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Oxidation of Methanol and Formaldehyde on Fe_2O_3 in Comparison with MoO_3 and a Mixed $Mo^{6+}Fe^{3+}O$ Catalyst

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The oxidation of methanol and formaldehyde was followed on Fe_2O_3 at 220°C with and without oxygen in the gaseous phase. The main difference between these two processes is the formation of hydrogen during the reaction without oxygen and the evolution of water in the opposite case.

The effect of small amounts of preadsorbed pyridine on the oxidation of methanol was also studied. The inhibition effect of preadsorbed pyridine on methanol oxidation on the mixed $Mo^{6+}Fe^{3+}O$ catalyst together with the infrared spectra of adsorbed pyridine may be explained by a cation–ligand interaction of both reactants with the transitional metal ions of the catalyst.

The behavior of the mixed $Mo^{6+}Fe^{3+}O$ catalyst in the oxidation of methanol resembles in many aspects that of MoO_3 in an unreduced state.

INTRODUCTION

A preceding paper (*1*) dealt with the oxidation of methanol on MoO_3. This paper is devoted to the study of the same reaction on Fe_2O_3, because Fe^{3+} is the other cation contained in the mixed $Mo^{6+}Fe^{3+}O$ catalyst (further denoted as MC, mixed catalyst) for selective oxidation of methanol to formaldehyde.

In an attempt to explain the nature of active sites on MC, the effect of preadsorbed pyridine on methanol oxidation has been studied on MC and some other oxides. Also the oxidation of pyridine was followed on some oxides including MC. Infrared spectra of pyridine adsorbed on MC were also recorded. In the discussion, the oxidation of methanol on MoO_3, Fe_2O_3 and MC is compared.

EXPERIMENTAL

The experimental procedure used in the present work was the same as in our paper on MoO_3 (*1*). The oxidation of small amounts of methanol and formaldehyde, usually about 0.2 cm^3 NTP, was followed on 1 g of Fe_2O_3 previously heated in vacuo (10^{-5} Torr) to 400°C for 15 hr. If the influence of preadsorbed pyridine on the oxidation of methanol was studied, small amounts of pyridine were adsorbed on the oxides at room temperature. The composition of the gaseous phase was continuously followed by means of a mass spectrometer MCH 1302 (USSR). Methanol and pyridine were the same as in previous work (*2*, *3*). The sources and surface areas of oxides (BET method, Ar 78°K, cross section of Ar 16.6 Å^2) are given in Table 1.

Infrared spectra of adsorbed pyridine on MC were recorded in the region of the ring vibrations by means of a Perkin Elmer 225 infrared spectrometer in the usual way (*4*) at the temperature of the infrared beam. A plate of MC (thickness, 13 mg/cm^2) in a vacuum cell was first evacuated at 380–400°C for 4 hr (10^{-4} Torr), and then at the

TABLE 1
SOURCES AND SURFACE AREAS OF THE SAMPLES USED

Sample	Surface area (m^2/g)	Preparation, composition
Mo–Fe–O MC	6.9	Commercial catalyst, data of analysis (17.5% Fe_2O_3, 82.5% MoO_3)
MoO_3	2.6	Merck, p.a.
Fe_2O_3	7.2	Lachema, p.a.
V_2O_5	1	"
CuO	20.9	By the decomposition of $Cu[OH]_2$ in vacuo

same temperature the catalyst was oxidized by 150 Torr of air and dried by passage through a trap with solid CO_2 for 1 hr. After cooling in air to the temperature of the infrared beam, and after 20 min evacuation, pyridine was adsorbed at a pressure of 10 Torr for 30 min. The cell was then evacuated for 10 min and the spectrum was recorded, the latter being unchanged for 12 hr. Infrared spectra of MC plates in vacuo before pyridine adsorption were also taken.

RESULTS

Oxidation of Methanol and Formaldehyde on Fe_2O_3

The oxidation of methanol on Fe_2O_3 could be repeated at 220°C several times, with the sample being evacuated between the individual doses of methanol at 400°C for 1 hr. The composition of gaseous products was not changed; they consisted mainly of H_2, CO_2, and CO, and the formation of H_2O was not observed. The amount of lattice oxygen of Fe_2O_3 consumed in methanol oxidation exceeded at least two surface layers.

The time course of the oxidation of one dose of methanol on Fe_2O_3 without oxygen in the gas phase is shown in Fig. 1a. Figure 1b shows the oxidation of methanol with a five-fold excess of oxygen in the gas phase. The main difference in these two cases is the appearance of hydrogen in case (a) and water vapor in case (b). The decrease of methanol concentration at the beginning of the reaction is larger in case (a) than in case (b). The concentration of CO_2 in case (b) is much higher than in the experiment without oxygen in the gaseous phase. In both cases, the amount of formaldehyde evolved is very small.

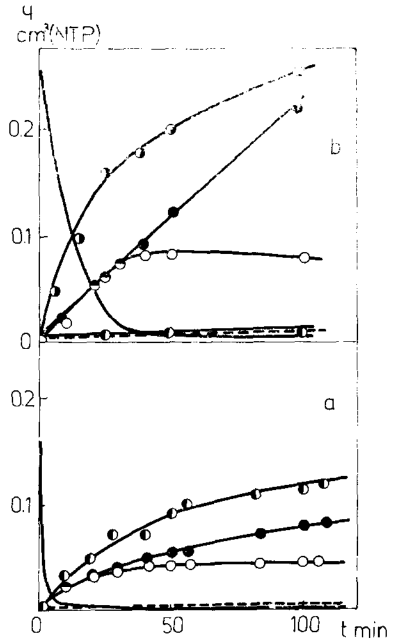

FIG. 1. The change of gas amounts with time during methanol oxidation on Fe_2O_3 at 220°C where in case (a) there is no oxygen in the gas phase; (b) an excess oxygen in the gas phase, with — representing methanol; ---- representing formaldehyde; ○ as CO; ● as Co_2; ◐ as H_2, and ◑ as H_2O.

In Fig. 2, the same experiment is shown as in Fig. 1 with formaldehyde instead of methanol. The results are similar to those in Fig. 1: appearance of hydrogen in case (a), water in case (b); faster decrease of formaldehyde concentration in case (a) than in case (b); larger amount of CO_2 in case (b) than in case (a).

Similar experiments were carried out with the oxidation of CO on Fe_2O_3 under the same conditions as the oxidation of methanol and formaldehyde without oxygen in the gaseous phase. The oxidation of CO proceeded with approximately the same rate as the oxidation of methanol, but no CO was found to be adsorbed on the surface of Fe_2O_3.

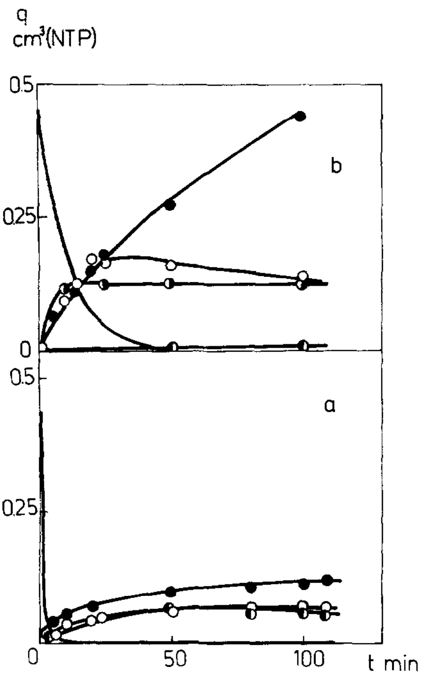

FIG. 2. The change of gas amounts with time during formaldehyde oxidation on Fe_2O_3 at 220°C where in case (a) there is no oxygen in the gas phase; (b) an excess of oxygen in gas phase, with — representing formaldehyde; ○ as CO; ● as CO_2; ◑ as H_2, and ◑ as H_2O.

The Effect of Preadsorbed Pyridine on the Oxidation of Methanol

The inhibition effect of preadsorbed pyridine on methanol oxidation on MC was already described (*2*, *3*, *5*). We poisoned the surface of MC with increasing amounts of preadsorbed pyridine (Fig. 3a–e). Pyridine was adsorbed at room temperature; then methanol was admitted at the same temperature. The sharp decrease of methanol concentration at time t = 0 is due to the adsorption of methanol at room temperature. This adsorbed methanol decreased with increased amount of preadsorbed pyridine. After 30 min of methanol adsorption, the sample was immersed in an oil bath at 100°C. A part of the methanol desorbed in the first few min. In the experiments from (a)–(d), no pyridine desorbed. The converted amount of methanol decreased with increasing amounts of preadsorbed pyridine.

The same inhibition effect of preadsorbed pyridine on the methanol oxidation was found for the oxides Fe_2O_3, MoO_3, CuO, and V_2O_5. No change in the composition of the gaseous products of methanol oxidation was observed for the oxides of deep methanol oxidation; only the amount of gaseous products decreased with increasing amount of preadsorbed pyridine.

Oxidation of Pyridine

The oxidation of pyridine was followed on various oxides at slowly increasing temperatures without oxygen in the gas phase. In Table 2, the temperatures of the onset of pyridine oxidation are shown in comparison with the same values for methanol oxidation. The oxides used for the selective oxidation of methanol to formaldehyde (MoO_3, V_2O_5) do not oxidize pyridine up to 400°C. The only exception we have found was MC previously heated in vacuo to 400°C. This sample oxidized pyridine at a relatively very low temperature of 200°C. In the preceding papers (*2*–*6*), the effect was found of the degree of dehydration of MC on the composition of the products of methanol oxidation. The more pronounced the dehydration of the sample, the higher the amount of formaldehyde and carbon monoxide. Only on the most dehydrated MC did the oxidation of pyridine proceed.

TABLE 2

TEMPERATURE OF THE ONSET OF THE OXIDATION OF METHANOL (T_1) AND PYRIDINE (T_2) IN °C

Sample	T_1 (°C)	T_2 (°C)
Mo–Fe–O MC	80	200
MoO_3	300	Inactive up to 400
Fe_2O_3	220	320
V_2O_5	120	Inactive up to 400
CuO	220	260

IR Spectrum of Adsorbed Pyridine on MC

The ir spectra of adsorbed pyridine on MC in the region of the ring vibrations are shown in Fig. 4, where the lower curve is the spectrum of adsorbed pyridine, and the higher curve is the spectrum of the catalyst

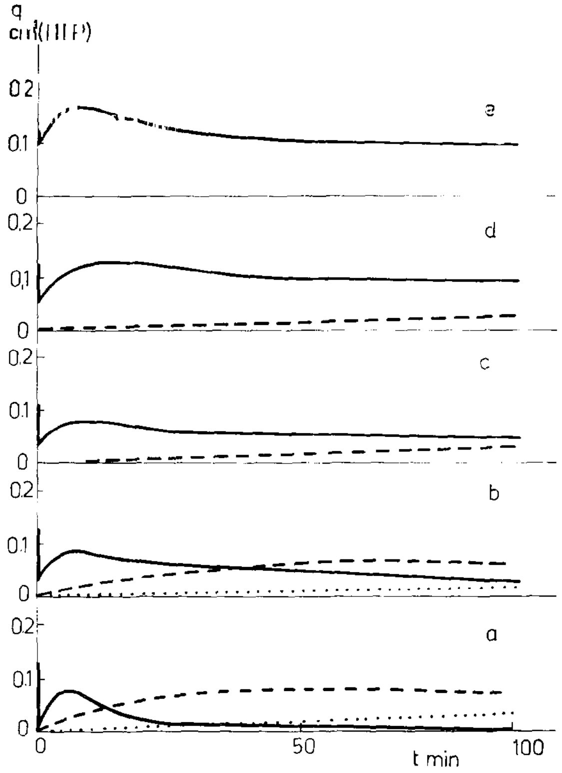

FIG. 3. The effect of preadsorbed pyridine on the oxidation of methanol at 100°C on Fe–Mo–O catalyst, where the — is used for the time function of the amounts of methanol; the ---- is used for the time function of the amounts of formaldehyde, and the ···· is used for the time function of the amounts of carbon monoxide, with a = 0, b = 2, c = 4, d = 12, and e = 20 μmole of preadsorbed pyridine/1g of Fe–Mo–O catalyst.

plate before pyridine adsorption. We also recorded the ir spectrum before and after the adsorption of pyridine in the region of 3000–3800 cm^{-1}. No bands with hydrogen bridge bonding characteristics for OH groups appeared in the vicinity of 3200 cm^{-1}.

DISCUSSION

Oxidation of Methanol and Formaldehyde on Fe_2O_3.

Under the above-mentioned experimental conditions, methanol and formaldehyde on Fe_2O_3 are oxidized in a similar way; at the same temperature they give the same gaseous products. The hydrogen in methanol and formaldehyde molecules is probably not bonded to the lattice oxygen of Fe_2O_3 or its bond is only weak, because during the oxidation without oxygen in the gas phase, molecules of hydrogen are released. In the presence of oxygen, water is released instead of hydrogen. In the latter case, the hydrogen of methanol and formaldehyde reacts either with sorbed oxygen or directly with the oxygen from the gas phase. If sorbed oxygen participates in the oxidation of hydrogen, it is not identical with the lattice oxygen of Fe_2O_3. The qualitative composition of other gaseous products is not changed in the presence of oxygen. The carbonyl part of the molecules might be, at least partially, bonded to the lattice oxygen of Fe_2O_3. Lattice oxygen takes part in the oxidation of methanol and formaldehyde, because CO_2 together with CO is released from the onset of the reaction.

The smaller amount of adsorbed methanol and formaldehyde on Fe_2O_3 in the

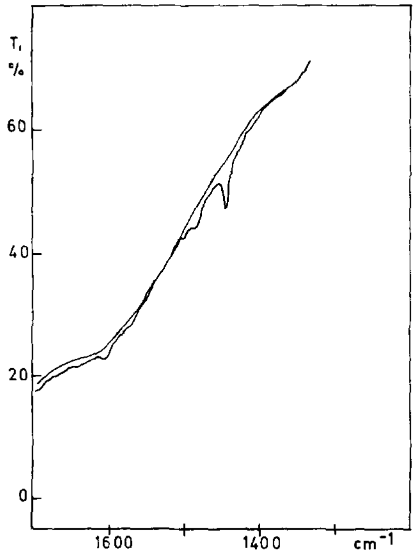

FIG. 4. Infrared spectrum of pyridine adsorbed on Fe–Mo–O catalyst at the temperature of the ir beam. The upper curve is the spectrum of the catalyst before pyridine adsorption, and the lower curve is the spectrum after pyridine adsorption and after evacuation of the gas phase.

presence of gaseous oxygen might be explained by the effect of evolved and probably partially adsorbed water. A similar effect on Bi-Mo catalysts was described (*7*) by the relation $2OH' \rightleftharpoons H_2O + \square + O''$. A competitive adsorption of water and methanol has already been described (*2, 6, 8*). The role of anion vacancies in the oxidation of NH_3 on Fe_2O_3 has been demonstrated by Pernicone *et al.* with the aid of ir spectra (*9, 10*).

Pyridine on MC

An increasing poisoning of MC in methanol oxidation with increasing amounts of pyridine was demonstrated in Fig. 3. This fact together with the previously described similarity in adsorbed amounts of irreversibly bonded pyridine and methanol and their similar heats of adsorption might be explained by the same type of bonding of methanol and pyridine on the surface of MC. From ir spectra (Fig. 4) of pyridine adsorbed on MC, a conclusion might be drawn about a coordination of pyridine to the cations of this catalyst. This conclusion follows from the region of ring vibrations (*11–13*) and from the following two facts: No bands at 1540 cm^{-1} were found which would indicate a donation of protons from the surface to the adsorbate with the production of a pyridinium ion (*11–13*), and no band of OH group affected by the hydrogen-bridge type bonding in the region of 3200 cm^{-1} was observed (*14*).

The very low temperature of the deep oxidation of pyridine on MC, dehydrated in vacuo at 400°C, is worth noting. According to this fact MC is one of the catalysts which can act as an excellent selective catalyst in one reaction as well as a good catalyst for deep oxidation in another reaction. Such an effect cannot be explained only by the role of the mobility of the lattice oxygen of the catalyst, as sometimes proposed (*15*).

Comparison of MoO_3, Fe_2O_3, and MC in the Oxidation of Methanol

The oxidation of small amounts of methanol (and formaldehyde in some cases) was carried out in the same way on MoO_3, Fe_2O_3, and MC. By the analysis of the gaseous products, it was shown that

(i) On MoO_3 at 320°C (without oxygen in the gas phase), the first dose of methanol produced mainly formaldehyde and water. Formaldehyde does not react with the pure surface of MoO_3.

(ii) With a further dose of methanol mainly CO, CO_2, and H_2 are produced. On this sample formaldehyde is oxidized, too.

(iii) On Fe_2O_3 at 220°C without oxygen in the gas phase, mainly CO, CO_2, and H_2 are produced during the oxidation of methanol as well as formaldehyde. This composition of the gaseous products is the same with several doses of methanol. During the oxidation of methanol and formaldehyde with oxygen in the gaseous phase CO_2, CO, and H_2O are produced.

(iv) On MC at 100°C without oxygen in the gas phase formaldehyde and water are produced. This composition of the product does not change with several doses.

According to these facts it seems reasonable to suppose that the mechanism of methanol oxidation is the same on MC and on MoO_3 in its unreduced state. The main difference is the substantially lower temperature of methanol oxidation on MC compared with MoO_3. In both cases water formed with the lattice oxygen is released.

In connection with the conclusion about the coordination bond of pyridine and also most probably of methanol with MC, we further suppose that the selective oxidation of methanol is caused by Mo^{6+} ions. An alcoholate bonding might be formed. If a similar complex is formed on Fe_2O_3, it is very unstable, because we have observed mainly products of complete oxidation and decomposition.

We complete our earlier views (*2*) on the prevailing role of Fe^{3+} ions in a selective mixed catalyst for methanol oxidation by the suggestion that ions of Fe hinder the reduction of Mo^{6+} cations and increase the lability of lattice oxygen available for the oxidation process.

The prevailing role of the Mo^{6+} cation in methanol oxidation is also assumed by other workers (*5–16*). These authors found the same kinetic data, activation energy and number of Lewis' acid sites for MC and MoO_3. According to their opinion, Fe^{3+} ions increase the number of anion vacancies (identical with Lewis acid sites) on which methanol is bound, and simultaneously facilitate the desorption of the products.

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