Reduction-Reoxidation Behavior of Silver(I) Ions in X-Type Zeolites

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The reduction of Ag^+ ions in X zeolites by hydrogen, the reoxidation of Ag atoms by oxygen, and the formation of silver particles were studied kinetically. The reduction is suggested to be a catalyzed reaction requiring an activation of hydrogen at some specific sites on the basis of the influence of exchange levels and hydrogen pressures on the reduction rates. At elevated temperatures the reduction of Ag^+ ions proceeded quantitatively and resulted in formations of Ag particles with a diameter between 10 and 25 nm and of highly dispersed Ag clusters. The clusters were easy to be reoxidized by oxygen at 473 K or below, while the particles were difficult to revert into the zeolite matrix. The diameter of the Ag particles was dependent on the reduction temperature and ion-exchange level and independent on the reduction time. It is discussed that this is due to the slow nucleation and the fast nuclear growth of Ag particles.

Many efforts have been made to develop finely dispersed metal clusters or particles upon reduction of transition metal ions in zeolites.[1,2] These zeolites can be used as highly active and/or bifunctional catalysts for a wide range of chemical reactions. Interest was stirred when Rabo *et al.*[3] reported an active catalyst consisting of Pt metal supported in a Y-type zeolite. To date, X and Y zeolites containing several metals such as Ni,[4] Cu,[5] and Pt[3,6] have been well investigated. The following reaction stoichiometry has been suggested to the hydrogen reduction of a metal

$$Me^{x+} + {}^1/_2xH_2 \longrightarrow Me^0 + xH^+ \qquad (1)$$

ion in the zeolite. Here, Me^{x+} represents a transition metal ion. It is also reported that variations of methods in preparing supported metal catalysts affect a dispersion of the metal particles and an activity of the catalyst.

An endeavor to form small silver clusters or particles in or on zeolite framework is very interesting and desirable, since silver metal is a highly active catalyst for not only the epoxidation reaction of ethene but also oxidations of various organic compounds. In fact, Kagawa *et al.*[7] reported an active silver catalyst which was prepared by the reduction of Ag^+ ions in X zeolites followed by the dissolution of zeolite matrix with a concentrated alkali solution. Tsutsumi and Takahashi[8] found that Ag^+ ions in Y zeolites could be reduced to particles of Ag atoms with a diameter 15—30 nm upon a treatment with alkylbenzenes and alcohols. Riekert[9] reoxidized Ag–Y zeolites reduced with hydrogen and found the reproduction of the original Ag^+–Y zeolites. Beyer *et al.*[10] also performed a kinetic and physicochemical study on the reduction of Ag^+ ions in Y zeolites. Recently, Kimm and Seff[11] reported the formation of small silver clusters in A zeolites without reducing agents. Upon an evacuation and oxidation at elevated temperatures, Ag^+ ions were found to form Ag_6 clusters surrounded by 8 Ag^+ ions.

Since the number of metal ions exchangeable in a unit cell of X zeolites is greater than that of Y zeolites, the redox behavior of silver ions in X zeolites is of interest though the X-type lattices are less stable than the Y-type lattices. In the present paper, therefore, a systematic study has been carried out on various Ag^+–X zeolites to clarify the following problems: the kinetics of the reduction and reoxidation of Ag^+ ions in X zeolites, the mechanism of Ag particles formation, and the influence of an extent of exchange between Ag^+ and Na^+ ions on the reduction. This would serve to further progress in the standardization of methods of catalyst preparations.

Experimental

Materials. Eight AgNaX samples with different Ag^+ contents were prepared from Linde NaX zeolite of a composition $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$. The zeolite was washed with diluted $NaNO_3$ solution in order to eliminate cation deficiency, ion-exchanged in aqueous silver nitrate solutions with adequate concentrations,[12] washed with water and dried at 473 K. The respective exchange levels of Ag^+ ions were analyzed by conventional analytical procedures. The compositions of the samples are summarized in Table 1. All the samples obtained were sieved to 30—60 mesh for use.

Hydrogen, oxygen, and nitrogen gases were of high purity grade (above 99.9% purity). Before use in reduction-reoxidation experiments, these gases were passed through a cold trap cooled at the liquid nitrogen temperature for removal of a trace amount of water.

Methods and Procedures. Reduction by hydrogen and reoxidation by oxygen were carried out in two ways of a static system and a flow system.

(a) Static System: An uptake of hydrogen could be followed accurately as a function of time by measuring the pressure drop in a static system. Reoxidation was also investigated by measuring the oxygen consumption in the same apparatus. The change of pressure was followed on a mercury manometer. A liquid nitrogen cold trap was

Table 1. The AgNaX zeolites used

Sample	Exchange level (%)	Number of Ag^+ ions per unit cell	Amount of silver supported (g-Ag/g-AgNaX)
AgNaX- 6	5.6	4.8	0.038
15	14.7	12.6	0.094
24	24.4	21.0	0.149
39	38.6	33.2	0.221
45	45.1	38.8	0.250
72	71.8	61.7	0.357
84	83.8	72.1	0.398
99	98.6	84.8	0.444

equipped between a reactor and a vacuum pump to avoid a possibility of contamination due to vapors flowing backward from the pump. In the reactor, each zeolite sample was degassed at 673 K for more than 1 h, exposed to oxygen at the same temperature for more than 30 min, and then reevacuated for 5 min. This pretreatment[13] was always carried out for a fresh sample in order to remove water, carbon dioxide, and possible hydrocarbon impurities on the zeolite surface. Following the pretreatment, the sample was cooled to a chosen temperature in static vacuum and exposed to hydrogen at a desired pressure for a prescribed time. Subsequently, the sample was evacuated for 30 min and subjected to X-ray analysis or reoxidation. Reoxidation was carried out at a prescribed temperature, period, and pressure in the presence of oxygen. In this paper, the experiments were performed by this procedure unless otherwise specified.

(b) Flow System: After being mounted in a reactor, samples were purged with nitrogen at ambient temperature and an atmospheric pressure, and then heated to a chosen temperature. At that temperature a mixture of nitrogen and hydrogen diverted to flow through the reactor. A constant flow of the mixture, 30 cm^3/min, were maintained for a prescribed period. The reduced samples were cooled down to ambient temperature in a nitrogen atmosphere. This procedure was applied to the study on the formation of silver particles under severe reduction conditions.

Characterization of Samples. In order to ascertain the change of the zeolite framework and to determine the average size of Ag particles formed, a X-ray diffraction pattern was taken on each sample after the reduction or the reoxidation. The line width of (111) reflection of the Ag crystal was used to determine the average size of the Ag particles by a simplified Scherrer relation.

Results and Discussion

Kinetics of the Reduction. Amounts of hydrogen consumption over AgNaX-45 are shown in Fig. 1 as functions of the reaction temperature and time. A reduction level was evaluated from a theoretical uptake of hydrogen based on Eq. 1. Evidently the rate and the amount of hydrogen uptake increased at the higher temperatures. At 723 K the sample consumed an amount of hydrogen corresponding to complete reduction of the Ag^+ ions within a few minutes and there was no further consumption of hydrogen. In each case the catalyst turned black from white with a progress of the hydrogen consumption, indicating the reduction of Ag^+ ions to Ag atoms. The plots of the logarithm of initial rates of the reduction, calculated from the amount of hydrogen consumption for 10 s, versus reciprocal absolute temperatures between 273 and 471 K gave a straight line. This linearity would indicate that the mechanism is essentially unchanged in the initial stage of the reduction between 273 and 471 K; therefore, the apparent activation energy was evaluated to be 23.4 ± 1.6 kJ/mol. This value seems to be reasonable because the activation energy of reduction of copper ions in X zeolites has been reported to be 49 kJ/mol[14] and silver ions are well known to be reduced more easily than copper ions. However, it should be noted that this value (23.4 kJ/mol) might be lower than the average value of activation energies for the whole silver ions, since first the distribution of Ag^+ ions is somewhat heterogeneous as suggested by the dependence of the achievable degree of the reduction on the reaction temperature, and secondly the extent of reduction at 471 K for 10 s was about 50% which was too much to measure the initial reduction rate.

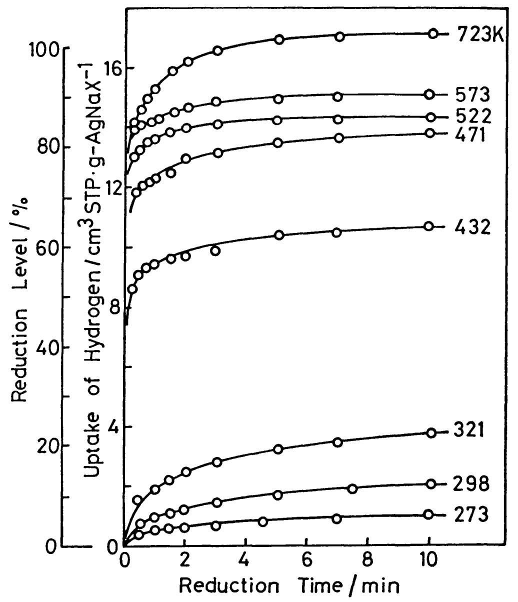

Fig. 1. Kinetic curves of the reduction of AgNaX-45 at various temperatures. The initial pressure of hydrogen was 13.3 kPa.

It was confirmed in a separate experiment that the rate of the reduction at 323 K did not depend on the partial pressure of hydrogen in the range 6.7—40.0 kPa. Beyer *et al.*[10] have reported that the reduction rate was proportional to the hydrogen pressure. However, it is very difficult to discuss the difference between these two results, since there was no description about the pressure range of hydrogen in their paper.

All samples reduced in the experiments of Fig. 1 were subjected to X-ray analyses. The reduction of AgNaX-45 at a temperature of 471 K or below did not give peaks in the diffraction pattern which are attributable to metallic silver particles. By contrast, the diffraction pattern of the sample reduced at a temperature higher than 522 K for 10 min showed a significant peak corresponding to the (111) reflection of metallic silver particles. These results lead to the conclusion that, under such mild reduction conditions as a treatment at 471 K for 10 min, the growth of silver particles should not proceed, or should stop below *ca.* 3.5 nm[15] in diameter.

The effect of an exchange level on the initial reduction rate of Ag^+ ions is depicted in Fig. 2. The reduction rate was calculated approximately from the amounts of hydrogen consumption during an initial short period, 10 sec, at 323 K. It was found that the reduction rate exhibited a characteristic correlation with the exchange level; the rate was very small for low-exchanged AgNaX zeolites until it increased rapidly above *ca.* 20% of the exchange level. This

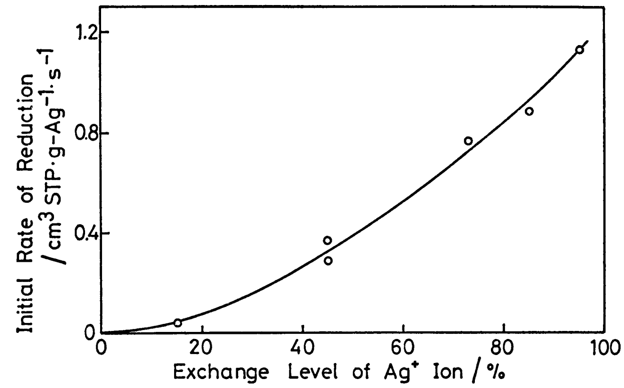

Fig. 2. Dependence of the initial rate of reduction at 323 K on the exchange level of silver(I) ions.

fact reflects that the reduction rate relates to the distribution of Ag$^+$ ions on several exchange sites in the zeolite framework. Ag$^+$ ions exhibit a tendency to occupy the interior sites (S_I or S_I') in dehydrated zeolites.[16] It is reasonable that the Ag$^+$ ions located at S_I and S_I' sites are difficult to be reduced with hydrogen. The influence of the exchange level and hydrogen pressure on the reduction rates at elevated temperatures could not be clarified, since the reduction rates were too fast to measure it accurately.

On the basis of the relation in Fig. 2, the activation energy of the reduction process, and the independency of the reduction rate on the hydrogen pressure, it is likely that the reduction is a catalyzed reaction in which the activation of hydrogen at some specific site S is required. This mechanism is acceptable

$$S + H_2 \rightleftharpoons S\text{-}H_2 \tag{2}$$

$$S\text{-}H_2 + Ag^+ \longrightarrow SH\text{-}Ag + H^+ \tag{3}$$

$$SH\text{-}Ag \longrightarrow SH + Ag \tag{4}$$

$$SH + Ag^+ \longrightarrow S\text{-}Ag + H^+ \tag{5}$$

$$S\text{-}Ag \longrightarrow S + Ag \tag{6}$$

if the exchange reaction of a Ag$^+$ ion with a H atom (Eq. 3) is a rate determining step. This cooperative exchange would be the reason for the lower activation energy of the process than that of a sole migration of univalent cations[17] (74.2 and 90.3 kJ/mol for Na$^+$ and Li$^+$ ions, respectively). This can explain the phenomenon shown in Fig. 2; that is, the reduction rate increased rapidly when Ag$^+$ ions began to situate inside or on the periphery of the supercage where Eq. 3 would become easy. The active species would be hydrogen atoms, since the hydrogen atoms have an average diameter small enough (0.1 nm)[18] to enter in the hexagonal or sodalite cavities through the hexagonal windows whose diameter is 0.22 nm,[19] while the diameter of hydrogen molecules is 0.24 nm.[20] Very recently, Che *et al.*[21] have reported that the reducing power of hydrogen atoms was higher than that of hydrogen molecules. In addition, in work on the equilibration of H_2–D_2 mixture over Y zeolites Heylen *et al.*[22] have shown that impurities such as iron ions are centers for the activation of hydrogen. These two findings support our assumption that the reduction is a catalyzed reaction requiring activation of the hydrogen at the site S. In the reduction process of Ag$^+$ ions located in S_I or S_I', it might be suggested that the generated Ag atoms are centeres for the activation of hydrogen and a spillover step of a hydrogen atom becomes significant.

Prior to the reduction experiments water vapor was introduced onto the sample which was dehydrated in the pretreatment. The reduction process was greatly inhibited in the presence of water, as shown in Fig. 3. This would result from the hydration of the active sites S or Ag$^+$ ions itself.

Kinetics of the Reoxidation. Reoxidation were performed on AgNaX reduced by a treatment with hydrogen at 573 K for 10 min. The uptakes of oxygen are illustrated in Fig. 4 as a function of time at dif-

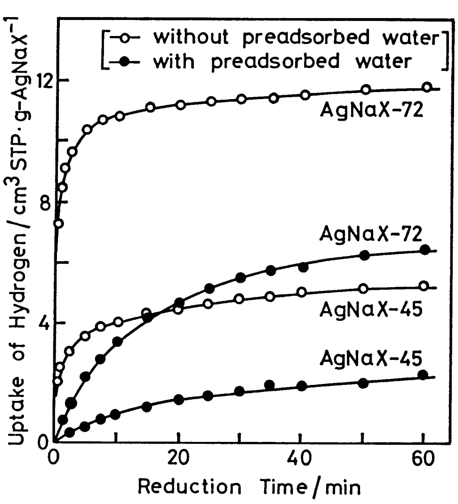

Fig. 3. Influence of the water addition on the reduction process of AgNaX-45 at 323 K. Water was introduced at 2.6 kPa into the system prior to the reduction and briefly evacuated at reaction temperature.

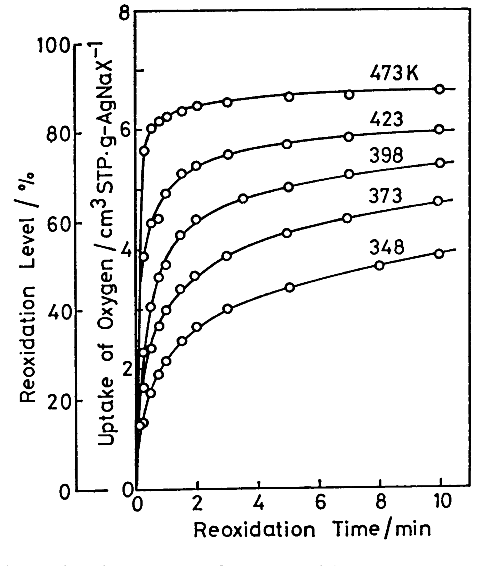

Fig. 4. Kinetic curves of the reoxidation of AgNaX-45 pre-reduced at 573 K for 10 min. The numerical values in the figure are the reoxidation temperatures. The initial pressure of oxygen was 13.3 kPa.

ferent temperatures. The reoxidation was slow at low temperatures. The achievable degree of reoxidation was nearly constant over the temperature range 348—473 K. For example, the uptake of oxygen in the reoxidation at 348 K for 2 h was 6.61 cm^3 STP/g-AgNaX-45, which was the same as that (6.65 cm^3 STP/g-AgNaX-45) at 473 K for 30 min within the experimental error. The apparent activation energy of the reoxidation, 20.1±2.0 kJ/mol, was calculated from the initial rates of Fig. 4 in the manner similar to that of the reduction. The extent of the reoxidation, evaluated from the amount of consumed oxygen on the basis of Eq. 7, was also graduated in Fig. 4. The

$$Ag + H^+ + {}^1/_4O_2 \longrightarrow Ag^+ + {}^1/_2H_2O \qquad (7)$$

reoxidation of the sample reduced at 573 K could not be achieved completely.

The stoichiometry of the reduction and reoxidation is quantitatively summarized in Table 2. Here, the reductions were carried out at two different temperatures for comparison. The amounts of reduced Ag^+ ions and reoxidized Ag atoms were determined by the quantities of the hydrogen and oxygen consumptions, respectively. The silver particles were defined here as the aggregates of silver metal which was detectable by X-ray analysis. Its quantities were measured by the method described in the following section. The remained Ag atoms were treated as silver clusters existing in the zeolites.

The hydrogen reduction of AgNaX-45 at 323 K for 30 min resulted in the production of 13.9 Ag atoms per unit cell. The formation of silver particles was not observed. Upon the treatment of this sample with oxygen at 473 K for 10 min, 3.01 cm^3 of oxygen was consumed and 14.0 Ag atoms were reoxidized to Ag^+ ions. This value is actually identical with the number of the produced Ag atoms. It is concluded that under these experimental conditions the reduction and reoxidation of Ag^+ ions in the zeolite are completely reversible. In contrast, among 34.8 Ag atoms generated by the reduction at 573 K 4.0 Ag atoms were found to form silver particles. Upon the reoxidation the amount of Ag^+ ions regenerated (30.9) is in fair agreement with that of silver clusters before the reoxidation (30.8). This is well interpreted by finding both amounts of silver particles before and after the reoxidation to be the same. These results lead to the conclusion that the silver particles remained unchanged even after the treatment of oxygen at 473 K and the reoxidation affected only the silver clusters presumably located inside the large cavities of the zeolite.

TABLE 2. STOICHIOMETRY OF REDUCTION AND REOXIDATION OF AgNaX-45 SAMPLE

Run	A	B
Reduction		
Temperature/K	323	573
Time/min	30	10
Uptake of H_2/cm^3 STP	5.99	14.97
Reduced Ag^+ ions[a) /atoms per unit cell	13.9	34.8
{ Silver particles[b)	0	4.0
{ Silver clusters	13.9	30.8
Reoxidation		
Temperature/K	473	473
Time/min	10	30
Uptake of O_2/cm^3STP	3.01	6.65
Reoxidized Ag atoms[c) /atoms per unit cell	14.0	30.9
Silver particles[b) /atoms per unit cell	0	4.0

a) This value was evaluated from the amount of hydrogen consumption. b) This value was calculated from the peak area of a Ag(111) diffraction line. c) This value was evaluated from the amount of oxygen consumption.

It is perhaps worthy of remark that there was no induction period in the reoxidation process and no effect of water addition on the reoxidation rate, in contrast to the observations for Ag–Y zeolites reported by Beyer *et al.*[10)

Formation of Metallic Silver Particles. The rates of particle formation during the reduction in the static system were evaluated from the increment of peak areas of Ag(111) diffraction pattern in the range 522—573 K. The apparent activation energy of the particle formation was 74.0±5.8 kJ/mol.

Next the reduction of Ag^+ ions was performed under severe conditions, *i.e.*, a treatment with hydrogen at 673 K and 101.3 kPa for 1 h in the flow system. The results were plotted in Fig. 5. The amounts of silver particles shown in Fig. 5A were essentially equal to those obtained when the reduction temperature and time were set to 773 K and 5 h. In addition, a good linear correlation evidently exists between the amounts of Ag^+ ions supported in the zeolite and the quantities

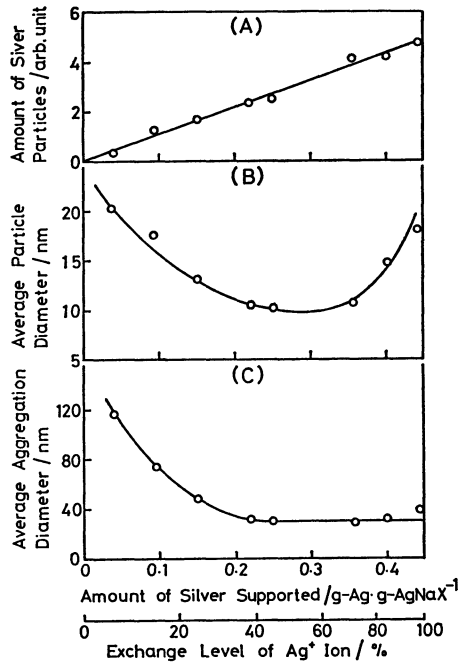

Fig. 5. Changes of amount of silver particles(A), particle diameter(B), and average aggregation diameter(C) with amount of silver supported. Reduction was performed at 673 K for 1 h by 101.3 kPa of hydrogen in the flow system.

of silver particles formed. Based on these facts, it was concluded that all Ag^+ ions were transferred into Ag particles. In Table 2, the amounts of Ag atoms converted into Ag particles were estimated by using this relation as a calibration.

In the experiments of Fig. 5, an irreversible destruction of the zeolite framework during the severe reduction was indicated by change in X-ray diffraction patterns. The diffraction patterns attributable to the zeolite structure were eliminated in proportion to the exchange level. After the reduction of AgNaX-99, for example, the diffraction patterns from the zeolites were completely disappeared and the formation of an amorphous phase was shown by the appearance of very broad and not intense peak. Under mild reduction conditions, however, the extent of the destruction was not so thorough, though the quantitative analysis concerning this phenomenon was not carried out.

The average diameters of the silver particles deduced from the line widths are shown in Fig. 5B. The diameter varied specifically with the Ag^+ ion-exchange level. It was approximately 20 nm for the low-exchanged AgNaX samples and decreased gradually with an increase in exchange level. The diameter increased after passing a minimum around 50% of the exchange level. The particle diameter were in the range 10—21 nm under these conditions. This value is in good agreement with 21 nm observed by Beyer *et al.*[10] and 15—30 nm by Tsutsumi and Takahashi.[8] Average aggregation diameters were evaluated by the following method from the results of Fig. 5B.

Since the crystal lattice of silver is of F. C. C., the number of Ag atoms included in a silver particles is given by $2\pi D_1^3/3A^3$ where D_1 represents the diameter of the silver particles and A is the lattice constant of silver crystal (0.4086 nm). On the other hand, the number of Ag^+ ions located in a unit cell of the X zeolite is $86E$, where E is an exchange level of Ag^+ ions. Therefore, writing the lattice constant of the zeolite (2.49 nm) as B, all silver ions situated in a volume of the zeolite given by $(2\pi D_1^3/3A^3)$ $(B^3/86E)$ were required to aggregate in order to form the silver particle. With an introduction of D_2 as a diameter of a sphere, whose volume is the same as that calculated above, Eq. 8 is

$$\frac{4}{3}\pi\left(\frac{D_2}{2}\right)^3 = \left(\frac{2\pi D_1^3}{3A^3}\right)\left(\frac{B^3}{86E}\right) \qquad (8)$$

$$D_2 = \frac{D_1 B}{A}\left(\frac{2}{43E}\right)^{1/3} \qquad (9)$$

set up and then Eq. 9 is derived. Here, D_2 is named an average aggregation diameter. This value indicates a range of the migration and aggregation of silver in the reduction process to yield a silver particle.

The results of the calculation using Eq. 9 are shown in Fig. 5C. The aggregation diameter took a large value as 120 nm at the low exchange level and gradually decreased with increasing the exchange level. In order to understand this phenomenon and gather more informations about the process of particles formation, following experiments were performed. Amounts and diameters of silver particles produced by the reduction of AgNaX-99 with 10.1 kPa of hydrogen in the flow system are plotted in Fig. 6 as functions of the reaction temperature and time. Clearly the amount of silver particles increased with the reaction time, while the particle diameters remained approximately constant irrespective of the reaction time. Moreover, the diameter showed a tendency to become larger at the higher temperatures.

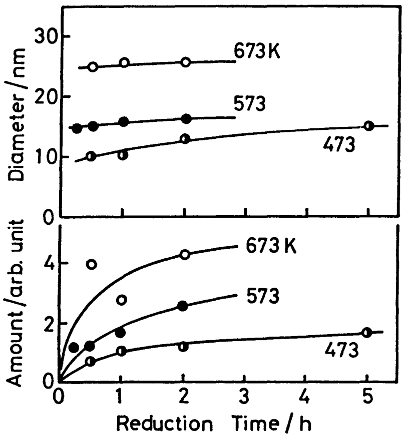

Fig. 6. Variations of amount and diameter of silver particles with reduction time at various temperatures. The reduction was performed by hydrogen at 10.1 kPa on AgNaX-99 in the flow system.

The above observations suggest that in the formation of silver particles a step of nucleation is rate-determining and a process of subsequent nuclear growth is relatively fast. The constant particle diameters independent on the reduction time in Fig. 6 would be understood as a result of a phenomenon that once a nucleus generates, all silver ions located in the aggregation diameter are rapidly gather to its nucleus. At the higher reaction temperatures the nucleation becomes more difficult because of the unstability of nucleus and the rate of the nuclear growth is more facilitated. These result in the formation of larger particles at the higher reduction temperatures, as shown in Fig. 6. In a similar manner to the above, the low exchange level of the Ag^+ ions makes the nucleation more difficult. This is the reason why the average aggregation diameter changed with the extent of the Ag^+ ion-exchange in Fig. 5C.

Conclusions

The reduction of the Ag^+ ions and the reoxidation of Ag atoms in X zeolites are found to proceed with ease, while the silver particles with a diameter of 10—25 nm produced in the severe reduction are difficult to be reoxidized. The processes are summarized in Eq. 10, where E_a represents an activation energy

$$\mathrm{Ag}^+ \underset{E_a=20.1\pm2.0}{\overset{E_a=23.4\pm1.6}{\rightleftarrows}} \mathrm{Ag}^0 \xrightarrow{E_a=74.0\pm5.8} \mathrm{Ag(particle)} \qquad (10)$$

of each step (kJ/mol). The reduction requires a catalytic activation of hydrogen at specific sites in the zeolites. Upon mild reduction some of the reduced silver atoms would form clusters in the supercage of the zeolites. The cluster might have a partial charge by the participation of unreacted silver ions, in a manner analogous to suggestions by Beyer *et al.*10) or Kimm and Seff.11) In the process of the particle formation it is suggested that the nucleation is rate-determining and its rate is varied with the reaction conditions. Che *et al.*21) have recently found that Ni^{2+} ions in X zeolites were reduced to Ni atoms at very low temperatures (77—273 K) by hydrogen atoms and that the growth of clusters was achieved by gradually heating of the reduced sample above the reduction temperatures. These results indicate the possibility that the formations of Ag clusters and particles might be carried out by a migration of Ag atoms.

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