The Formation of Metallic Silver in Silver-Form Zeolites

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The formation of silver crystallites in silver-form zeolites was investigated, mainly by means of X-ray diffraction analysis. Silver ions were reduced to the zero-valent state; they aggregated to metals in three cases in this study—first, when silver-form zeolites were heated in a helium flow at above 600°C; secondly, when they were reduced by hydrogen, and lastly, when they were treated with the alkyl benzenes or alcohols above 300°C. The silver crystallites had sizes of 150—400, 150—200, and 200—300Å respectively when Ag(31.6%)-Na-$Y_{4.6}$ was re-reduced in the three cases mentioned above. If the silver ions are reduced, the zeolite becomes decationated-form, in which metallic silver is dispersed. The silver metals formed in the zeolite have peculiar interactions with oxygen.

Zeolite has been known to be useful as a catalyst in various organic reactions,[1] since it is so highly crystalline that theoretical studies of its activity and active site seem easier than those of many other catalysts. Furthermore, the activity is much higher than that of conventional silica-alumina catalysts, so it has been widely used as a practecal catalyst.

The present authors previously found that the cumene-cracking activities of transition metal-form zeolites gradually increase with each slug of cumene, eventually attaining maximum values.[2] The data of magnetic susceptibility indicate that paramagnetic nickel-form zeolite becomes ferromagnetic during the reaction as a result of the formation of metallic nickel. Thus, transition metal cations, such as Ni^{2+}, Fe^{3+}, Co^{2+}, Cd^{2+}, and Cr^{3+}, incorporated into the zeolite were reduced to the metals when these zeolites were used for catalysts in the cumene-cracking reaction.

The formation of metal in zeolite has already been reported by many authors. Lawson *et al.* studied nickel-crystallite formation in a Ni-Y zeolite using a reduction with a hydrogen flow above 300°C, as detected by electronmicroscope and X-ray diffraction.[3] A significant portion of these crystallites appeared on the outside surface, destroying any possible size-selective characteristics. Mild pretreatment reduced the rate of crystal growth and produced a catalyst with a slightly improved poison resistance. Lewis reported on the platinum crystallite formation in a Pt-Y zeolite.[4] The X-ray absorption edge data showed that all the platinum was reduced to a zero-valent state, and that, on the average, this platinum was smaller in size than that found in conventional reforming catalysts. Sixty percent of the reduced platinum was estimated to be 10Å size or less. Yates found that reducible metal cations such as Cd^{2+}, Mg^{2+}, and Zn^{2+} can be removed from zeolites by hydrogen treatment.[5] The reduced nickel and silver were held loosely in the zeolite lattice because of their low vapor pressures. The average nickel crystallite size was 240Å. In each case, no free metals were formed when the samples were heated in a vacuum. Rabo *et al.* investigated, by ESR, the oxidation state of nickel ions contained in Ni-Y which had been treated by either sodium vapor or by hydrogen; they found the formation of Ni^0 at 575°C.[6] Gioia has reported the reduction of Ni-X by hydrogen.[7]

Alloy fromation on zeolite Y was reported by Reman *et al.*[8] If two types of metal ions were present, for instance Ni^{2+} and Cu^{2+}, reduction by hydrogen, under favorable circumstances, led to the formation of crystals of alloys. Alloy formation was found to have a profound influence on the type of conversion of *n*-hexane.

In almost all the cases mentioned above, the reductions were performed by hydrogen.

In this paper, the formation of silver crystallites in Ag-form zeolites with reduction by hydrocarbons, mainly cumene, and other substances were investigated by X-ray diffraction analysis.

Experimental

The starting materials were synthetic sodium faujasite (Na-$Y_{4.6}$,$Na_2O \cdot Al_2O_3 \cdot 4.6SiO_2 \cdot nH_2O$) and synthetic mordenite (Na-M,$Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot nH_2O$).

The ion exchange of sodium ions for the silver ion was performed by stirring an aqueous suspension of the Na-form zeolite in the presence of a proper amount of silver nitrate. This treatment was done in the dark to prevent the silver ion being reduced. The degree of ion exchange was determined from chemical analysis.

Hydrocarbons were guaranteed-grade samples which had been dehydrated with a molecular sieve 4A before use.

For studying the catalytic activity, a pulse microreactor was used. The details were described in a previous paper.[9] The reactants (or the reducing agents), alkylbenzene, alcohol, or hydrogen, were injected by means of a syringe and were fed to the catalyst with a flow of dry helim, the flow rate of which was 60 cc/min. The products were trapped and analyzed by gas chromatography.

The electronmicrographs were taken by means of a Hitachi HU-11A-type electronmicroscope.

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[2] K. Tsutsumi, S. Fiji, snd H. Takahashi, *J. Catal.*, **24**, 8 (1972).

[3] J. D. Lawson, and H. F. Rase, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 317 (1970).

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[6] J. A. Rabo, C. L. Angell, P. H. Kasai, and V. Schomaker, *Disc. Faraday Soc.*, **41**, 328 (1966).

[7] F. Gioia, G. Greco, Jr., and E. Drioli, *Chem. Ind.* (Milan) **71**, 457 (1969).

[8] W. G. Reman, A. H. Ali, and G. C. A. Schuit, *J. Catal.*, **20**, 374 (1971).

[9] K. Tsutsumi and H. Takahashi, *ibid.*, **24**, 1 (1972).

The X-ray powder diagrams were recorded by means of a X-ray diffractometer. The experimental conditions were as follows. Copper radiation was used; the scanning speed was 1° or 1/4° 2θ/min; the time constant was 2 sec; the receiving slit was 0.15 mm; the angular aperture was 1°. Silicon was used as the internal standard for the measurement of the crystallite size.

Results and Discussion

In Fig.1, the change in the cumene-cracking activities over Ag–Na–$Y_{4.6}$ with an increase in the Ag^+ exchange is shown in relation to the pulse number of the added cumene. The pretreatment was carried out at 450°C, and the reaction temperature was 350°C. As is clearly, the activities gradually increase with each slug of cumene until they attain a maximum value. The higher the extent of ion exchange or the reaction temperature, the greater the saturated activity. These tendencies are similar to those of transition metal-form zeolites such as Ni, Fe, Co, Cd, and Cr.[2] Therefore, the silver ion must be reduced to zero-valent silver, which aggregates to metal, during the reaction. At the same time, an active site, a decationated site, is newly formed. The activity was greatly decreased by the addition of oxgen at 450°C, and it could not be restored even if excess cumene was fed in. This behavior was surely connected with the formation of metallic silver.

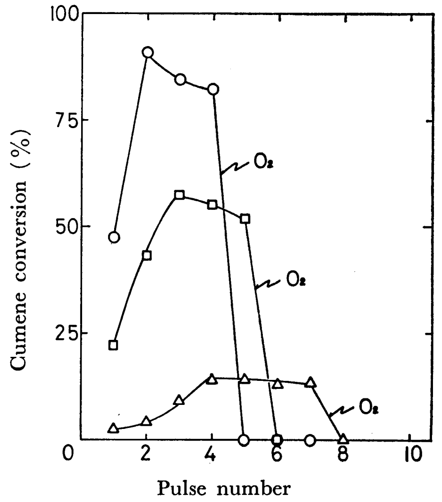


Fig. 1. Conversion of cumene over Ag-Na-$Y_{4.6}$ as a function of cumene pulse number and effect of oxygen addition.
—○— Ag(86.1%)-Na-$Y_{4.6}$
—□— Ag(31.6%)-Na-$Y_{4.6}$
—△— Ag(14.4%)-Na-$Y_{4.6}$

Table 1 shows the cumene-cracking activity of Ag(31.6%)–Na–$Y_{4.6}$ at 350°C after various hydrocarbons, alcohols, and water were added at 450°C. The addition of hydrocarbons and alcohols clearly induces the activity increase; thus, the reduction of the silver ion by such reagents must occur in the zeolite. Water molecules, however, have no influence on the catalytic activity.

The X-ray diffraction diagrams of Ag(31.6%)–Na–$Y_{4.6}$ treated in various ways are illustrated in Fig.2. The B, C, E and F samples have a new prominent peak at about $2\theta = 37.5°$ and 44.0° which is not observed in the original. Since these peaks correspond to the (111) and (200) reflections of crystalline silver, it is confirmed that silver ions are reduced to Ag, which then aggregates to metal. Metallic silver can be formed even by heat treatment in a helium

Table 1. Effects of the additives on the cumene conversion rate on Ag(31.6%)-Na-$Y_{4.6}$[a)]

Additives	Conversion rate (mol%)
Without addition	23.0
Toluene	46.0
Ethylbenzene	57.6
Cumene	60.7
t-Butylbenzene	56.9
p-Xylene	45.0
Mesitylene	34.1
Ethyl alcohol	22.1
i-Propyl alcohol	51.0
t-Butyl alcohol	54.2
Water	23.0

a) After 60 mg of Ag(31.6%)-Na-$Y_{4.6}$ was pretreated at 450°C and followed by addition of 5.7×10^{-5} mol of hydrocarbons, alcohol or water, the conversion rate of 5.7×10^{-5} mol cumene pulse was examined.

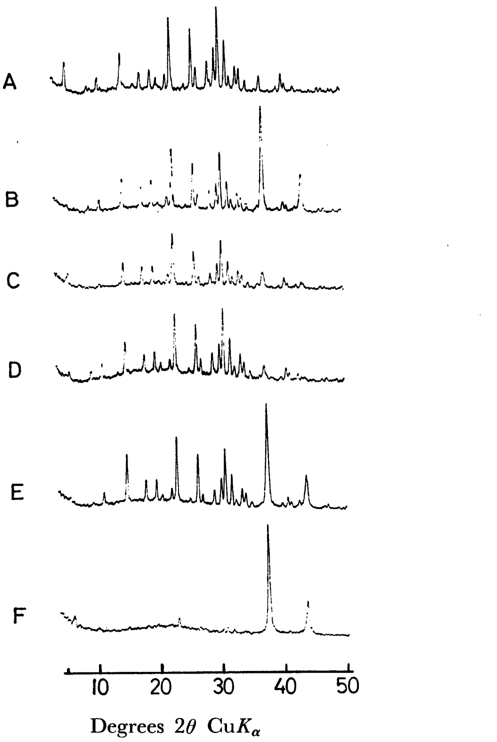


Fig. 2. X-ray diffraction patterns of Ag(31.6%)-Na-$Y_{4.6}$.
A: original.
B: treated in He at 750°C.
C: treated in He at 600°C.
D: pretreated in He at 450°C and followed by addition of cumene at 250°C.
E: pretreated in He at 450°C and followed by addition of cumene at 350°C.
F: pretreated in He at 450°C and followed by addition of cumene at 350°C and oxygen at 450°C.

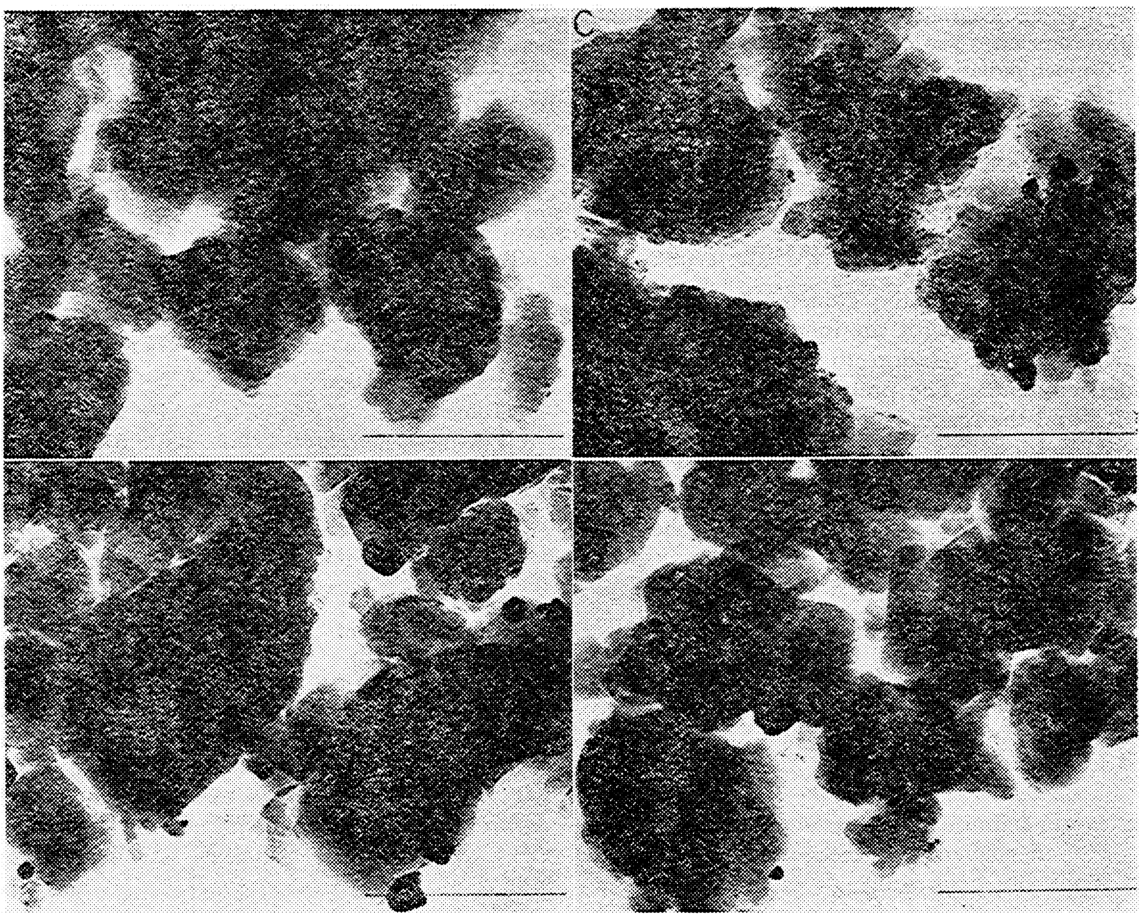


Fig. 3. Electronmicrographs of Ag(31.6%)-Na-$Y_{4.6}$. The linear dimension on electronmicrographs represents 0.5 μ.
A: original.
B: treated in He at 750°C.
C: pretreated in He at 450°C and followed by addition of cumene at 350°C.
D: pretreated in He at 450°C and followed by addition of cumene at 350°C and oxygen at 450°C.

flow at above 600°C; no such formation was observed in the case of Ni-form zeolites. The conversion of cumene and the formation of silver metal did not occur during the reaction below 250°C when the catalyst had been pretreated at 450°C. The oxygen addition destroyed the structure of the zeolite, as is shown in F: this agrees with the decrease in catalytic activity. The water addition under similar conditions induced no destruction of the structure and no decrease in the catalytic activity of zeolite.

The electronmicrographs of Ag(31.6%)–Na–$Y_{4.6}$ under various conditions are shown in Fig.3. There was no metallic silver in the original sample; however, its formation can be clearly observed in the B, C, and D species. The particle-size distribution in B is comparably uniform. The crystallite size of B is measured as 363Å by X-ray diffraction analysis, so the particle consists of several crystallites. The particle sizes in C are widely distributed. As is shown in D, the oxygen addition makes the particle size larger.

Judging from the particle size of metallic sliver, silver atoms which are formed with the reduction of ions are mobile and grow to the metallic state on the external surface.

Crystallite sizes of (200) faces of silver metals formed in Ag–Na–$Y_{4.6}$ under various conditions are listed in Table 2. The change in the crystallite sizes of the silver metals formed in Ag(31.6%)–Na–$Y_{4.6}$ with the heat treatment tempteature in the He flow is illustrated in Fig. 4. No formation of silver metal

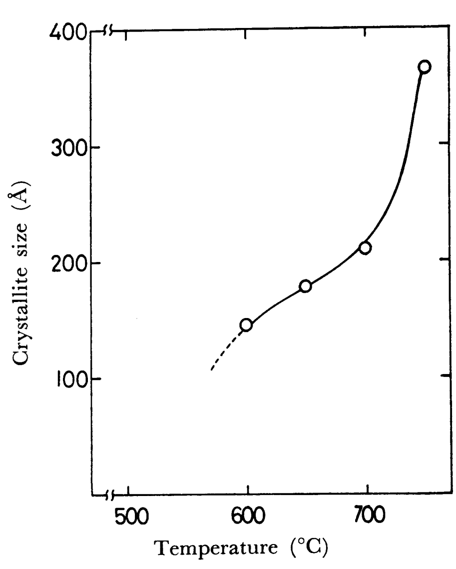


Fig. 4. Change of crystallite size of silver formed in Ag (31.6%)-Na-$Y_{4.6}$ with heat treatment temperature.

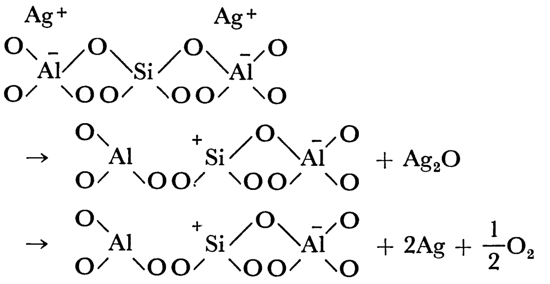
TABLE 2. CRYSTALLITE SIZES (L_{200}) OF SILVER FORMED IN Ag-Na-$Y_{4.6}$ UNDER VARIOUS CONDITIONS

Degree of Ag-exchange (mol%)	Pretreatment temperature (°C)	Reactant	Reaction temperature (°C)	L_{200} (Å)
31.6	450			—
31.6	550			trace
31.6	600			146
31.6	650			178
31.6	700			211
31.6	750			363
14.4	450	Cumene[a)]	350	179
22.3	450	Cumene	350	216
31.6	450	Cumene	350	253
86.1	450	Cumene	350	298
31.6	450	Cumene	250	—
31.6	450	Cumene	300	213
31.6	450	Cumene	450	285
31.6	750	Cumene	250	416
31.6	750	Cumene	300	436
31.6	750	Cumene	350	439
31.6	750	Cumene	450	428
31.6	450	Cumene 1[b)]	350	176
31.6	450	Cumene 3	350	219
31.6	450	Cumene 5	350	225
31.6	450	Cumene 7	350	226
31.6	450	Cumene 9	350	253

a) More than 1.4×10^{-3} mol-cumene was added to 200 mg of Ag-Na-$Y_{4.6}$.

b) One pulse of 1.4×10^{-4} mol-cumene was added to 200 mg of Ag-Na-$Y_{4.6}$.

is observed under a heat treatment at temperatures lower than 600°C. The higher the temperature, the larger the crystallite. The mechanism of metal formation under heat treatment is thought to be as follows:



(1)

Since Ag_2O could not be detected by X-ray diffraction analysis, Ag_2O probably exists in the transition state.

An increase in the degree of silver-exchange facilitates the formation of comparably large crystallites, as is shown in Fig.5. In view of the relation between the degree of exchange and the crystallite size, the number of crystallites formed seems to be nearly constant regardless of the degree of exchange. The number of cages necessary for the formation of one crystallite are 1.7, 1.9, 2.2, and 1.6×10^5 in the samples of Ag-Na-$Y_{4.6}$ where the degrees of exchange are 14.4, 22.3, 31.6, and 81.6% respectively.

The change in crystallite size with the pulse number

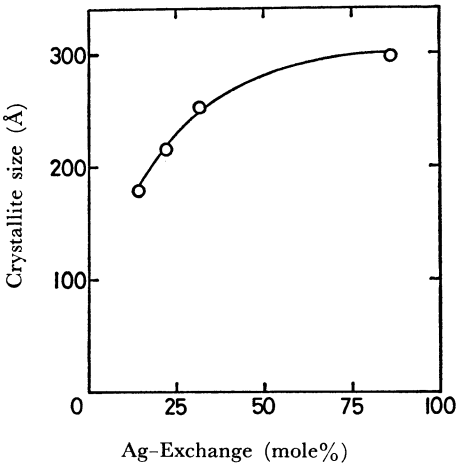


Fig. 5. Change of crystallite size of silver formed in Ag-Na-$Y_{4.6}$ with degree of Ag-exchange.

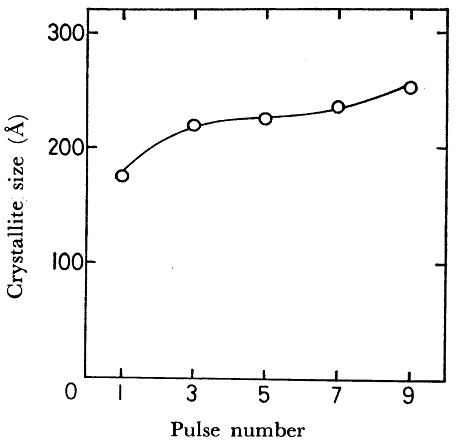


Fig. 6. Change of crystallite size of silver formed in Ag (31.6%)-Na-$Y_{4.6}$ with cumene pulse number.

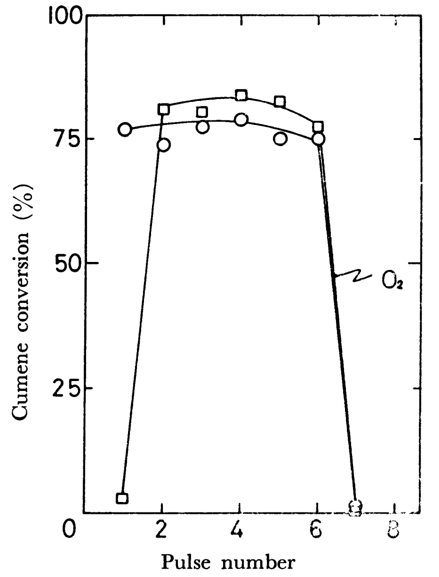


Fig. 7. Conversion of cumene over Ag (31.6%)-Na-$Y_{4.6}$ as a function of pulse number and effect of oxygen addition.

—○— pretreated in He at 450°C and followed by addition of hydrogen at 450°C before the reaction.

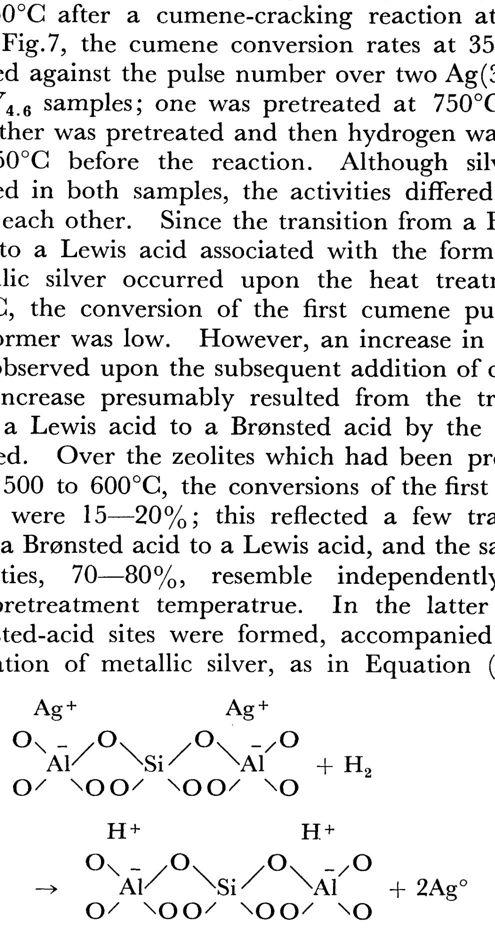
—□— pretreated in He at 750°C.

in Ag(31.6%)-Na-$Y_{4.6}$ is illustrated in Fig.6. The figure shows that the growth of the crystallite is related to the amount of cumene converted.

The dependence of the crystallite formation upon the reaction temperature in Ag(31.6%)-Na-$Y_{4.6}$ which has been pretreated at 450°C or 750°C is also shown in Table 2. When the zeolite is pretreated at 450°C, the crystallite size depends remarkably upon the reaction temperature; however, when it is pretreated at 750°C, the crystallite size formed in the reaction as 250°C is relatively large even though no cumene conversion occurred, and it merely changes at higher temperatures.

The crystallite size was increased to 261 or 320Å when oxgen was added to Ag(31.6%)-Na-$Y_{4.6}$ at 350 or 450°C after a cumene-cracking reaction at 350°C.

In Fig.7, the cumene conversion rates at 350°C are plotted against the pulse number over two Ag(31.6%)-Na-$Y_{4.6}$ samples; one was pretreated at 750°C, while the other was pretreated and then hydrogen was added at 450°C before the reaction. Although silver was formed in both samples, the activities differed greatly from each other. Since the transition from a Brønsted acid to a Lewis acid associated with the formation of metallic silver occurred upon the heat treatment at 750°C, the conversion of the first cumene pulse over the former was low. However, an increase in activity was observed upon the subsequent addition of cumene; this increase presumably resulted from the transition from a Lewis acid to a Brønsted acid by the cumene reacted. Over the zeolites which had been pretreated from 500 to 600°C, the conversions of the first cumene pulse were 15—20%; this reflected a few transitions from a Brønsted acid to a Lewis acid, and the saturated activities, 70—80%, resemble independently upon the pretreatment temperatrue. In the latter zeolite, Brønsted-acid sites were formed, accompanied by the formation of metallic silver, as in Equation (2):



(2)

Therefore, the reduction by cumene and the increase in activity no longer occurred. The crystallite size of the silver formed in this zeolite before the reaction was 176Å, much smaller than that of the silver formed in the earlier case. This fact suggests that the catalytic activity is not essentially influenced by the formation and the size of silver crystallite, but by the formation of the Brønsted acid site.

The radiation by ultraviolet rays did not facilitate reduction of silver ions in Ag-Na-$Y_{4.6}$ under various conditions—that is, at 35, 200°C in air or at 300°C in a vacuum.

In Fig.8, the conversion rates of cumene at 350°C over silver-exchanged mordenite-type zeolite pretreated at 450°C are shown. The silver formed in Ag(35.1%)-Na-Mord. by cumene addition at 350°C after pretreatment at 450°C has a relatively large crystallite size, though the pore diameter of mordenite is smaller than that of faujasite. The heat treatment at 750°C also induced the formation of large crystallites of silver. However, since the X-ray diffraction peak of the (200) face of silver is overlapped by the peak of mordenite, the measurement of the crystallite size by X-ray-diffraction analysis is difficult The conversion of cumene was decreased with each slug of cumene over Ag(35.0%)-H(64.7%)-Na-Mord. and only traces of silver formation were found. In Ag(68.6%)-H(26.8%)-Na-$Y_{4.6}$, no formation of silver was observed. In these cases, H-form sites contribute to the activity and cumene molecules interact more strongly with H^+ than with Ag^+. This behavior agrees with the finding of Richardson that the reducibility of supported nickel was small if the support had an increased acidity.[10]

Some work has been done on the reducibility of Ag(36.1%)-Ni(50.6%)-Na-$Y_{4.6}$ zeolite. The reduction of silver was preferred to that of nickel, and the

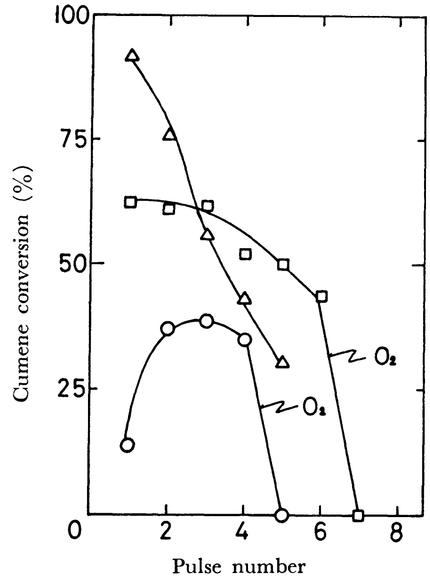


Fig. 8. Conversion of cumene over Ag-exchanged mordenite as a function of pulse number and effect of oxygen addition.

—○— Ag(35.1%)-Na-M pretreated at 450°C.
—□— Ag(35.1%)-Na-M pretreated at 750°C.
—△— Ag(35.0%)-H(64.7%)-Na-M pretreated at 450°C.

TABLE 3. CRYSTALLITE SIZES (L_{200}) OF SILVER FORMED IN Ag(36.1%)-Ni(50.6%)-Na-$Y_{4.6}$

Condition	L_{200} (Å)
Pretreated in He at 750°C	343
Pretreated in He at 450°C and followed by addition of cumene at 350°C	295
Pretreated in He at 450°C and followed by addition of hydrogen at 450°C	161

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[10] J. T. Richardson, *J. Catal.*, **21**, 122 (1971).

formation of alloy, which was reported by Reman *et al.* in the case of Ni–Cu–Y,[8) was not observed. The crystallite sizes of the silver in this zeolite are shown in Table 3. The sizes are similar to those of silver formed in Ag–Na–$Y_{4.6}$ under similar conditions.

We wish to thank Mr. Takashi Akeboshi for his assistance in carrying out the experiments.