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ENHANCING EFFECT OF HYDROGEN ON ACID-CATALYZED REACTION OVER SILVER EXCHANGED Y TYPE ZEOLITE

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Abstract—The catalytic activity of *o*-xylene transformation and cyclopropane isomerization over hydrogen reduced AgY was greatly enhanced by the presence of gaseous hydrogen. This enhancing effect was reversible by the presence and absence of gaseous hydrogen, and was confirmed by the catalytic activity changes and infrared spectroscopy. While, HY had not enhancing effect in the presence of hydrogen. This hydrogen enhancing effect and its reversibility over reduced AgY may be related to the redox properties of the small silver clusters which can be chemisorbed gaseous hydrogen. This effect was also affected by the partial pressure of hydrogen, and the extent of Ag^+ ion-exchange.

INTRODUCTION

Zeolites, supported metal particles which can be used as catalysts for a variety of chemical reactions, are in general prepared by ion-exchange of corresponding transition metal ion into the zeolite structure, followed by reduction of ions with gaseous hydrogen. Silver ions in the zeolite can be reduced to silver atom, charged silver cluster, uncharged silver cluster, and silver metal by the hydrogen reduction.

There is currently much interest in silver clusters entrapped in various silver exchanged zeolites. Jacobs et al.[1-3] reported that the hydrogen reduction of Ag^+ ions in silver exchanged Y type zeolites and zeolon results in the formation of highly dispersed silver clusters with concomitant formation of acidic hydroxyl groups. It was also found that hydrogen was adsorbed over reduced silver exchanged Y type zeolite and zeolon. The same authors[4] found that hydrogen was dissociatively adsorbed on dehydrated AgA zeolites.

The structure and location of the various silver clusters have been extensively characterized by many spectroscopic techniques. Gellens et al.[5-7] studied the silver clusters of AgA and AgY by X-ray crystallography. Ozin and coworkers[8-11] studied the systems with diffuse reflectance spectroscopy and far-infrared spectroscopy and suggested the reversible cluster redox process of Ag_3^{2+} and Ag_3^0 by treatment with oxygen and hydrogen in AgA.

Although the physicochemical states of silver clusters have been extensively studied, the fate of chemisorbed hydrogen attracted less attention. Since chemisorbed hydrogen is expected to be retained in the zeolite as protons, the catalytic activity of acid-catalyzed reactions should give an important clue of monitoring the behavior of chemisorbed hydrogen species.

In the previous paper[12], we reported that the enhancing effect of hydrogen was observed in the dehydration of alcohols over reduced AgY. In this study, we report in detail the enhancing effect of hydrogen over reduced AgY by investigating adsorption of hydrogen, hydrogen partial pressure, the extent of Ag^+ ion-exchange, infrared spectroscopy, and HD exchange reaction. Cyclopropane isomerization and *o*-xylene transformation were carried out as the model reaction of acid-catalyzed reactions.

EXPERIMENTAL

1. Materials

As starting zeolite, NaY($SiO_2/Al_2O_3 = 5.6$) from Toyo Soda Manufacturing Co.(Japan) was used. The Na^+ ion was partially exchanged by Ag^+ ions in silver nitrate aqueous solution at room temperature according to the conventional ion-exchange procedures. After the samples were washed until complete disappearance of any ions in the washing waters, air dried at 393K for 1 day. In order to prevent a reduction from light, preparation, handling, and the storage of the silver exchanged zeolites were performed in the dark. The extent of Ag^+ ion-exchange was determined by the chelatometric methods using a murexide as a metal indicator[13].

For sample identification, the extent of ion exchange of zeolites as usual follows the sample name. For example, AgY-98 represents that the extent of Ag^+ ion-exchange for Na^+ ions is 98%.

2. Methods

Cyclopropane isomerization was carried out with a closed-circulating reaction system. Cyclopropane (99.92% pure) was purchased from Sowa Chemical Co.(Japan) and used without further purification. The catalyst which was pressed and pelletized into grains of 16-32 mesh was packed in a reactor, outgassed, reduced with hydrogen, and then outgassed again at 623K for 1hr, respectively. The reaction products were taken periodically from the gas sampling port and analyzed with Porapak Q column at 343K.

o-Xylene transformation was carried out with a continuous flow reactor system operating at atmospheric pressure. The catalyst was packed in a reactor of silica tubing (10 mm i.d.) placed in a vertical furnace, pretreated in an air stream at 773K for 1 hr, and successively reduced in a hydrogen stream at 623K for 1 hr. *o*-Xylene was delivered by motor-driven syringe and vaporized in the preheating zone of the reactor containing of silica sands. Nitrogen and hydrogen was fed through flowmeters, respectively. The reaction products were taken periodically from the outlet of reactor, and analyzed by a gas-chromatograph (FID) with a PEG-6000 column at 433K.

The amount of chemisorbed hydrogen on the reduced silver zelolites was measured by volumetric method in the conventional high-vacuum system.

Infrared spectra were recorded by using a Shimadzu IR-460. The zeolites were pressed into self-supporting wafers, containing about 8×10^{-2} kg of zeolite per m^2. They were mounted in a vacuum cell, which could be heated and connected with a conventional high-vacuum system. All spectra were recorded at beam temperature.

RESULTS AND DISCUSSION

1. Enhancing effect of hydrogen

Cyclopropane isomerization is shown in Figure 1. This reaction was carried out in a closed-circulating reaction system at 453K. After pretreatment of catalyst, cyclopropane and hydrogen were introduced with an initial pressure of 12 kPa and 27 kPa, respectively. In the absence of hydrogen, only cyclopropane with a pressure of 12 kPa was introduced.

Starting material, NaY had not catalytic activity for this reaction. The reaction rate of the system with hydrogen was faster than that of the system without hydrogen, and propylene was a unique product.

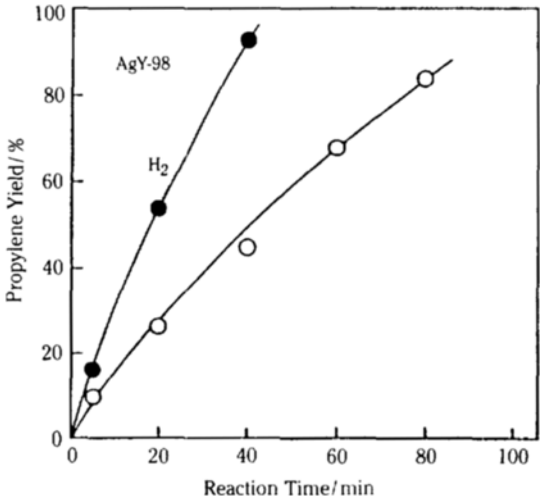

Fig. 1. Catalytic activity of AgY-98 with reaction time for the cyclopropane isomerization in the closed-circulating reaction system.
Reaction conditions: Catalyst weight = 0.02 g, Reaction temperature = 453K, Initial pressure of H_2 = 27 kPa, Initial pressure of cyclopropane = 12 kPa.
● : H_2 (27 kPa) + cyclopropane (12 kPa)
○ : cyclopropane (12 kPa)

o-Xylene transformation was carried out over AgY-98 at 523K, W/F = 1.0 g·hr·mol^{-1}, and *o*-xylene partial pressure of 10 kPa. As products, benzene, toluene, *m*-, and *p*-xylene, 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene were observed. The catalytic activity with the type of carrier gas is shown in Figure 2.

When nitrogen(91 kPa) alone was fed to the reac-

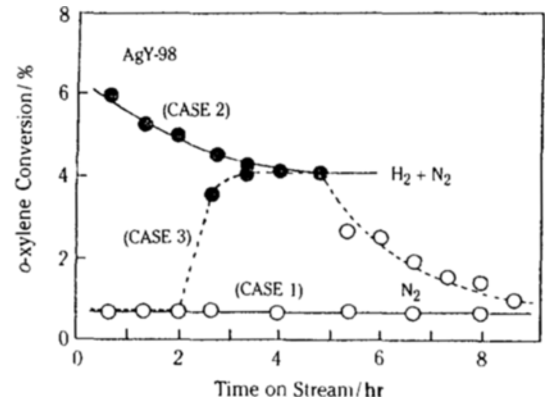

Fig. 2. Enhancing effect and reversibility on the catalytic activity of AgY-98.
Reaction conditions: Catalyst weight = 0.15 g, Reaction temperature = 523K, W/F = 1.0 g·hr·mol^{-1}, Partial pressure of *o*-xylene = 10 kPa.
● : H_2 (60 kPa) + N_2 (31 kPa) + *o*-xylene (10 kPa)
○ : N_2 (91 kPa) + *o*-xylene (10 kPa)

tion system as carrier gas(case 1), the conversion was only 0.8%, and did not change with time on stream. However, when the mixed carrier gas of hydrogen (61 kPa) and nitrogen (30 kPa) was fed to the system (case 2), the conversion was gradually decreased from 6% to 4.2% with time on stream. The catalytic activity in the presence of hydrogen was much higher than that of nitrogen alone. After the steady state conversion with nitrogen alone was attained, hydrogen was fed to the system (case 3). While, the partial pressure of o-xylene and the contact time were kept constant with decreasing pressure of nitrogen, and partial pressure of hydrogen and nitrogen was the same pressure of case 1. The conversion increased sharply from 0.8% to 4.2%, and then gradually decreased as hydrogen was eliminated from the system.

It clearly shows that the presence of gaseous hydrogen enhances the rate of acid-catalyzed reactions, and this enhancing effect of hydrogen is at least partially reversible.

2. Effect of hydrogen partial pressure

Before investigating the effect of hydrogen partial pressure, hydrogen adsorption on reduced silver exchanged zeolite was examined. The amount of reversible hydrogen adsorption was measured by checking the pressure drop in the vacuum system. The sample was previously reduced with hydrogen at 623K for 1hr, and degassed at a predetermined adsorption temperature for 1hr. Hydrogen was reversibly adsorbed on the reduced AgY-98, and the adsorbed amount of hydrogen was 3.1×10^{-2}mmol·g^{-1} at 31.2 kPa of hydrogen pressure and 523K.

The influence of hydrogen partial pressure on this enhancing effect is shown in Figure 3. This data was obtained after 4 hr from hydrogen and nitrogen was fed to the reaction system. In the absence of hydrogen, the conversion of o-xylene over AgY-98 was only 0.8%. The conversion increased with increasing hydrogen partial pressure, and remained constant as 4.2% above the hydrogen partial pressure of 40 kPa. From this result, it is noted that the number of the proton formed or catalytic activity is dependent on the hydrogen partial pressure in the system. However, the conversion of o-xylene over HY was not affected by increasing the hydrogen partial pressure. This shows that the silver species which were formed by hydrogen reduction are active site to chemisorb the gaseous hydrogen. Because the silver metal did not chemisorb the gaseous hydrogen[14,15], this active silver species must be small silver clusters.

Two possibilities of the proton formation over reduced AgY can be represented as follows;

$$Ag_n^+ + ZO^- + 1/2H_2 \rightleftharpoons Ag_n^0 + ZOH \qquad (1)$$

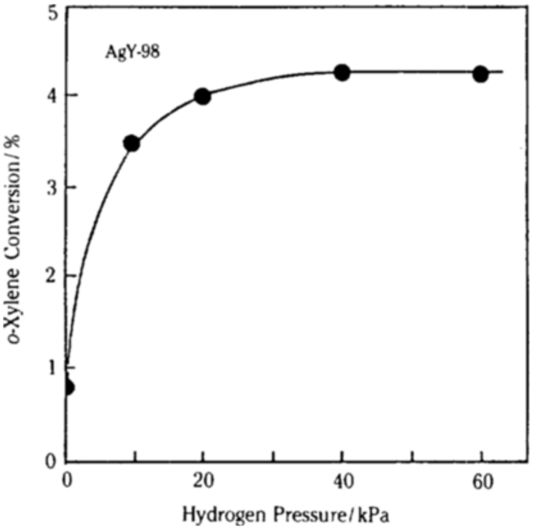

Fig. 3. Effect of hydrogen partial pressure on catalytic activity of AgY-98.

Reaction conditions: Reaction temperature = 523K, W/F = 1.0 g·hr·mol^{-1}, Partial pressure of o-xylene = 10 kPa.

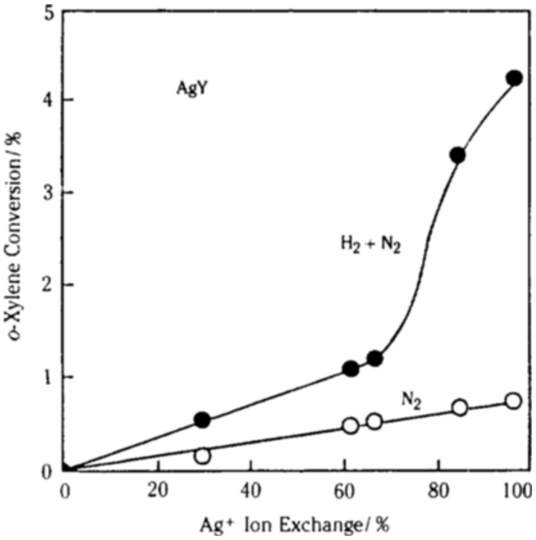

Fig. 4. Effect of the Ag$^+$ ion-exchange extent on catalytic activity of AgY.

Reaction conditions: Reaction temperature = 523K, W/F = 1.0 g·hr·mol^{-1}, Partial pressure of o-xylene = 10 kPa.

● : H_2 (60 kPa) + N_2 (31 kPa) + o-xylene (10 kPa)

○ : N_2 (91 kPa) + o-xylene (10 kPa)

$$Ag_n^+ + ZO^- + H_2 \rightleftharpoons Ag_nH + ZOH \qquad (2)$$

One of the possibilities, Eq.(1) was proposed by Uytterhoeven and coworkers[1,2,5]. Where, ZO^- and ZOH denotes the zeolite framework and acidic OH groups, respectively. The other possibility, Eq.(2) is the heterolytic dissociative chemisorption of hydrogen[16,17].

3. The extent of Ag^+ ion-exchange

Figure 4 shows the effect of Ag^+ ion-exchange extent in the AgY zeolites. The starting zeolite, NaY had not catalytic activity for o-xylene transformation in the presence and absence of hydrogen. In the absence of hydrogen, the conversion was slightly increased with increasing the extent of Ag^+ ion-exchange. However, the conversion in the presence of hydrogen was normally increased, and then sharply increased above the extent of Ag^+ ion-exchange of 67%. The difference of conversion between the presence and the absence of hydrogen was much greater at higher extent of Ag^+ ion-exchange. This implies that the number of active site where hydrogen can be chemisorbed increases with increasing the extent of Ag^+ ion-exchange.

4. Infrared spectroscopy

The appearance of deuteroxyl groups in the silver zeolite upon reduction was proved by infrared spectroscopy as shown in Figure 5. When silver zeolite was pretreated with oxygen at 623K for 1 hr (Figure 5.(A)), the absorbance in the OH stretching region could be ignored. In order to maximize the transmittance, AgY-61 was used as a sample and deuterium gas as a reductant. On reducing the catalyst at 523K for 1 hr (Figure 5.(B)), two distinct bands appeared at 2615 cm^{-1} and 2680 cm^{-1}, which were proved both acidic by infrared spectra of adsorbed pyridine. These two deuteroxyl bands are similar to the high frequency and low frequency bands in DY zeolites[18]. The very intense in-

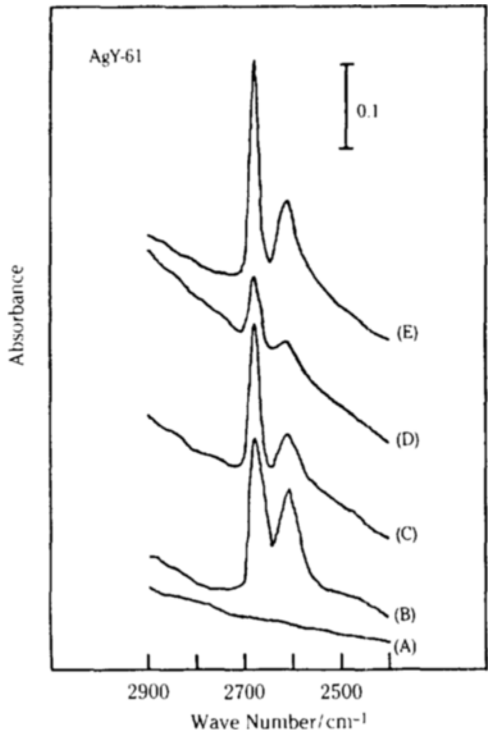

Fig. 5. Infrared spectra of the deuteroxyl bands in AgY-61.

(A): Calcination with O_2 for 1 hr at 623K.
(B): Reduction with D_2 for 1 hr at 523K.
(C): Evacuation for 1 hr at 523K.
(D): Evacuation for 4 hr at 523K.
(E): Exposure to D_2 for 0.5 hr at 523K.

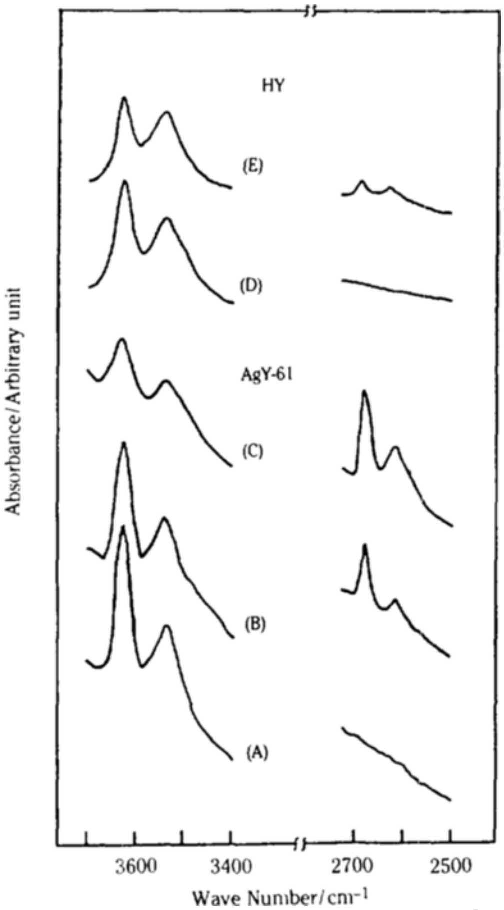

Fig. 6. Infrared spectra of the deuteroxyl and hydroxyl bands for HD exchange reaction in AgY-61 (A-C) and HY (D,E).

(A): Calcination with O_2, reduction with H_2, and then evacuation for 0.5 hr at 623K, respectively.
(B): Exposure to D_2 for 0.33 hr at 353K.
(C): Exposure to D_2 for 0.33 hr at 423K.
(D): Evacuation for 1 hr at 623K.
(E): Exposure to D_2 for 0.33 hr at 423K.

itial bands indicate a large number of active site where deuterium could be chemisorbed. These OD groups disappeared to a minor extent after degassing at 523K for 1 hr (Figure 5.(C)), and then disappeared to a major extent after degassing at the same temperature for 4 hr (Figure 5.(D)). These spectra changes show that the chemisorbed deuterium is desorbed upon degassing a reduced AgY zeolite. These deuteroxyl bands increased again in intensity after a subsequent deuterium introduction at the same temperature (Figure 5.(E)). These changes of intensity in OD stretching region indicate that deuterium (or hydrogen) chemisorption on reduced silver zeolites is partially reversible.

5. HD exchange reaction over HY and reduced silver zeolite

In order to study the activation of hydrogen (or deuterium) on reduced AgY-61 and HY, HD exchange reaction was performed with deuterium gas as shown in Figure 6. All spectra were taken in both OH stretching and OD stretching regions. The reduction of silver zeolite was carried out with hydrogen, and the reduced zeolite was successively degassing at the same temperature. Such a reduction results in the appearance of two hydroxyl bands (Figure 6.(A)). HD exchange reaction was started with introducing deuterium gas of 28.4 kPa at 353K for 0.33 hr (Figure 6.(B)). In OD stretching region, two new deuteroxyl bands were observed. This shows that HD exchange reaction occured between the proton of reduced silver zeolite and the gaseous deuterium at 353K. Figure 6.(C) shows the spectra which were obtained after subsequent exchange reaction at 423K for 0.33 hr. The extent of HD exchange reaction increased with increasing the reaction temperature. Proton exchanged zeolite, HY was prepared by degassing NH_4Y at 623K for 1 hr. Such a treatment results in the appearance of two hydroxyl bands (Figure 6.(D)). HD exchange reaction on HY did not occur at 353K, and then occured very small extent at 423K (Figure 6.(E)).

When Ag^+ ion was ion-exchanged in the zeolite and reduced with hydrogen, the rate of hydroxyl exchange increased, namely, the exchange reaction rate on reduced silver zeolite was faster than that on HY at the same temperature. This active exchange reactivity of reduced AgY may be related to the silver clusters which gaseous deuterium can be chemisorbed and activated.

CONCLUSION

The enhancing effect of hydrogen on acid-catalyzed reaction was observed for cyclopropane isomerization and o-xylene transformation over AgY, and was reversible by the presence and absence of gaseous hydrogen in the system. This enhancing effect of hydrogen and its reversibility indicate that protons are formed by hydrogen chemisorption on the reduced AgY and this proton formation is reversible. This effect was much greater at higher extent of Ag^+ ion-exchange, and increased with increasing the partial pressure of gaseous hydrogen in the system. Also, it is very significant that the HD exchange reaction activity of AgY is much higher than that of HY at the same reaction conditions. Because the silver metal did not chemisorb the gaseous hydrogen, it is clear that the active site where gaseous hydrogen can be chemisorbed and activated must be small silver clusters in the reduced AgY zeolites, and acidic OH groups as well as silver species take part in the catalysis.

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