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Studies on Chromium-Molybdenum Oxide Catalyst by Temperature Programmed Desorption Method

Formaldehyde is manufactured by partial oxidation or dehydrogenation of methanol. The mixed oxide catalysts including molybdena have been mainly employed in the manufacture of formaldehyde by methanol oxidation. The partial oxidation method is carried out by using a lean mixture of methanol and air. Many papers have been published on the mechanism and kinetics of methanol oxidation over mixed oxide catalysts, especially iron–molybdenum oxide mixture (*1–4*). The mechanism of methanol oxidation on these oxide catalysts have been reported to involve a surface redox process.

Previously we have reported that chromia–molybdena mixed catalyst is effective for methanol oxidation to formaldehyde and investigated the structure of this catalyst (*5, 6*). However, it was not clear whether the mechanism of methanol oxidation over chromia–molybdena catalyst is similar to that over iron–molybdenum oxide catalyst or not. In the present work, the method of temperature programmed desorption (TPD) as devised by Amenomiya and Cvetanovic (*7*) was applied to the investigation of surface of chromia–molybdena catalyst. Desorption of methanol, water or oxygen from the catalyst and from a slightly reduced sample have been studied in an attempt to obtain information on the catalyst surface. Furthermore, TPD of methanol in helium or air flow has been compared in order to elucidate the mechanism of methanol oxidation over Chromia–molybdena catalyst.

EXPERIMENTAL METHODS

In the present work, helium or air was employed as carrier gas for TPD. Helium from the cylinder was passed through charcoal cooled with liquid nitrogen to remove traces of water. Air from a cylinder was dried by passing it through charcoal cooled with dry ice and acetone. Conven- ventional thermal conductivity cells were employed as the detector. The temperature of the catalyst bed was raised at a uniform rate by the use of a programming controller.

Catalyst, $(MoO_3)_{10}(Cr_2O_3)$, (abbreviated MC) was prepared from molybdic acid and chromium hydroxide as previously described (*5*). Before use, the catalyst was evacuated at 250°C for 2 hr. On the other hand, a slightly reduced sample [abbreviated MC(R)] was prepared as follows: (a) the catalyst was pretreated by the same method described above; (b) the catalyst was exposed to methanol vapor (30 mm Hg) at 200°C for 30 min; (c) the sample was evacuated at 250°C for 30 min and the temperature of sample was lowered to room temperature. Following this pretreatment, CH_3OH, H_2O, or O_2 were adsorbed. After adsorption equilibrium was reached at the room temperature, the sample was evacuated for 20 min at the same temperature and then exposed to the carrier gas flow.

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When the base line of recorder attached to the detector was found to be unchanging, TPD was started.

RESULTS AND DISCUSSION

The TPD chromatogram from a typical experiment using MC or MC(R) is shown in Fig. 1. When the desorption of O_2 from MC and MC(R), curves a and b, are compared, the first peak formed was similar and the second peak was quite different. The amount of O_2 desorbed from MC was small in the vicinity of 310°C and a larger amount of O_2 was detected by the desorption from MC(R) at a lower temperature, 290°C. It may not be possible to disregard the likely prospect that a part of vacancies were reoxidized in the process of TPD. However, curve b suggests that the amount of oxygen related to the reoxidation required a very small part of the adsorbed oxygen. It was concluded that O_2 from MC in the second peak was formed from lattice oxygen similar to the desorbed O_2 observed from MoO_3 and that O_2 from MC(R) was the result of desorption of chemisorbed oxygen on the reduced surface. That is to say, the second peak found on MC(R) is made up by the desorption of O_2 chemisorbed on the vacancy which was introduced by the reduction. This fact indicates that a new site which is able to adsorb O_2 had been induced by reduction. Perhaps this site is an oxygen ion vacancy in the surface. As described in our previous report (*8*), MC is more reducible than MoO_3 because of strain introduced into the lattice of MoO_3 by the presence of chromia, i.e., lattice

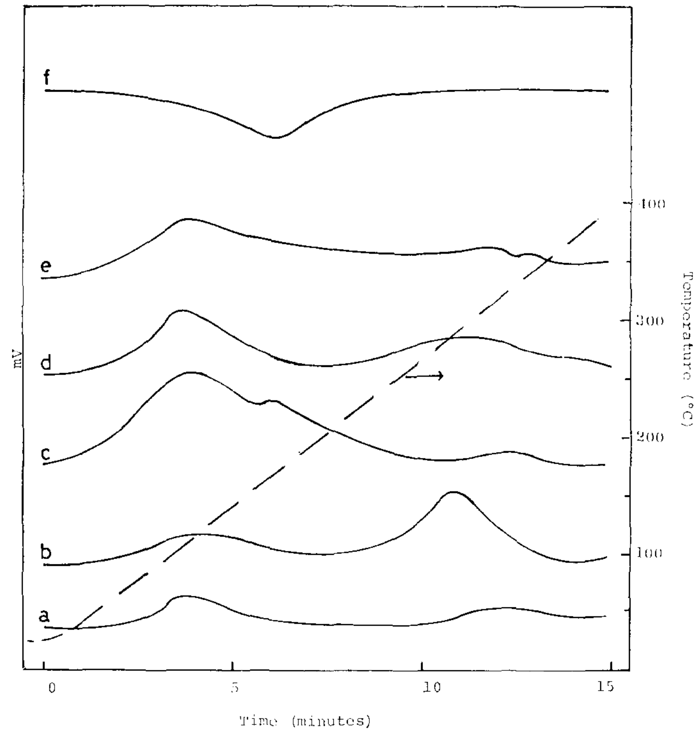

FIG. 1. TPD chromatograms from MC or MC(R). (a) O_2; (c, f) CH_3OH; and (e) H_2O were adsorbed on MC before TPD under 50 mm Hg at a room temperature. (b) O_2; and (d) CH_3OH were adsorbed on MC(R) before TPD under 50 mm Hg at a room temperature. Carrier gas: (a–e) helium; (f) air.

oxygen reactivity of MC is greater than that of MoO_3.

When H_2O was introduced onto MC, the peak maximum appeared at 110°C and the desorption curve decreased slowly (curve e). It is inferred that a part of the H_2O adsorbed on surface oxygen by hydrogen bonding, therefore, desorbing such H_2O slowly introduced the tail of the peak.

The TPD chromatogram of CH_3OH from MC, curve c, had the first peak at 100°C and the desorbed material was CH_3OH. A definite second peak at low temperature was observed; its maximum appeared at 160°C and the desorbed materials were CH_3OH and CH_2O. The amount of desorbed CH_2O in this peak was larger than that of CH_3OH. This peak, due to the desorbed CH_2O from MoO_3, did not show a maximum; it could only be detected by the presence of CH_2O in the tail of the first peak. The third peak at 340°C was made up by the desorption of ($CO + CO_2$) formed from CH_3OH and it was usually observed to be small. In similar experiments with MC(R) instead of MC, only two peaks were observed (curve d). The first peak at 100°C was CH_3OH and the second peak at 300°C consisted of ($CO + CO_2$). The desorption of ($CO + CO_2$) from MC(R) occurred at lower temperature than that from MC. There were three peaks on the TPD curve from MC. It is assumed that these peaks have a one to one correspondence to weak, medium and strong adsorption of CH_3OH. The weakly adsorbed CH_3OH (CH_3OHwa) is desorbed without change at 100°C, the medium adsorbed CH_3OH (CH_3OHma) is desorbed with conversion to CH_2O at 160°C, and CO and CO_2 from the decomposition of strongly adsorbed CH_3OH (CH_3OHsa) is desorbed at 340°C. The experimental results indicated that the amount of CH_3OHma was smaller on MoO_3 than MC. This fact suggests there are three types of surface oxygen on MC. It is reasonable to assume that the situation of adsorption of CH_3OH was determined by the nature of surface oxygen. Thus, the surface oxygen atoms of the catalyst were classified into three types (conveniently named types 1, 2, and 3). That is to say, CH_3OH adsorbed weakly on oxygen atoms belonged to type 1, with intermediate strength on oxygen atoms belonged to type 2, and strongly on oxygen atoms belonged to type 3. It is presumed that oxygen atoms in type 1 are the most stable and that oxygen atoms in the other two classifications are related to the catalytic activity for oxidation. When CH_3OH was desorbed with increasing temperature, the oxygen in type 2 should react with CH_3OH in the process, and then CH_2O is produced. The oxygen of type 3 should produce CO and CO_2 from CH_2OH in the course of TPD. The location corresponding to the surface oxygen in types 2 or 3 is defined as site 1 or 2 for oxidation of methanol. The results of TPD showed that site 1 was more prominent on the surface of MC than MoO_3. However, our experiments on the reduced sample MC(R), did not indicate the existence of site 1. When MC(R) was reoxidized with air at 350°C, the second peak reappeared on the TPD curve of CH_3OH desorption from MC(R). It seems to be reasonable to assume that most of the oxygen atoms of type 2 on MC were lost upon reduction. On the other hand, the desorbed amount of CH_3OH converted to ($CO + CO_2$) from MC(R) at 300°C was more than that found from MC. Apparently there are more sites of type 3 on the surface of MC(R) than on MC. The temperature at which the peak of ($CO + CO_2$) appeared from MC(R) was lower than that from MC. These facts suggest that the site from which ($CO + CO_2$) desorbs from MC(R) is not the same as site 2. It is postulated that this site on MC(R) was introduced by the reduction. Perhaps, the oxygen of site 2 is lost in the reduction and another unstable oxygen is produced neighboring the vacancies formed. Similarly, the unstable oxygen may be also produced by the reduction of site 1. Figure 1 shows that most of such unstable oxygen atoms produced by reduction are similar in nature to site 2 (type 3) and a slight part of such oxygen atoms should be analogous with site 1. MC is more active than MoO_3 for the methanol oxidation and it is ascertained that there are more sites of type 2 on the surface of MC than on MoO_3.

The kinetics of methanol oxidation over oxide catalysts of iron and molybdenum have been reported by Boreskov *et al.* (*1*) and Jiru *et al.* (*2*). Boreskov *et al.* reported the rate to be independent of oxygen pressure and first order in methanol and Jiru *et al.* indicated a rate equation based on the redox mechanism. Mann and Hahn (*4*) deduced a rate expression assuming a steady state involving a two stage irreversible redox process over MnO_2–MoO_3 catalyst. Furthermore, Novakova *et al.* (*3*) suggested a change in the oxidation mechanism due to the lowering of the vacancy of Mo^{6+} to Mo^{4+}. Thus, their reports have shown that the catalysis of metal oxide molybdena mixture in methanol oxidation is based on the redox mechanism. If molybdena catalyst promoted with another oxide and used for methanol oxidation does involve redox of its surface as the above-mentioned reports indicate, MC should involve a similar mechanism and the two sites on MC detected by TPD are assigned to active centers for oxidation.

Curve *f* is typical of TPD curves obtained by using air as a carrier gas and may be compared with He TPD. CH_3OH was used as the absorbate in these experiments. The TPD chromatogram of CH_3OH purged with He was shown in curve a, however, curve f had only one broad peak at a temperature in the neighborhood of 150°C. This contained a large amount of CH_2O and small amount of CH_3OH, CO_2, and CO; the temperature of desorption was approximately equal to the second peak of curve a. It was thought that the desorbed materials were formed by oxidizing a large portion of the adsorbed CH_3OH with O_2 from the air stream. However, the form of the desorbed peak was indicative of amount of desorbed CH_2O from site 1, because the temperature of the maximum in air flow was approximately the same as that of the desorbed peak of CH_2O from site 1 in He flow. Consequently, it is concluded that methanol oxidation over MC is accomplished by both oxygen on the surface and O_2 in the gas phase. If methanol oxidation were to be carried out in an air rich mixture, the mechanism of reaction is probably similar to the situation that ensues with TPD with air.

On the basis of above-mentioned results, it is concluded that methanol oxidation under air rich conditions is accomplished by the reaction between surface oxygen (lattice oxygen) and adsorbed methanol and/or oxygen in air and adsorbed methanol and, moreover, there are two active centers on MC.

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