CHEMISTRY LETTERS, pp. 1295-1298, 1975. Published by the Chemical Society of Japan

MEASUREMENT OF Mo^{+5} SPECTRA DURING METHANOL OXIDATION

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Oxidation of methanol into formaldehyde on SnO_2-MoO_3 catalyst proceeds according to the redox mechanism of $Mo^{+5} \rightleftarrows Mo^{+4}$.

ESR spectra of Mo^{+5} offer us some informations concerning activities of mixed and supported molybdenum oxide catalysts.1-6) It has already been reported in the cases of various reactions that the catalytic activities were correlated with the signal intensity of Mo^{+5}. However, the catalytic action of Mo^{+5} is not fully understood, and it is not confirmed that these observed Mo^{+5} sites are significantly available for the reaction. The authors will report here the behaviors of Mo^{+5} on SnO_2-MoO_3 under the reaction conditions of oxidation of methanol.

SnO_2-MoO_3 system catalysts were prepared by mixing of tin hydroxide gel with ammonium molybdate solution, drying, and then followed by calcination at 500°C for 3 hrs in the air stream. ESR measurements have been done in the X-band with a JEOL spectrometer (JES-ME-1X). An ESR in situ cell was made of a 3 mm i.d. Pyrex outer tube and a 1 mm o.d. inner tube, and set in a cavity with a temperature variant equipment.4) Because the width of Mo^{+5} spectrum was not varied, the intensity was expressed in terms of the relative peak-peak height of the resonance line.

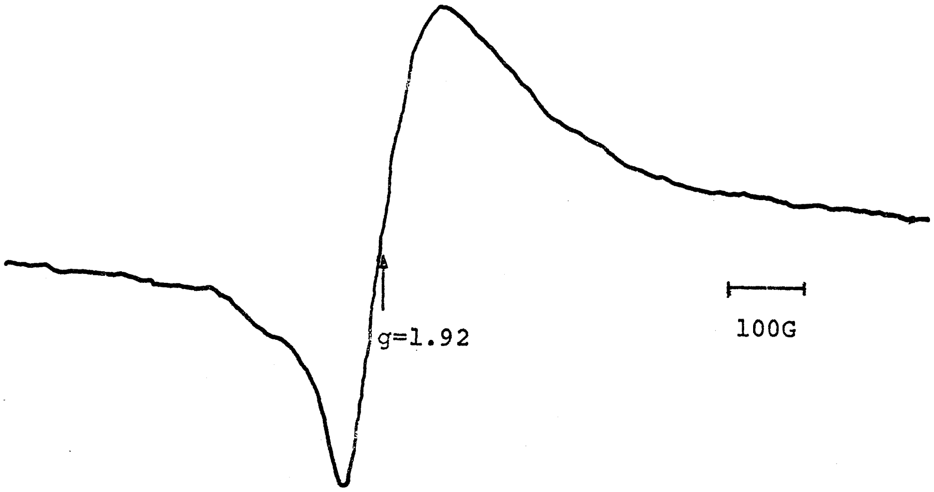

Fig. 1. ESR spectrum of Mo^{+5} on SnO_2-MoO_3.

The SnO_2-MoO_3 system catalysts had higher activities in the methanol oxidation than Fe_2O_3-MoO_3(1/1), TiO_2-MoO_3(1/1), and Co_3O_4-MoO_3(1/1) catalysts, as far as our experiments are concerned. On SnO_2 catalyst, methanol was only converted into carbon oxides. On MoO_3 catalyst, methanol was selectively oxidized into formaldehyde over 350°C. On the other hand, the mixed SnO_2-MoO_3 catalysts possessed selective activities over 180°C. Therefore, it is clear that the activity of SnO_2-MoO_3 system catalyst is substantially based on the action of molybdenum oxide.

An anisotropic signal was observed around $g = 1.92$ in the ESR spectrum of SnO_2-MoO_3 catalysts, as shown in Fig. 1. This signal was identified as paramagnetic Mo^{+5}. Furthermore, a qualitative relation was found between the relative intensity of Mo^{+5} and the catalytic activity over SnO_2-MoO_3 with different components.

Then, the reactivity of Mo^{+5} has been examined using the in situ cell. The ESR signal of Mo^{+5} was observed in exactly the same conditions as the continuous-flow reaction, in reaction temperature, catalyst weight, total flow rate, and partial pressures. As shown in Fig. 2, the Mo^{+5} signal showed the greatest intensity in the methanol-free condition, and it decreased as the Pm/Po increased.

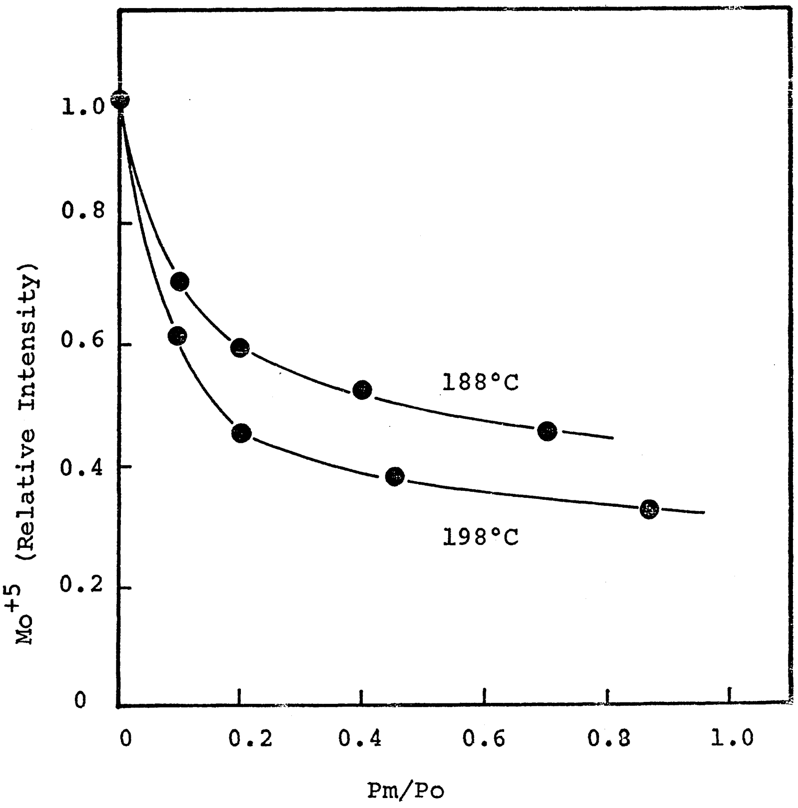

Fig. 2. Variation in relative intensity of Mo^{+5} with Pm (partial pressure of methanol) / Po (partial pressure of oxygen) on SnO_2-MoO_3(3/7)[9] using in situ cell.

No hysteresis of the intensity of Mo^{+5} spectrum was observed throughout this experiment. It is therefore considered that the observed Mo^{+5} site was reduced to Mo^{+4}, but Mo^{+6} was not reduced to Mo^{+5}. In other words, it can be said that the oxidation of methanol over SnO_2-MoO_3 system catalysts proceeds according to the redox mechanism of $Mo^{+5} \rightleftarrows Mo^{+4}$.

Jiru et al. have previously reported that oxidation of methanol over Fe_2O_3-MoO_3 proceeds in the oxidation-reduction mechanism,[7, 8] viz.,

$$CH_3OH + (O) \xrightarrow{k_1} HCHO + H_2O + (\ )$$

$$(\ ) + 1/2\ O_2 \xrightarrow{k_2} (O)$$

where (O) and ( ) denote active site and reduced site, respectively. The coverage of active site (θ) and the rate of methanol oxidation (r) can be described in the following.

$$\theta = \frac{k_2 Po^{1/2}}{k_1 Pm + k_2 Po^{1/2}} \qquad (1)$$

$$\frac{1}{r} = \frac{1}{k_1 Pm} + \frac{1}{k_2 Po^{1/2}} \qquad (2)$$

The validity of this kinetic equation (2) was confirmed by plotting 1/r against 1/Pm or $1/Po^{1/2}$. The rate constants, k_1 and k_2, were determined from

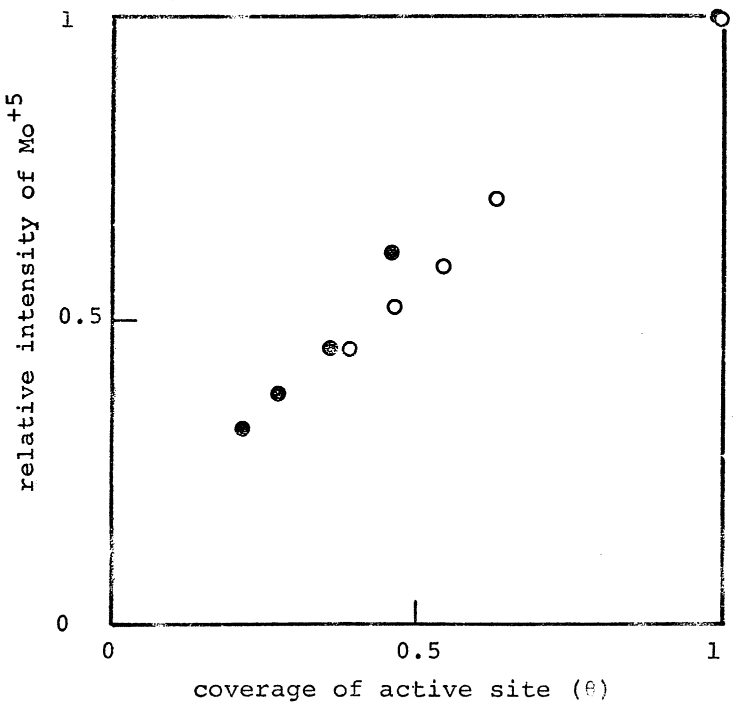

Fig. 3. Relationship between coverage of active site (θ) derived from kinetic measurement and relative intensity of Mo^{+5} on SnO_2-MoO_3(3/7) at 198°C (●) and 188°C (○).

slope and intercept, and the coverage θ thus obtained is plotted against the relative intensity of Mo^{+5} as observed by in situ ESR measurement. The quantitative consistency between θ and Mo^{+5} are clearly observed. It is therefore reasonable that the observed Mo^{+5} is the active site for methanol oxidation, and the reaction proceeds according to the redox mechanism of $Mo^{+5} \rightleftharpoons Mo^{+4}$.

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(9) Represents the atomic ratio (Sn/Mo).

(Received October 15, 1975)