CHEMISTRY LETTERS, pp.305-308, 1972. Published by the Chemical Society of Japan

VAPOUR PHASE OXIDATION OF BUTADIENE OVER SUPPORTED MOLYBDENA CATALYSTS

Masamichi AKIMOTO and Etsuro ECHIGOYA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo

Reactivity of Mo^{5+} with oxygen which is formed in supported molybdena catalysts was investigated by ESR spectroscopy and discussed as a carrier effect with reference to the selectivity in maleic anhydride formation during vapour phase oxidation of butadiene. Mo^{5+} formed on SiO_2 and TiO_2, showed good selectivity and appeared to be the active site for the production of maleic anhydride.

Catalytic oxidation of butadiene was carried out using a conventional flow system at a pressure of one atmosphere. Gaseous products were analysed by gas chromatography and maleic acid formed was absorbed into water followed by titration with aqueous sodium hydroxide. Catalysts were prepared by mixing either alumina sol, silica sol, titania sol or magnesium hydroxide with an aqueous solution of ammonium molybdate and calcination of dried mass in air current at 540°C for 4 hours. The amount of Mo^{5+} was determined by ESR spectroscopy using Mn^{2+} as internal standard.

Fig. 1 shows the result of vapour phase oxidation of butadiene over MoO_3-TiO_2 catalysts and also the relative amount of Mo^{5+} modified by surface area formed in the catalysts by evacuation at 365°C for 30 minutes. Catalytic activity was found to be enhanced with increase in the amount of Mo^{5+} formed on the catalyst surface. With the exception of MoO_3-Al_2O_3, the other catalysts showed similar results. Therefore, Mo^{5+} appears to be the active site in the oxidation of butadiene. Based on the selectivity to maleic anhydride formation, these carriers can be broadly divided into (a) MgO, Al_2O_3 selectivity 10-12% and (b) SiO_2, TiO_2 selectivity 40-42%. As strong solid acids are formed on the surface of these catalysts during prepation, it is possible that their presence may affect the selectivity of reaction.

Poisoning of the catalysts with pyridine during the oxidation resulted in a decrease of activity and conversion of butadiene, but the selectivity remained unchanged. Hence it can be concluded that the selectivity is independent of the presence of strong solid acids but may be attributed to the nature of the Mo^{5+} formed in the catalyst.

Fig. 2 shows the reactivity of Mo^{5+} with oxygen which is formed in the various catalysts by evacuation at 365°C for 30 minutes. It is of interest to note that unlike the Mo^{5+} in MoO_3-SiO_2 catalyst, the Mo^{5+} in MoO_3-MgO and MoO_3-Al_2O_3 catalyst can not be oxidized even at 450°C. Thus, there appears two kinds of Mo^{5+}, Mo^{5+}(A) and Mo^{5+}(B), in MoO_3-TiO_2 catalyst. Mo^{5+}(B), presumably formed at the sites where lattice oxygen is lost, appears to be easily oxidized and reduced. The higher activity and selectivity of Mo^{5+}(B) than of Mo^{5+}(A) can be attributed to the different nature of

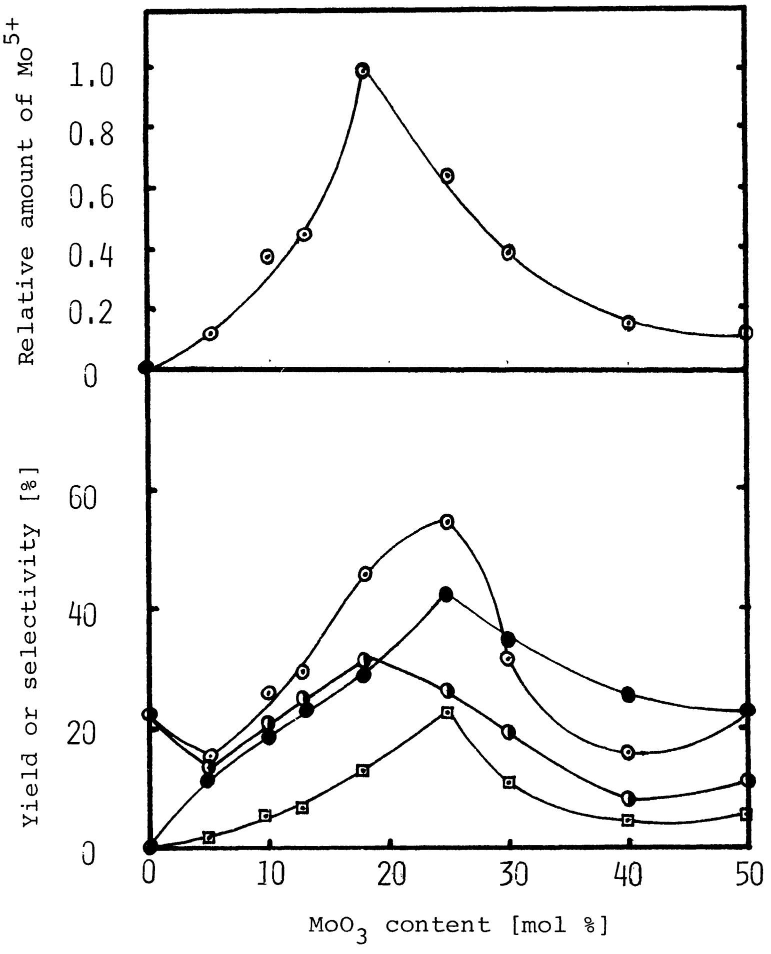
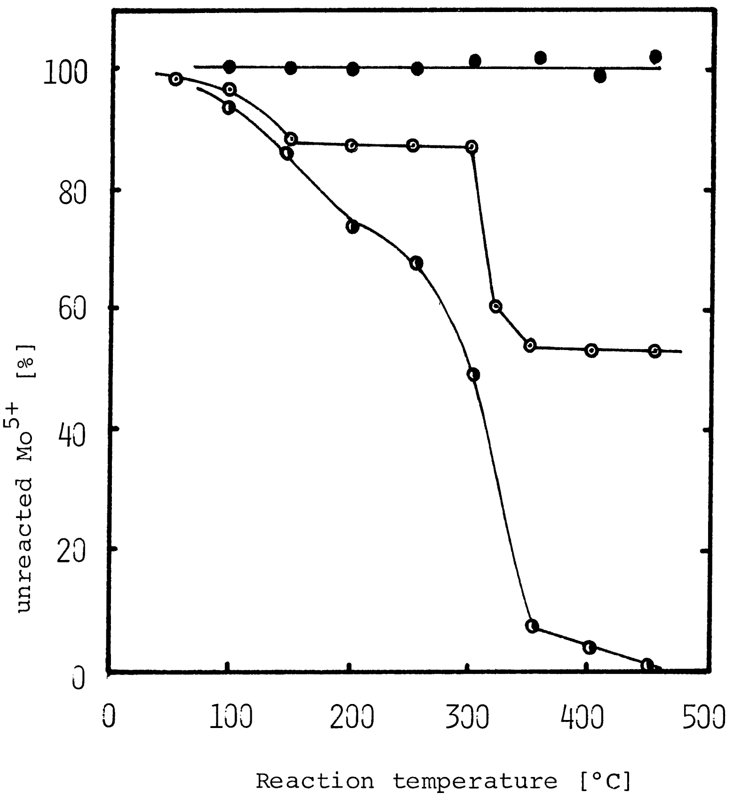


Fig. 1 Correlation between relative amount of Mo^{5+} and activity of MoO_3-TiO_2 catalyst in vapour phase oxidation of butadiene.
reaction temp. : 380°C, butadiene concentration: 1.5 vol % in air,
contact time: W/F=0.51 [g-cat.hr/mol]
◎ : conversion of butadiene,
◐ : yield of (CO_2+CO),
▣ : yield of maleic anhydride,
● : selectivity to maleic anhydride.



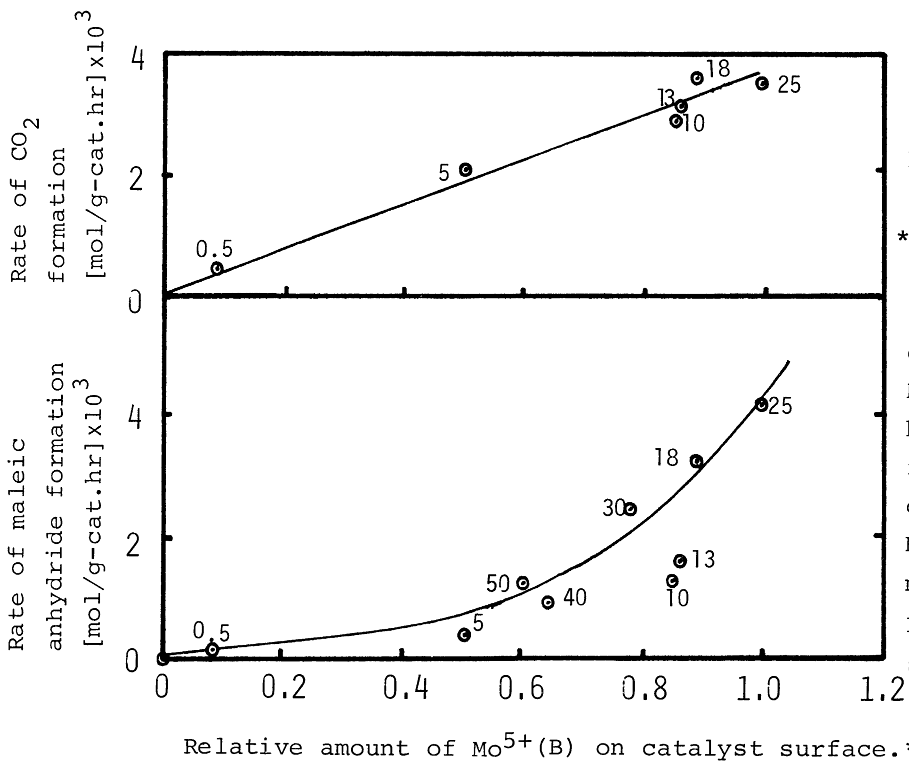
catalyst weight: 0.100 (g),
reaction time: 30 minutes,
pressure of oxygen: 20 mm Hg,

⊙ : Mo/Ti=1/3

◐ : Mo/Si=1/9

● : Mo/Al=1/9, Mo/Mg=1/9

Fig. 2 Reactivity of oxygen with Mo^{5+} formed in catalysts.



reaction temp.: 365°C, butadiene concentration: 1.5 vol % in air,

*The amount of Mo^{5+} on the surface of catalyst equals to the decreased amount of Mo^{5+} when Mo^{5+} formed by evacuation at 365°C for 30 minutes is oxidized by oxygen (20 mm Hg) at 225°C for 30 minutes.

Each number in Fig. 3 shows MoO_3 content [mol %].

Fig. 3 Rate of CO_2 and maleic anhydride formation vs relative amount of Mo^{5+} on catalyst surface.

the adsorbed oxygen species.

The relative concentration of Mo^{5+}(B) per gram MoO_3 formed by evacuation at 365°C for 30 minutes was as follows;

MoO_3-TiO_2 > MoO_3-ZnO > MoO_3-SiO_2 (Mo ≤ 10 atom %)

It is interesting to note that the amount and quality of Mo^{5+} are controlled by the nature of the support. The results showed that titania anatase is the best carrier for the production of Mo^{5+}(B). A detailed investigation of MoO_3-TiO_2 catalyst appears as logical choice. X-ray revealed that MoO_3 can dissolve in anatase type titania to the extent of about 30 atom percent, to form solid solution. Active sites, which are responsible for the production of CO_2 and maleic anhydride, were shown by kinetic measurement to be unchanged within the maximum solubility, and the reaction seems to follow the Langmuir-Hinshelwood mechanism instead of the redox type pathway.

Correlations between the amount of Mo^{5+}(B) on the surface of the MoO_3-TiO_2 catalyst and the rate of CO_2 and maleic acid formation are shown in Fig. 3. The results showed a linear relationship between the CO_2 formation and the amount of Mo^{5+}(B) on the catalyst surface, thus indicating that at the rate controlling step oxygen absorbed on1) Mo^{5+}(B) reacted with butadiene adsorbed on Ti^{4+} to form CO_2. Fig. 3 also shows that maleic anhydride is produced by the reaction of oxygen and butadiene2) adsorbed on Mo^{5+}(B).

These results were also supported by temperature-programmed desorption studies and regularity3) of CO_2 formation over oxides of group VA-TiO_2 and group VIB-TiO_2 catalysts. The above results clearly demonstrate that selectivity to maleic anhydride formation is affected by the nature of adsorbed oxygen and butadiene species.

REFERENCES

1) Y. Ishii and I. Matsuura, Nippon Kagaku Zasshi, 89, No. 6 533 (1968)
2) G. K. Boreskov, V. A. Dzisko, V. H. Emelyanova, Y. I. Pecherskaya and V. B. Kazanskii, Dokl. Akad. Nauk SSSR, 150, 829 (1963)
3) M. Akimoto and E. Echigoya, 24th annual meeting of Chemical Society of Japan, Oosaka (1971)

(Received February 9, 1972)