PREPARATION AND CHARACTERIZATION OF Mo/Y-ZEOLITE AND ITS CATALYTIC ACTIVITY FOR PROPENE METATHESIS

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ABSTRACT

The adjustment of the oxidation state of molybdenum in Mo/HNa-Y zeolite and the properties of the catalytically active sites for propene metathesis were investigated.

Mo/HNa-Y zeolite was prepared by the adsorption of $Mo(CO)_6$ vapor on HNa-Y(proton exchange degree; 0 — 74 %) dehydrated at 473 — 873 K, followed by the decomposition of adsorbed $Mo(CO)_6$ at 573 K. We could control the average oxidation number (AON) of molybdenum in the range of 0 — +2 by changing the concentration of proton in Y zeolite.

The catalytic activity for propene metathesis increased with decreasing the AON of molybdenum on HNa-Y. The data of oxygen titration at 97 K and UV diffuse reflectance spectroscopy suggested that the dispersion of Mo species played the important role for the catalytic activity. From these results, it was concluded that the slightly aggregated Mo^0 species showed the highest catalytic activity for propene metathesis.

INTRODUCTION

There have been so many reports in the field of zeolite catalysis in recent years. The major part of them has been related to the solid acid catalysis. On the other hand, the transition metal cations can be supported in a variety of oxidation state on the zeolites by an ion exchange method. These transition metal cations have the high catalytic activities in some organic reactions [1]. We have reported the polymerization of ethene on CrY zeolite [2], the selective dimerization of ethene on NiY and RhY zeolites [3], and the carbonylation of methanol to produce acetic acid on RhY zeolite [4].

Molybdenum oxides and sulfides have been used in chemical industries as catalysts for the hydrodesulfurization of petroleum products, the oxidation, the polymerization and the metathesis of

alkenes. Most of these commercial catalysts are prepared by the impregnation method using oxide supports and ammonium molybdate aqueous solution.

Recently, well-defined molybdenum catalysts were prepared by Yermakov et al. [5] and Iwasawa et al. [6]. Both researchers prepared their catalysts by using $Mo(\pi\text{-}C_3H_5)_4$ and silica or alumina and adjusted the oxidation number of molybdenum to +2, +4 or +6. Bowman et al. [7] have reported that the low oxidation state molybdenum, whose average oxidation number is less than +1, can be prepared by using $Mo(CO)_6$ and highly dehydroxylated alumina.

MoY zeolite cannot be prepared by a conventional cation exchange process, because molybdenum species is not a cation but a molybdic anion as a stable state in aqueous solution. Lunsford et al. [8] have prepared MoY using $MoCl_5$ and HY by means of a solid-solid ion exchange method without solvent. They have reported that their MoY shows the catalytic activity for the oxidation of cyclohexene and that the oxidation number of molybdenum is +6. On the other hand, Gallezot et al. [9] have reported that Mo/HNa-Y zeolite can be prepared by the adsorption of $Mo(CO)_6$ on HNa-Y followed by the thermal decomposition of $Mo(CO)_6$ and the simultaneous oxidation of molybdenum by the protons of HNa-Y.

We have reported [10] that the oxidation state of molybdenum in MoY zeolite derived from $Mo(CO)_6$ and HNa-Y zeolite is changed by the decomposition temperature of $Mo(CO)_6$ and the pretreatment temperature of HNa-Y. Namely, the average oxidation number (AON) of molybdenum increased with increasing the decomposition temperature or with decreasing the pretreatment temperature. We could adjust the AON of molybdenum in the range from +0.6 to +3.8. It has been found that Mo/HNa-Y shows the very high catalytic activity for ethene polymerization at the AON of about +1. It has been pointed out that the dispersion of molybdenum is a very important factor on the catalytic activity.

In this paper, we present a control method of AON of molybdenum by changing the proton exchange degree of HNa-Y and discuss the oxidation states and the dispersion of molybdenum in Mo/HNa-Y catalyst for the propene metathesis.

EXPERIMENTAL

Catalysts preparation. Na-Y zeolites(Toyo Soda Ind. Co., Lot Y-30) were treated with 0.05 N NH_4Cl aqueous solution at room temperature to form NH_4Na-Y. After calcination at 743 K in air, H(x)Na-Y was obtained, where x is the percent degree of proton exchange.

A certain amount of HNa-Y powder set in a quartz tube was heated in vacuo at various temperatures to get dehydrated HNa-Y. The desired amount of $Mo(CO)_6$ was added to the dehydrated HNa-Y in nitrogen or argon atmosphere. After the nitrogen or argon gas was pumped out for 20 s, the tube was put in a thermostated oven at 333 K and allowed to stand for 15 h to adsorb $Mo(CO)_6$ on HNa-Y. Mo/HNa-Y was obtained by heating in vacuo at 573 K.

The content of sodium in HNa-Y and that of molybdenum in Mo/HNa-Y were analyzed by flame emission spectroscopy and atomic absorption spectroscopy, respectively.

Average oxidation number of molybdenum. The average oxidation number (AON) of molybdenum in Mo/HNa-Y after the decomposition of $Mo(CO)_6$ adsorbed on HNa-Y was determined by the O_2 titration method.

Mo/HNa-Y was exposed to oxygen which was introduced into the system at the rate of 20 Torr/min up to 200 Torr at room temperature. Then the sample was heated at 573 K for more than 30 min. The amount of O_2 consumed by the oxidation of molybdenum was measured volumetrically by subtracting the amount of physisorbed O_2. The AON of Mo was calculated by taking account of the observation that all of the Mo species were oxidized to Mo^{6+} [11].

Metathesis of propene. The metathesis of propene on Mo/HNa-Y which was prepared from a certain amount of $Mo(CO)_6$ and 0.2 g of HNa-Y, was carried out at 274 K with a usual closed circulation system of 230 ml dead volume. Propene was purified using a freeze-pump-thaw tequnique. The initial presure of propene was 190 Torr.

The reaction products were analyzed by gas chromatography using a 4 m column of propylene carbonate.

The turnover frequency calculated from the amount of ethene produced for 1 h and the amount of molybdenum in catalyst was used as the catalytic activity of Mo/HNa-Y.

Oxygen chemisorption. The oxygen chemisorption on Mo/HNa-Y was investigated with a static system. First, the amount of oxygen adsorbed at 77 K was measured volumetrically. The pressure of oxygen used was lower than 110 Torr(the vapor pressure of oxygen at 77 K is 156 Torr). After evacuation at 195 K for 30 min, oxygen was readsorbed at 77 K. The amount of chemisorbed oxygen was calculated from the difference between the amounts of oxygen in the first and the second adsorptions.

Ultraviolet spectra. The diffuse reflectance technique was used to obtain the ultraviolet(UV) spectra on a Shimadzu UV-240 spectrometer.

HNa-Y(28 — 60 mesh) was put into a pyrex tube having a branch of
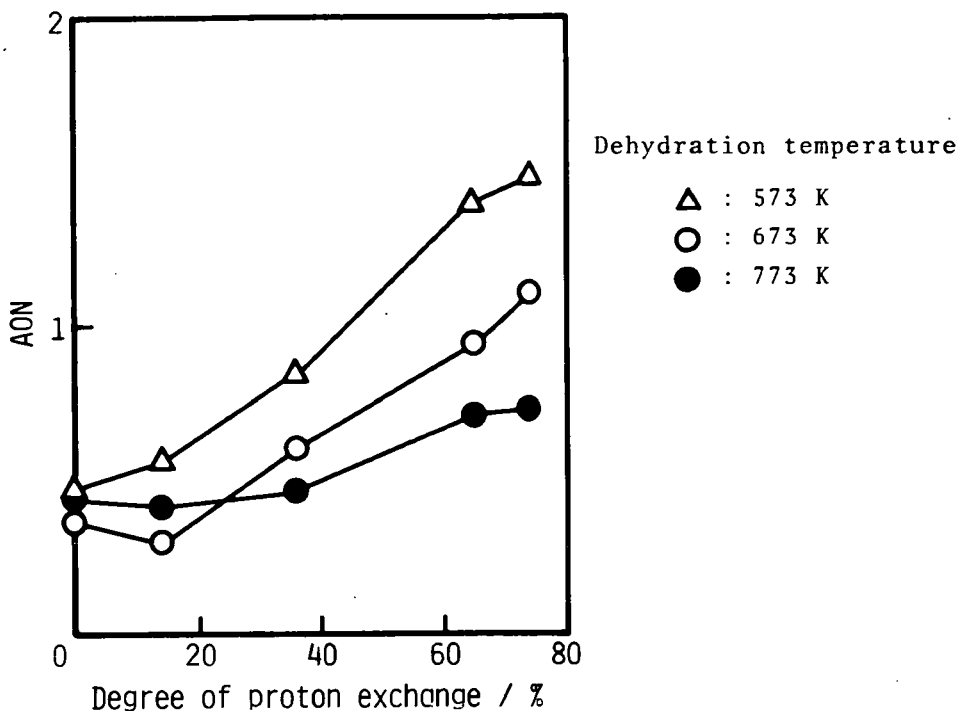
Fig. 1 Effect of degree of proton exchange in HNa-Y on AON of Mo

quartz cell. After Mo/HNa-Y was prepared in the tube, molybdenum was oxidized by O_2 in the same manner as the O_2 titration. Then Mo^{6+}/HNa-Y sample was transferred into the quartz cell in vacuo. The UV-diffuse reflectance spectra were recorded at room temperature in the range of 190 − 700 nm using the parent HNa-Y as a reference.

RESULTS AND DISCUSSION

    Oxidation state of supported molybdenum. It has been reported [9 that molybdenum is oxidized by the surface hydroxyl groups of HNa-Y zeolite during the decomposition of $Mo(CO)_6$ adsorbed on the HNa-Y. Therefore, it is expected that the oxidation state of the supported molybdenum is dependent on the concentration of the hydroxyl groups of HNa-Y. We have reported [10] that the average oxidation number (AON) of molybdenum decreases with the increase of the pretreatment temparature of the HNa-Y zeolite. On the other hand, the concentration of the hydroxyl groups of HNa-Y can be varied with the degree of the proton exchange in Na-Y zeolite. In this study, we changed the proton exchang degree from 0 %(parent Na-Y) to 74 % by using the various amounts of NH_4Cl aqueous solutions in the NH_4^+ exchange process.

    Fig. 1 shows the AON of molybdenum supported on the HNa-Y

zeolites with various degrees of proton exchange. It was found that
the AON of molybdenum increased with increasing the degrees of proton
exchange when HNa-Y were dehydrated at the same temperature. It is
concluded that the higher content of the hydroxyl groups of HNa-Y
causes the higher oxidation degree of molybdenum. In this study, AON
of molybdenum was measured by the O_2 titration method. We have
evaluated [11] the AON of molybdenum also by the measurement of H_2
formed during the simultaneous oxidation of molybdenum by proton with
the decomposition of adsorbed $Mo(CO)_6$. The decomposition and oxidation
of $Mo(CO)_6$ was described as follows;

$$Mo(CO)_6 + n(-OH) \longrightarrow (-O-)_n Mo^{n+} + 6CO + \frac{n}{2} H_2 \qquad (1)$$
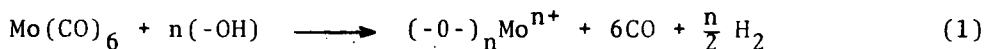
The AON obtained by this method agreed with that measured by the O_2
titration.

The maximum content of molybdenum for this catalyst system has
been reported [9,10] to correspond to one Mo atom per supercage of Y
zeolite. However, we found [11] that the maximum content corresponded
to two Mo atoms per supercage in the case of H(x)Na-Y (x = 0 − 74 %)
supports. The surface area of H(82)Na-Y used as a support in the
earlier work [10] was considerably smaller than that of the parent Na-Y.
From this result we suggested that the partial destruction of the
zeolite crystal structure caused the decrease in the maximum content of
molybdenum to some extent. The content of molybdenum used in this
study usually corresponded to two Mo atoms per supercage of Y zeolite
to avoid the heterogeneous distribution of molybdenum.

In order to prepare Mo/HNa-Y catalysts having various AONs of
molybdenum, we varied the dehydration temperature of HNa-Y in addition
to the degree of proton exchange. The results are shown in Fig. 2.
Less effect of the dehydration temperature on AON was observed in the
case of the HNa-Y supports having the lower degrees of proton exchange,
because these zeolites have a small amount of protons.

Propene metathesis. The metathesis of propene was carried out at
274 K on Mo/HNa-Y catalysts. Ethene, trans- and cis-2-butenes and a
trace amount of 1-butene were detected as reaction products. The
amount of ethene formed was larger than that of butenes in every case.
We expressed the catalytic activity of Mo/HNa-Y for the propene
metathesis in terms of the ternover frequency of the ethene formation.

Fig. 3 shows the relation between the catalytic activity of
Mo/HNa-Y and the AON of molybdenum. The catalysts used were Mo/HNa-Y
whose AON were controlled by changing the proton exchange degree and the
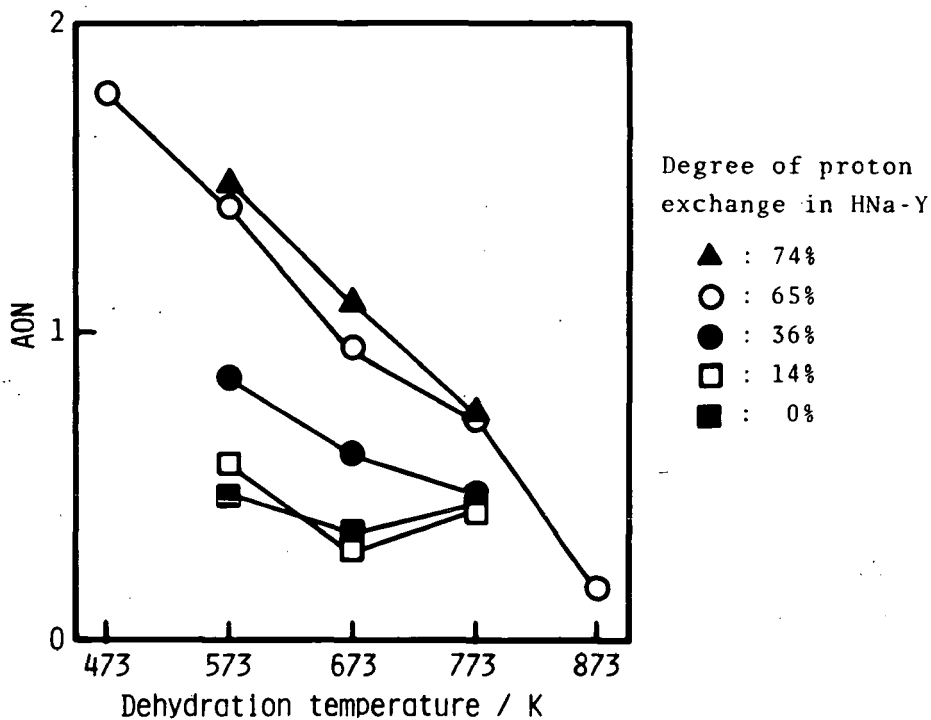dehydration temperature of HNa-Y zeolites as presented in Fig. 2.

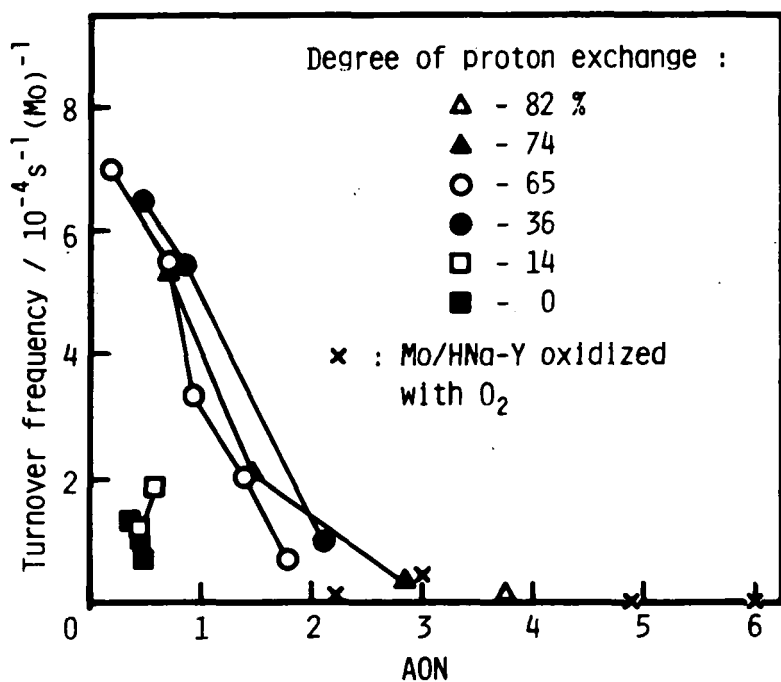Fig. 2   Effect of dehydration temperature of HNa-Y on AON of Mo

Fig. 3   Change in activity for propene metathesis with AON of Mo

In addition, Mo/H(74)Na-Y(Mo content=0.68 Mo atoms/supercage; AON=2.83), Mo/H(82)Na-Y(Mo content=0.68 Mo atoms/supercage; AON=3.75) and Mo/HNa-Y oxidized with oxygen at room temperature or 573 K were used as catalysts.

In the cases of Mo/H(74)Na-Y, Mo/H(65)Na-Y and Mo/H(36)Na-Y, the catalytic activity increased with decreasing the AON of molybdenum. When Mo/HNa-Y was oxidized with oxygen at room temperature, the AON increased from +1.1 to +3.0, while Mo/HNa-Y oxidized at 573 K had the AON of +6. These oxidized catalysts exhibited very low activities compared with the parent Mo/HNa-Y.

The active Mo species for the propene metathesis have been reported to be Mo^{4+} [12,13] or Mo^{3+} [14] in some supported molybdenum catalysts. In the case of Mo anchored catalysts prepared from Mo(π-$C_3H_5)_4$ and SiO_2 or Al_2O_3, it has been reported [12,13] that the activity was increased by oxygen treatment of Mo^{2+} species at room temperature. Similarly, Brenner et al. [15] have reported that the activity of (σ-$O^-)_2$Mo species was increased by the oxygen treatment at room temperature.

In our catalyst system, however, the activities of the Mo species whose AON were around +4 were much lower than those of Mo species in a low oxidation state for propene metathesis. Besides, the oxygen treatment on the Mo species in the low oxidation states caused the decrease in activity to a considerable extent. Therefore, it is concluded that the oxidation number of the most active Mo species for propene metathesis is not +4 but less than +4, probably 0.

In the case of H(14)Na-Y and Na-Y supports, however, the catalytic activities were relatively low, though the AON of molybdenum in these Mo/HNa-Y were as low as those in more active catalysts using H(36)Na-Y or H(65)Na-Y support. It was suggested that some other differences in the supported Mo species caused the change in activity. We thought that one of these differences consisted in the dispersion of the Mo species. To confirm this speculation, we carried out the oxygen chemisorption studies using some Mo/HNa-Y catalysts.

Dispersion of Mo species. Table 1 shows the turnover frequency and the amount of chemisorbed oxygen in terms of the O/Mo atomic ratio. We have already reported [10] the apparent dispersion of Mo calculated from the amount of irreversibly adsorbed oxygen at 298 K. But at 298 K, the oxygen uptake was gradually increased for more than 40 h. This result suggested that the oxidation of molybdenum in bulk phase occured at 298 K. On the other hand, when oxygen adsorption was carried out at 77 K, the adsorption reached the equilibrium state in 20 min. Therefore, to get the information about the dispersion of Mo species,

Table 1

Oxygen chemisorption on Mo/HNa-Y

Zeolite support	Dehydration temperature /K	Amount of irreversible adsorption of O_2 /O atom(Mo atom)$^{-1}$	Turnover frequency /$10^{-4}s^{-1}$(Mo)$^{-1}$
Na-Y	573	0.27	0.69
H(36)Na-Y	773	0.58	6.47
H(65)Na-Y	573	1.26	2.00
	773	0.90	5.45

it is better to adsorb oxygen at 77 K. From Table 1 it is clear that the dispersion of molybdenum in Mo/Na-Y is considerably low compared with that in Mo/H(65)Na-Y prepared by a similar procedure. This difference in the dispersion corresponded to the difference in the activities. However, the dispersion of molybdenum in the highly active Mo/H(36)Na-Y pretreated at 773 K was lower than that in the less active Mo/H(65)Na-Y pretreated at 573 K. Similarly in the case of H(65)Na-Y support, the dispersion in the more active catalyst pretreated at 773 K was lower than that in the other pretreated at 573 K. It seems that the Mo^0 species aggregated slightly are the most active for propene metathesis.

We studied the dispersion of Mo species also using ultraviolet diffuse reflectance spectroscopy. It has been reported [16,17] that Mo^{6+} with tetrahedrally and octahedrally coordinated O^{2-} exhibit UV absorption bands at 260 — 280 nm and 300 — 320 nm, respectively. An additional band at 220 — 240 nm is common to tetrahedral and octahedral configurations. The Mo^{6+} species in the tetrahedral configuration were thought to be monomeric species, while those in the octahedral configuration were attributed to polymeric species with bridging O^{2-} [18].

Fig. 4 shows the UV diffuse reflectance spectra of two different Mo/HNa-Y measured after all of the Mo species were oxidized to Mo^{6+}, and the spectra of $Na_2MoO_4 \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The spectrum of Mo^{6+}/H(65)Na-Y had a peak at ca. 255 nm and a shoulder at around 220 nm similarly to the spectrum of $Na_2MoO_4 \cdot 2H_2O$ which consists of tetrahedrally coordinated molybdenum. The spectrum of Mo^{6+}/Na-Y had a peak at ca. 295 nm and three shoulders at around 230, 270 and 320 nm. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ which consists of octahedrally coordinated molybdenum exhibited two absorption peaks at ca. 260 and 295 nm and two shoulders at around 220 and 320 nm.

Accordingly it is clear that the Mo species in Mo^{6+}/H(65)Na-Y

d : Mo/Na-Y oxidized
     with O_2

c : $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
b : Mo/H(65)Na-Y oxidized
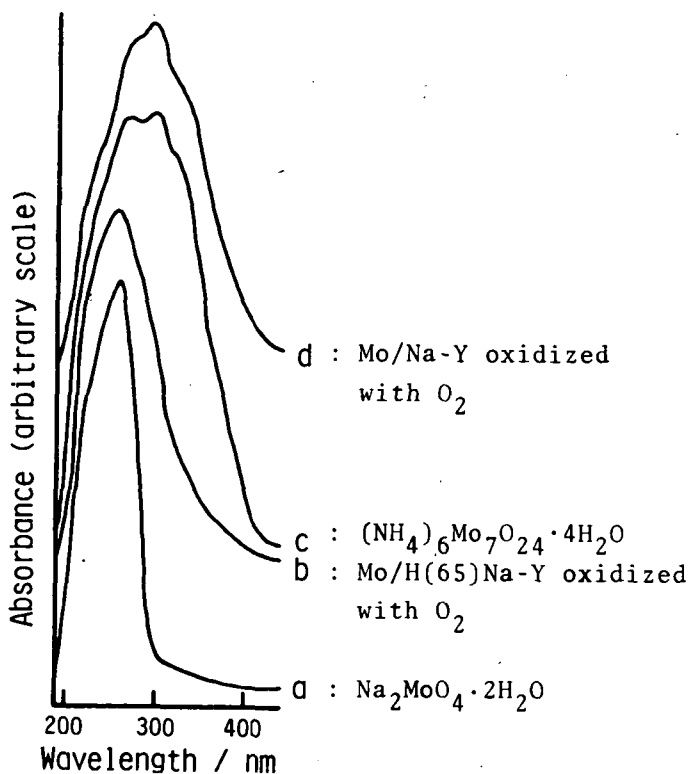   with O_2

a : $Na_2MoO_4 \cdot 2H_2O$

Fig. 4 UV diffuse reflectance spectra

consist almost exclusively of the tetrahedrally coordinated molybdenum. Therefore, the Mo species in this catalyst should be dispersed nearly monomerically in the zeolite. On the other hand, it seems that most of the Mo species in Mo^{6+}/Na-Y have the octahedral coordination, that is, the Mo species are probably aggregated to form bulk oxide. These results are consistent with the results of oxygen chemisorption.

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