CHEMISTRY LETTERS, pp. 115-118, 1982.

THE ACTIVE SITE OF ETHYLENE POLYMERIZATION ON MoY ZEOLITE DERIVED FROM $Mo(CO)_6/HY$

Seitaro NAMBA, Takayuki KOMATSU, and Tatsuaki YASHIMA
Department of Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The catalytic activity of MoY zeolite for ethylene polymerization and the apparent oxidation number of molybdenum changed with the activation temperature of HY zeolite and the decomposition temperature of $Mo(CO)_6/HY$. At 573K of the decomposition temperature, the maximum activity was observed when the apparent oxidation number was about 1.

A synthetic catalyst with a well-defined surface is very suitable for obtaining clear information on the active site. Well-defined molybdenum catalysts supported on silica and alumina have been reported by Yermakov et al.$^{1)}$ and Iwasawa et al..$^{2)}$ They have adjusted the oxidation number of molybdenum to 2, 4 or 6 and proposed the active sites of olefin hydrogenation and methathesis, etc. Bowman et el. have reported that the supported molybdenum, whose apparent oxidation number is less than 1, can be prepared by using $Mo(CO)_6$ and dehydroxylated alumina.$^{3)}$ Gallezot et al.$^{4)}$ have reported that MoY zeolite can be prepared by using $Mo(CO)_6$ and HY zeolite, one $Mo(CO)_6$ molecule can be introduced per supercage of Y zeolite at most, and the complete decomposition of $Mo(CO)_6$ and the oxidation of molybdenum by protons on HY take place by heating $Mo(CO)_6$ adsorbed on HY above 573K as following equation.

$$Mo(CO)_6 + n(O_z-H) \longrightarrow Mo^{n+}(O_z^-)_n + (n/2)H_2 \qquad O_z\text{: framework oxygen}$$

In this paper, we expected to adjust the oxidation state of molybdenum in MoY zeolite and to clarify the active site of MoY zeolite for ethylene polymerization.

A certain amount of HY zeolite set in a tube was heated for 2h in vacuo at various temperatures. A desirable amount of $Mo(CO)_6$ was added to the activated HY zeolite at room temperature in a nitrogen flow. The HY and $Mo(CO)_6$ were evacuated for a little while, heated at 333K and allowed to stand for 15h to complete the loading of $Mo(CO)_6$ on HY. The $Mo(CO)_6$ adsorbed on HY was decomposed in vacuo at various temperatures. The MoY zeolite thus prepared was used as a catalyst. The polymerization of ethylene was carried out in a static system (dead volume; 110ml). The extent of the reaction was monitored by measuring the pressure decrease in the system. The initial pressure of ethylene and the reaction temperature were 36kPa and 333K, respectively. The apparent oxidation number (AON) of the molybdenum in MoY zeolite was assayed by oxygen titration. When the temperature of the freshly prepared catalyst was brought to 573K in vacuo, a known amount of oxygen was introduced into the system. The temperature was raised to 773K in 0.5h and held for 1h. The AON of the molybdenum was calculated from the amount of oxygen consumed assuming that Mo(VI) was the final product.

Fig. 1 shows the effects of the activation temperature of HY zeolite and the decomposition temperature of $Mo(CO)_6$/HY on AON. The lower activation temperature and the higher decomposition temperature provided the higher AON. The higher activation temperature of HY zeolite should correspond to the lower concentration of OH group on the surface. Therefore, the oxidation of Mo(0) with surface OH group would become more difficult at the lower concentration. While, this oxidation would become easier at the higher decomposition temperature, probably because of the higher mobility of surface OH group as a water molecule. Similar phenomena in $Mo(CO)_6/Al_2O_3$ have been

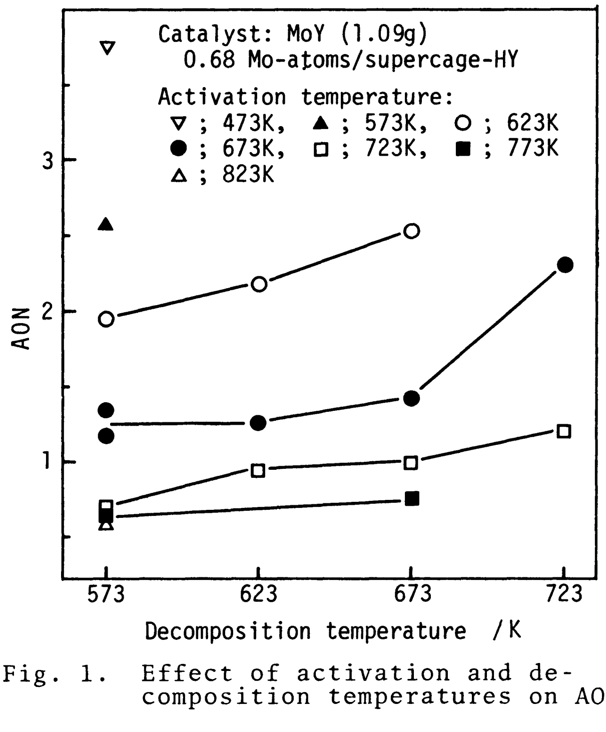

Fig. 1. Effect of activation and decomposition temperatures on AON

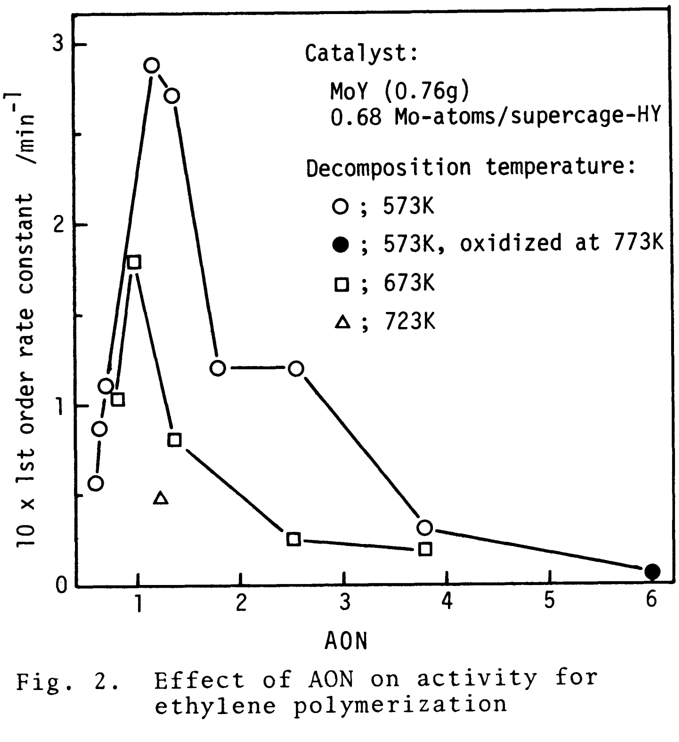

Fig. 2. Effect of AON on activity for ethylene polymerization

reported by Bowman et al..[3] As shown in Fig. 1, the fine adjustment of the AON is possible in the range of AON=0.6-2.6 by changing the activation temperature of HY zeolite and the decomposition temperature of $Mo(CO)_6/HY$. However, it is suggested that the oxidation state of molybdenum in MoY zeolite is not uniform, because the AON of molybdenum is not always integral, although the oxidation number of each individual molybdenum should be integral.

Fig. 2 shows the effect of the AON on the activity of MoY zeolite for ethylene polymerlyzation. The activity was very low when the AON was more than 3.7. While, the maximum activity was observed around AON=1. The data obtained at 573K of the decomposition temperature did not coincide with those obtained at 673K or 723K. Therefore, the catalytic activity of MoY zeolite are not governed solely by the AON. The dispersion of molybdenum and the distribution of the oxidation state of molybdenum in MoY zeolite may also affect the activity.

An information on the dispersion of molybdenum, whose AON is about 1, is shown in Table 1. The apparent dispersion was calculated from the amount of oxygen uptake at 298K for 1min assuming that the stoichiometry was O/Mo=1. At 573K of the decomposition temperature the apparent dispersion thus obtained was about 100%. However, the higher decomposition temperature provided the lower apparent dispersion, although the molybdenum was thought to be atomically dispersed before the decomposition of $Mo(CO)_6/HY$.[4]

Hashimoto et al. have reported that the active site for ethylene polymerization is a kind of Mo(V).[5] On the other hand, the AON of the most active MoY zeolite is about 1. Our ESR measurements showed that the fraction of ESR-sensitive Mo(V) in the most active MoY zeolite was less than 0.2% and that in less active MoY zeolite, whose AON was 3.8, was about 0.5%. The first order rate constant per molybdenum atom

Table 1. The apparent dispersion of molybdenum in MoY zeolite calculated from the amount of oxygen uptake

Activation temperature /K	Decomposition temperature /K	AON	Apparent dispersion /%[a]
673	573	1.16	102
673	673	1.42	63
773	773	0.88	24

[a] Calculated from the amount of oxygen uptake at 298K assuming O/Mo=1

measured at 313K on the most active MoY zeolite is more than that on the MoO_3/Al_2O_3 catalyst reduced with hydrogen at 823K[6] by a factor of about 25. Moreover, Soga et al. have reported that when the pore diameter of the support is less than 5nm, the less pore diameter provides the lower activity in the propene polymerization on Ti(III)/SiO_2.[7] Rommelfaenger and Howe have reported that the zeolite is able to stabilize low oxidation state molybdenum ions such as Mo(I).[8] From the facts mentioned above, the most active molybdenum in MoY zeolite would be a low oxidation state molybdenum, i.e. Mo(I), Mo(II), Mo(III), or a combination of one of them with Mo(0), etc..

References

1) Yu.I. Yermakov and B.N. Kuznetov, Prep. 2nd Japan-Soviet Catalysis Seminar (Tokyo, 1973), p.65.

2) Y. Iwasawa, Y. Nakano, and S. Ogasawara, J.C.S. Faraday I, 74, 2968 (1978): Y. Iwasawa and S. Ogasawara, ibid., 75, 1465 (1979): Y. Iwasawa, M. Yamagashi, and S. Ogasawara, Shokubai, 22, 313 (1980).

3) R.G. Bowman and R.L. Burwell, Jr., J. Catal., 63, 463 (1980).

4) P. Gallezot, G. Coudurier, M. Primet, and B. Imerik, "Molecular Sieves II," ACS Symp. Ser. 40, ed by J.R. Katzer, Amer. Chem. Soc., Washington D.C. (1977) p.144.

5) K. Hashimoto, S. Watanabe, and K. Tarama, Bull. Chem. Soc. Japan, 49, 12 (1976).

6) J. Engelhardt, J. Catal., 62, 243 (1980).

7) K. Soga, K. Izumi, M. Terano, and S. Ikeda, Makromol. Chem., 181, 657 (1980).

8) P. Rommelfaenger and R.F. Howe, J.C.S. Chem. Comm., 1979, 123.

(Received September 16, 1981)