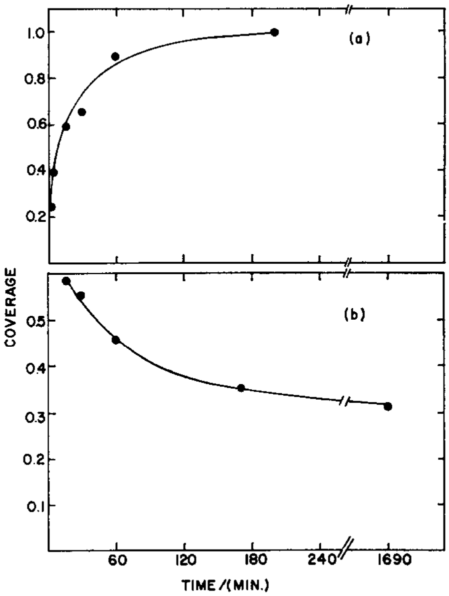

FIG. 4a. Dependence of amount of desorbed methanol on exposure time (at 10^{-5} Torr) for constant evacuation time (30 min). 4(b). Dependence of amount of desorbed methanol on evacuation time for constant exposure of 15 min at 10^{-5} Torr.

3. Surface Migration of Adsorbed Species

In order to determine whether methoxyl and hydroxyl migrate readily on the MgO surface at various temperatures, a series of experiments was performed in which methanol was desorbed in the usual way up to a specified temperature T_s, at which heating was abruptly terminated. After evacuation at room temperature for 2 hr, the thermal desorption mass spectrum was taken for the entire temperature range. Figure 5 shows the mass 31 peak for three different values of T_s. It is evident that a low coverage resulting from partial

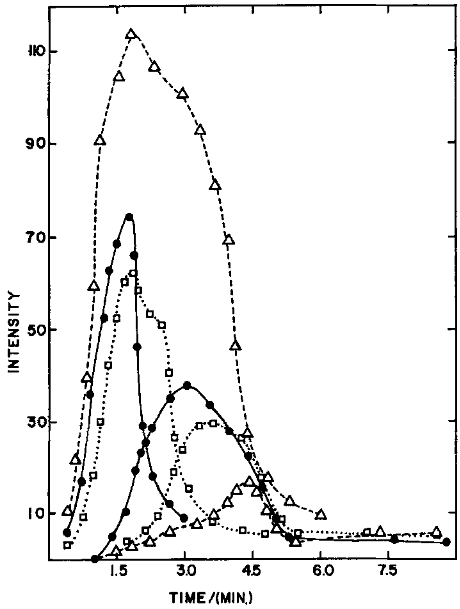

Fig. 5. Methanol desorption profiles after exposure to CH_3OH at 300 K and 10^{-4} Torr for 15 min. The three samples were desorbed to T_s = 448 (●), 523 (□), and 673 (△), respectively, after which heating was abruptly terminated and the sample was pumped for 2 hr at 300 K. At each temperature two curves are shown; the more intense is the first heating cycle, while the other is the desorption after the 2 hr pumping period. With the exception of points above T_s on the first heating cycle of each run, the temperature is given by $T = 100t + 268$ where t is the time (min).

desorption differs markedly from a low coverage due to short exposure time. In the latter case, the onset of methanol desorption and the position of the maximum are independent of coverage, whereas in the T_s experiments the onset occurs much later during the second desorption, and the maximum is reached only after T_s has been passed. This result indicates that the new surface condition induced by partial desorption is not greatly changed upon standing, i.e., that surface migration of the adsorbed species is quite slow at room temperature. However, it should be noted that the onset of the mass 31 peak during the second desorption occurred at 373–400 K for all three values of T_s. For similar experiments on Al_2O_3 (*4*), on the other hand, the onset of the second desorption was much sharper, except for the highest T_s employed. We conclude that surface migration, although slow in both cases, is somewhat faster and begins at a lower temperature for MgO than for Al_2O_3.

4. Homogeneity vs Heterogeneity of Adsorption Sites

The T_s data described above make it clear that partial desorption produces a state of the surface that differs qualitatively from any state obtained merely by adsorption and evacuation at room temperature. This fact can be explained in any of the following ways: (a) an intrinsically heterogeneous surface, with strong binding sites being occupied first and desorbing last; (b) an intrinsically homogeneous surface with coverage-induced heterogeneity, in which the ease of desorption increases with increasing number of

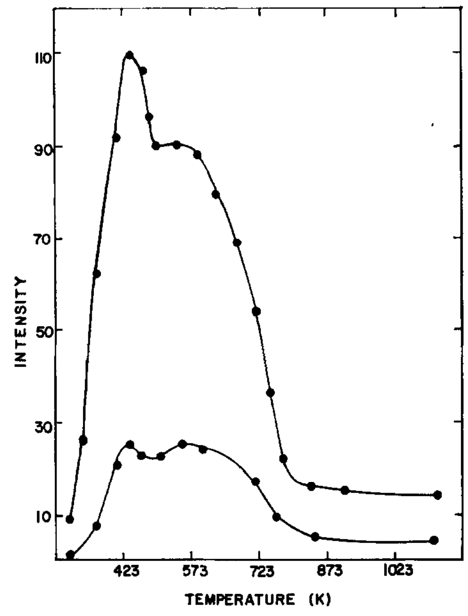

Fig. 6. Mass 31 (CH_3OH) desorption profiles following exposures of 2 min (lower) and 60 min (upper) at 300 K and 10^{-6} Torr, with equal evacuation times of 30 min.

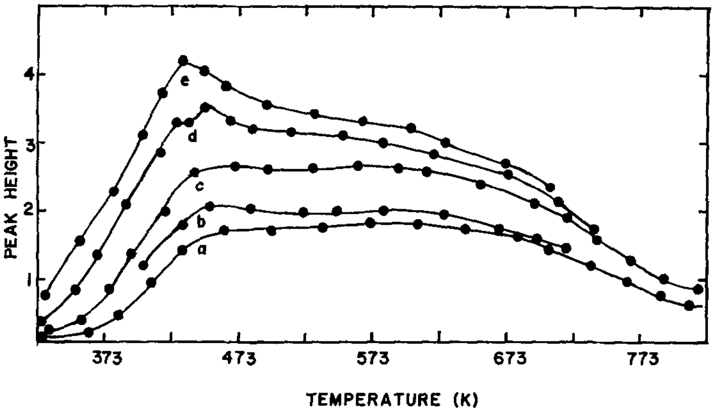

FIG. 7. Mass 31 (CH_3OH) desorption profiles following exposures of 15 min at 300 K and 10^{-6} Torr, with evacuation times (min): (a) 1690, (b) 170, (c) 62, (d) 30, and (e) 16.

methoxyl or hydroxyl nearest neighbors; or (c) a model intermediate between these two, in which methanol molecules adsorb in structurally different ways on an originally homogeneous surface. Model (b) has been proposed by Peri (*7*) for hydroxyl groups on alumina, and its correctness for methoxyl on alumina has been verified by Matsushima and White (*4*), who showed that the CH_3O remaining after the first cycle of a T_s experiment can in fact be desorbed as methyl ether below T_s during the second cycle, provided that the original near-neighbor condition is restored by adsorption of CD_3OD between the two cycles. Although the absence of ether production on MgO precludes the use of this particular technique, it is still possible to draw some tentative conclusions about the MgO sites on the basis of methanol desorption.

One important piece of evidence for model (b) for alumina is the fact that the onset temperature for methanol desorption and the position of the peak maximum are independent of exposure and evacuation time (*4*). In the case of MgO, however, the evidence is somewhat less clear. Figure 6 shows curves for mass 31 following exposures of 2 and 60 min, with constant evacuation time; and Fig. 7 shows curves for constant exposure of 15 min, but with evacuation times of 16, 30, 62, 170, and 1690 min. The onset and first maximum are indeed independent of exposure and evacuation time, indicating a homogeneous surface condition of type (b) with initial preferential adsorption in islands, and with induced heterogeneity arising as methoxyl sites with fewer near neighbors are produced in the course of random desorption (*4*, *7*). On the other hand, the desorption curves for MgO are distinguished from those for Al_2O_3 in that the former change in shape as a function of initial coverage, with the relative intensity of the low-temperature part of the curve increasing with increasing coverage (Figs. 6 and 7). These observations are most readily explained by means of model (a) or (c) in which different parts of the desorption curve correspond to different types of sites. In such a model the peaks at lower temperature (300–450 K) would be produced by more weakly bonded sites which are, on the average, the last to be occupied and the first to be desorbed. This model would account correctly for the fact that the low-temperature portion of the curve grows more slowly with exposure and decreases more rapidly with evacuation than the high-temperature portion. In order to explain these observations with a model of type (b) alone, it would be necessary to make the additional

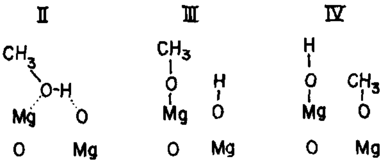

FIG. 8. Structural models of adsorbed methanol species on MgO [from Ref. (*2*)].

assumption that adsorption sites with large numbers of methoxyl near neighbors are relatively difficult to form and are favored by longer exposure times and higher total coverage. But this assumption is in conflict with the earlier assumption of initial preferential island adsorption that is required to account for the uniform onset temperature of the methanol desorption peak, regardless of exposure. These considerations indicate that a satisfactory explanation of adsorption on the MgO surface must combine aspects of model (b) with either model (a) or (c).

5. Correlation with Structural Models for Surface Species

On the basis of infrared absorption studies, Tench *et al.* (*2*) have proposed a type (c) model for methanol adsorption on MgO involving four distinct species of adsorbed alcohol on a homogeneous surface. These four species are characterized by distinctive CO stretching frequencies, and some of them are correlated with characteristic OH absorption peaks. Three of the four proposed structures (**II**, **III**, and **IV**) are shown in Fig. 8. Species **I** is a second layer of loosely adsorbed methanol whose ir spectrum resembles that of liquid methanol. Species **I** and **II** were largely removed by pumping overnight, and **II** was completely removed by heating for 15 min at 373 K; species **III** desorbed slowly below 373 K, and was finally completely removed by heating for 15 min at 573 K; species **IV** persisted at constant concentration from room temperature to 673 K, and was desorbed as CO at 673–773 K (*2*).

Although we cannot categorically rule out the possibility of type (a) heterogeneity, our high resolution thermal desorption studies are consistent with the proposal of Ref. (*2*) and serve to clarify and amplify certain of its features. The low-temperature thermal desorption of methanol, which increases more slowly with exposure than the higher-temperature desorption, is to be attributed to species **I** and **II**. The remainder of the methanol desorption curve is due to species **III**, the T_s data being explained by coverage-induced heterogeneity of type (b) as discussed above. The sudden CO desorption at 723 K is produced by decomposition of species **IV**.

Our data and that of Ref (*2*) are in agreement regarding the decomposition temperature of **IV**. However, we find that **II** and **III** persist to temperatures roughly 100 K higher than those previously reported (*2*). This difference can be attributed to the fact that we have heated the substrate at a constant and relatively rapid rate (100 K/min) while monitoring the desorbing species, whereas Tench *et al.* (*2*) increased the temperature in 50 K increments, maintaining a constant temperature for 15 min at each step before the sample was cooled to room temperature for ir analysis. Our data therefore reveal the state of the sample during heating more clearly than the ir experiments, in which the long heating times permit the restoration of the initial condition in which type **III** species are concentrated in islands, or at least are surrounded by hydroxyl species optimally located for desorption. In our experiments, on the other hand, the temperature increase is sufficiently rapid relative to surface migration so that regions of high coverage are thinned out, resulting in a progressive increase in average binding energy as species with the maximum number of near neighbors are depleted and other, less easily desorbed species of type **III** are formed. Thus the temperature dependence of desorption of species **III** reported in Ref. (*2*) is probably determined primarily by the rate of surface migration, whereas our data reflect primarily the relative ease of desorption of various subspecies of **III** having different local concentrations.

Finally, the fact that the desorption of species produced by surface migration begins at 373–400 K (Sect. III.3) is consistent with the observation of Tench *et al.* (*2*) that desorption of species **III** is small below this temperature. The small quantity of methanol desorbed below T_s during the second cycle is presumably due to small regions of high species **III** coverage (or of high local concentration of hydroxyl groups around type **III** methoxyl groups) produced by surface migration at or below T_s. It is significant that only one of the hydroxyl ir bands (3570 cm^{-1}) reported in Ref. (*2*) correlates in intensity with the species **III** CO stretching peak as the temperature is increased. Two others which persist well above 373 K, namely those at 3110 and 3332 cm^{-1}, decay more rapidly with temperature than type **III** methoxyl. It appears reasonable to attribute these bands to hydroxyl groups which are originally less favorably located for methanol desorption than the 3570 cm^{-1} species, but which are the source of hydrogen for the surface migration that replenishes the supply of 3570 cm^{-1} hydroxyl as the system is allowed to rearrange during each successive 15 min heating period.

The origin of the formaldehyde produced during desorption cannot be unambiguously assigned to one of the two surface methoxyl species discussed above, but the evidence suggests species **IV** as its most likely source. Formaldehyde desorption declines only slowly after the onset of CO desorption, continuing almost 50 K beyond the temperature at which methanol desorption, assigned to species **III**, levels off. Therefore, it seems reasonable to attribute formaldehyde production to the oxidation of species **IV**. The fact that ir studies (*2*) showed no decrease in species **IV** concentration below 673 K is not evidence against this assignment, since the quantity of formaldehyde produced below this temperature is quite small; even the formaldehyde maximum (at 723 K) is only ~4% of the CO maximum, which is a measure of species **IV** concentration.

6. Comparison with Alumina

The alumina and magnesia surfaces differ significantly in several ways. One of these is that methoxyl is less tightly bound to MgO than to Al_2O_3. This is shown by the slower adsorption, faster desorption at room temperature, and greater ease of migration on magnesia, as discussed above. The opposite order of binding strength would ordinarily be expected; alkoxide on the oxide of the more electropositive metal is typically more anionic (*9*, *10*), and since bonding of alkoxide to metal oxides is primarily ionic (*11*), the adsorption of methanol on magnesia should be stronger, other factors being equal, than on alumina. This apparent discrepancy can be accounted for if we assume, with some previous authors, that dissociative adsorption of alcohol on alumina is accompanied by the breaking of an Al–O bond (*7*), whereas the corresponding process on magnesia involves the formation of chemisorption bonds without major changes in the arrangement and bonding of Mg^{2+} and O^{2-} in the surface layer (*2*, *8*). These models for chemisorption make the assumption that adsorption takes place on the 100 plane of the relevant crystal lattice in each case, an assumption which, although not directly verified, has proven capable of accounting for a wide variety of observations for these two systems (*7*, *8*). The proposed difference in structure of chemisorbed species on MgO and Al_2O_3 can also account for the more intense and sharply peaked CO desorption curve for MgO which, unlike Al_2O_3 according to the above models, is capable of forming methoxyl species of type **IV**.

Finally, the failure of MgO to produce methyl ether from methanol may be due, at least in part, to the fact that adjacent methoxyl species on the model MgO surface will be of different types (**III** and **IV**), resulting in a nonoptimal orientation for ether formation; whereas on Al_2O_3, adjacent methoxyl groups will have corresponding atoms at an equal distance from the surface.

SUMMARY

The thermal desorption of methanol and its decomposition products from magnesium oxide powder, over the temperature range 300–1123 K, has been recorded mass-spectrometrically in an ultrahigh vacuum system, and the results of these experiments are correlated with structural models for the surface species (*2*). Adsorbed methanol molecules are desorbed below 450 K. Above this temperature, the methanol desorption arises primarily, if not exclusively, from methoxyl groups attached to surface Mg^{2+} ions [type **III** site of Ref. (*2*)]. The onset and peak maximum temperatures for methanol desorption are independent of initial exposure and room temperature evacuation times, indicating that the adsorbed species are initially concentrated in islands whose size varies with exposure time, but whose composition does not. The ease of desorption of this methoxyl species decreases as the coverage decreases during the course of desorption, and the initial condition of the surface is not restored by surface migration at room temperature. This effect is attributed to coverage-induced heterogeneity on a homogeneous surface.

Beginning at 723 K, CO and H_2 are evolved, together with a small amount of CH_4, from the decomposition of surface species in which the methyl group is bonded directly to a surface oxide ion [type **IV** site of Ref. (*2*)]. Formaldehyde production is tentatively assigned to this species, also.

Compared to the methanol/alumina system (*4*), the adsorption of methanol on magnesia is slower and the desorption at room temperature is more rapid, indicating that the adsorption bond is weaker in the magnesia case. This result is apparently due to the fact that methanol adsorption involves the breaking of metal–oxide bonds in the alumina system, but not in the magnesia system.

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REFERENCES

1. Kagel, R. O., and Greenler, R. G., *J. Chem. Phys.* **49**, 1638 (1968).
2. Tench, A. J., Giles, D., and Kibblewhite, J. F. J., *Trans. Faraday Soc.* **67**, 854 (1971).
3. Takezawa, N., Hanomaki, C., and Kobayashi, H., *J. Catal.* **38**, 101 (1975).
4. Matsushima, T., and White, J. M., *J. Catal.* **44**, 183 (1976).
5. Nelson, T. L., Tench, A. J., and Harmsworth, B. J., *Faraday Soc. Trans.* **63**, 1427 (1967).
6. Vaughan, R. W., private communication.
7. Peri, J. B., *J. Phys. Chem.* **69**, 211 (1965); **69**, 220 (1965).
8. Anderson, P. J., Horlock, R. F., and Oliver, J. F., *Trans. Faraday Soc.* 61, 2754 (1965).
9. Takezawa, N., and Kobayashi, H., *J. Catal.* **25**, 179 (1972).
10. Takezawa, N., and Kobayashi, H., *J. Catal.* **28**, 335 (1973).
11. Foyt, D. C., and White, J. M., *J. Vac. Sci. Technol.* **13**, 334 (1976).