Effects of Metal Particle Size in Gas-Phase Hydrogenation of Acetonitrile over Silica-Supported Platinum Catalysts

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The gas-phase hydrogenation of acetonitrile was studied with silica-supported platinum catalysts of which the degrees of metal dispersion were widely changed by reduction conditions. The activities were found to decrease gradually during the course of reaction for all the catalysts examined. The initial rate of reaction increased with an increase in the degree of platinum dispersion, *D*. Triethylamine was the only main product irrespective of *D* and period of reaction time. The initial turnover frequency, TOF_0, was shown to be smaller for larger *D* values. This dependence of TOF_0 on *D* was explained by the electronic state of the surface of the platinum particles and the state of acetonitrile molecules adsorbed on them on the basis of X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy measurements. The surface layer of smaller particles is more favorable for the adsorption of acetonitrile. The acetonitrile is adsorbed by platinum with the electron lone pair of nitrogen in the antibonding orbital, but electron back-donation does not takes place. As a result, the C≡N bonds of acetonitrile adsorbed on smaller particles are stronger and more difficult to hydrogenate.

1. Introduction

Amines have a wide range of applications such as solvents, agrochemicals, pharmaceuticals, and others. Catalytic hydrogenation of nitriles is an industrially important route for the production of a variety of amines. In the literature,[1,2] a number of works have described the liquid-phase hydrogenation of nitriles using transition-metal catalysts at high pressures of hydrogen, in which a mixture of primary, secondary, and tertiary amines is given as the products. The following reaction scheme is now well-accepted. Nitriles are hydrogenated to primary amines through aldimines. The primary amine reacts with the aldimine, yielding the 1-aminodialkylamine, which then changes to the secondary amine through elimination of an ammonia molecule and hydrogenation of the C═N group. The tertiary amine is formed analogously from the secondary amine and the aldimine. The control of activity and selectivity may be possible by changing catalysts and reaction conditions used.

A few groups have studied the catalytic hydrogenation of nitriles under gas-phase reaction conditions[3−10] and found interesting results that are different from those of liquid-phase hydrogenations. For example, Verhaak et al. indicated that the selectivity of supported nickel catalysts in acetonitrile hydrogenation depended on the acid−base properties of the support used.[6] Rode et al. showed that diethylamine was highly selectively formed by the hydrogenation of acetonitrile over supported platinum catalysts, in contrast to the selective formation of triethylamine by liquid-phase hydrogenations.[9]

Those results imply that the gas-phase hydrogenation of nitriles would be a suitable process for controlling the activity and selectivity in the production of amines. However, the features of these catalytic hydrogenations have not been well-understood. In the present work, our attention has focused on the influence of the degree of metal dispersion on the activity and selectivity. Recently Rode et al.[8] and Bond and Stone[7] examined the influence of metal dispersion on the hydrogenation of acetonitrile. The former group used nickel catalysts in which the degree of nickel dispersion was changed by using different supports and reduction temperatures, and the latter used magnesia-supported iron catalysts prepared by different methods. Rode et al. have showed turnover frequency (TOF) to increase with decreasing degree of nickel dispersion, while Bond and Stone have indicated an increase in the activity with the surface area of metallic iron.

The present work was undertaken to study the influence of metal dispersion of supported platinum catalysts on the gas-phase hydrogenation of acetonitrile. For this study, it is required to exclude the influence of support, including strong metal−support interactions and incompleteness of reduction of dispersed metal species, which were important in the previous studies. So, a silica gel was selected as an inert support, and the degree of platinum dispersion was changed by reduction conditions. The initial TOF was found to increase with a decrease in the platinum dispersion, similar to the cases of nickel catalysts.[8] Possible reasons for this structure (size) sensitivity were examined by characterizing the dispersed platinum particles by several techniques. It is significant to note here that the strength of carbon−nitrogen bonds of acetonitrile molecules is increased by the adsorption on smaller platinum particles, resulting in the lower specific activity in the hydrogenation.

A number of workers have been investigating the structure sensitivity for various catalytic reactions, and their results are reviewed in the literature.[11−14] The structure sensitivity includes a few different aspects, and it still remains a significant issue of catalytic chemistry.

2. Experimental Section

Catalyst Preparation. A silica gel, Davisil grade 646 of Aldrich Chemical Co., Inc., was used as a starting support

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material (nominal purity >99%). It was calcined in air at 973 K for 3 h, giving a BET surface area of 270 m^2 g^{-1}. Silica-supported platinum catalysts were prepared by wet impregnation by immersing the calcined silica gel in an aqueous solution of chloroplatinic acid, evaporating the solvent at around 320 K under reduced pressure, drying under vacuum at 383 K for 2 h, and reducing to metallic platinum by flowing hydrogen. The amount of metal loaded was 1 wt %, and the degree of metal dispersion was altered by changing reduction temperature in the range of 623 to 973 K and reduction period of time ranging from 0.5 to 3 h.

Activity Measurement. A fixed-bed reactor operated at atmospheric pressure was used for the measurement of activity for the hydrogenation of acetonitrile. Pure hydrogen was passed through a saturator of acetonitrile cooled at 273 K and then a catalyst bed of 0.01 g maintained at a constant temperature of 383 K. The inlet concentration of the acetonitrile was 7% in volume, and the products were analyzed by an on-line gas chromatograph. The details of activity measurements were described previously.[8,9] For three selected catalysts having different degrees of platinum dispersion of 0.13, 0.62, and 0.84, the weight of sample used was changed. It was found that the rate of reaction was proportional to the sample weight, showing that the reaction was under kinetic control under the present conditions.

Catalyst Characterization. Temperature-programed reduction (TPR) was conducted to make sure that the reduction was completed for all the catalysts prepared. The apparatus and procedures were the same as described elsewhere.[15] An unreduced silica-supported platinum (1 wt %) sample of 0.15 g was treated at 423 K under dynamic evacuation for 1 h. After the sample was cooled to room temperature, a mixture of hydrogen and argon (1:19 in volume) was passed through the sample at 50 mL min^{-1} and the sample temperature was raised at 10 K min^{-1}. A thermal conductivity detector (TCD) was used to detect the relative amount of hydrogen consumed.

The degree of platinum dispersion was measured by a static volmetric method using hydrogen. A catalyst sample (0.2 g) reduced at the desired temperature was reduced again by hydrogen at 623 K for 3 h and treated at 473 K under dynamic evacuation for 30 min. The hydrogen uptakes were then measured at room temperature and at different pressures in the range of 0.1−1.4 kPa. The monolayer coverage was determined by extrapolation of the square-root fit to zero pressure, and the number of exposed platinum atoms was calculated with a stoichiometry of H/Pt = 1.

The nature of surface layer of supported platinum particles was examined by X-ray photoelectron spectroscopy (XPS) with an ULVAC PHI ESCA 5600 with a resolution of 0.125 eV. The quantity of carbon species was observed to be less than 2 mol %, and so the measurements were performed without any pretreatment like Ar^+ sputtering. The binding energies measured were charge-referenced to a C 1s binding energy of 284.6 eV.[16]

Temperature-programed desorption (TPD) of hydrogen was conducted to examine the surface of catalysts with the same apparatus and procedures as used previously.[17,18] An unreduced sample was reduced by flowing hydrogen at the desired temperature for 3 h and heated at 30 K min^{-1} up to 973 K while passing a carrier gas of argon to remove the residual hydrogen. The reduced sample was exposed to a hydrogen stream at 383 K (reaction temperature) for 10 min and decreasing temperatures to room temperature for 10 min, a total of 20 min. The carrier gas was passed at room temperature until no desorption was detected by a TCD. Then, the sample was heated at 30 K min^{-1} and at a carrier gas flow rate of 30 mL min^{-1} to collect the TPD spectrum.

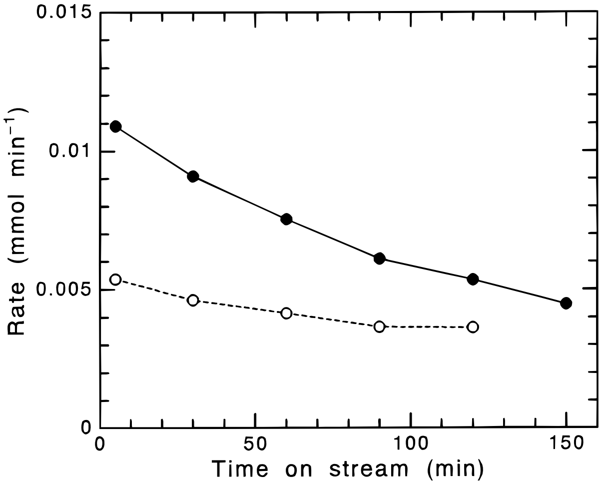

Figure 1. Rate of acetonitrile hydrogenation as a function of time on stream for two 1 wt % platinum/silica catalysts reduced at 673 K for 3 h (●) and at 1023 K for 5 h (○).

The state of acetonitrile adsorbed on the surface of catalysts was examined by Fourier transform infrared spectroscopy (FTIR) with a Perkin-Elmer 1600 model. A reduced sample of about 50 mg was ground in a mortar and pressed into a wafer of 2 cm in diameter. The wafer was treated in a glass cell by dynamic evacuation at 383 K for 3 h, and it was exposed to gaseous acetonitrile at an initial pressure of 9.3 kPa for 20 min at the same temperature and several minutes at decreasing temperatures to room temperature. The sample was then treated by dynamic evacuation at a certain temperature and subjected to the FTIR measurement, which was conducted in transmission mode with a nominal resolution of 2 cm^{-1} and an accumulation of 64 repeated times.

3. Results

Acetonitrile Hydrogenation. Figure 1 shows the rate of reaction (the rate of disappearance of acetonitrile reacted) as a function of time on stream for two selected catalysts reduced at 673 and 1023 K. For all the catalysts examined, it was found that they gradually lost their catalytic activities during the reaction and the extent of deactivation was smaller for less active catalyst. It was also found that triethylamine was the main product with very minor products of hydrocarbons for all the catalysts, for which the selectivities of triethylamine were around 95% and little changed with reaction time.

Figure 2 shows the influence of hydrogen treatment on the activity of a deactivated catalyst (originally reduced at 673 K). The catalyst can be regenerated by the treatment at a low temperature of 383 K (A and B) as well as 673 K (C), indicating that the deactivation during the reaction should not be due to serious causes including carbonaceous deposits, metal sintering, and poisoning. A possible explanation is that the active sites become covered by some products during the reaction. This possibility was examined by adding a small quantity of the main product, triethylamine, into the reaction mixture with a concentration of 0.17 mol %. Figure 3 shows the influence of triethylamine added on the initial catalytic activity. The activities are decreased by the addition of triethylamine, so the presence of triethylamine produced and adsorbed on the catalysts should be an important factor for their deactivation as observed during the reaction.

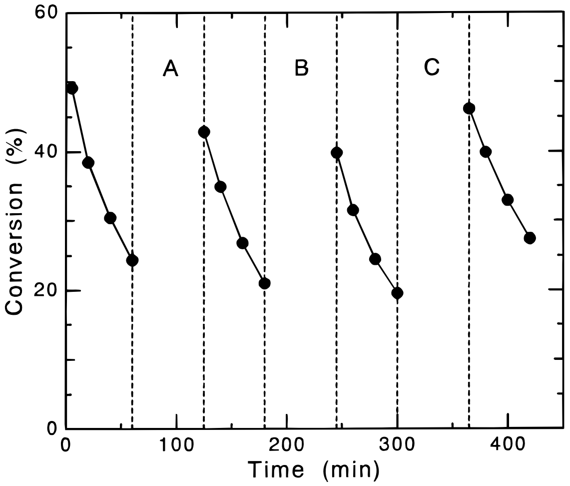

Figure 2. Influence of treatments with hydrogen (A, B, C) on regeneration of the activity of a catalyst originally reduced at 673 K. Between the activity measurements at 383 K, the catalyst was exposed to flowing hydrogen: (A, B) at 383 K for 60 min; (C) at 673 K for 30 min and at decreasing temperatures to 383 K for 30 min.

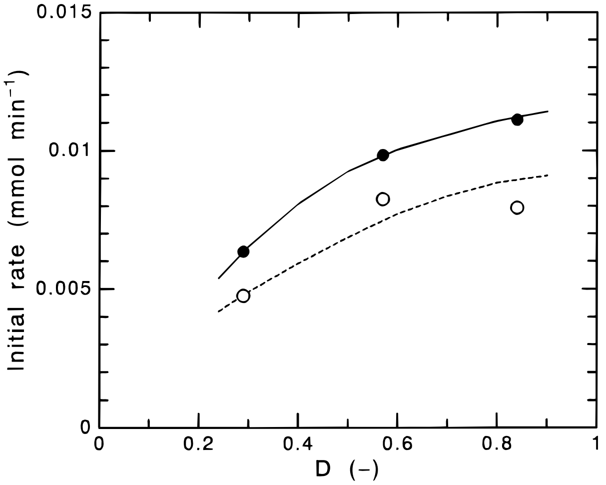

Figure 3. Initial rate of acetonitrile hydrogenation in the absence (●) and presence (○) of a small quantity of triethylamine added to the reaction mixture as a function of the degree of platinum dispersion, *D*, for 1 wt % platinum/silica catalysts.

Specific Activities. Either initial or steady activities may be used to compare the catalysts. Here we are mainly concerned with the former. Initial activities were obtained by extrapolation of such results as shown in Figure 1 to zero time on stream. Figure 4 shows the initial rate of reaction (sample weight 0.01 g) as a function of exposed platinum area. The activity does not linearly correlate to the platinum area. In Figure 5 the initial turnover frequency (TOF_0) is plotted against *D*, including results for 0.5 and 2.0 wt % platinum-loaded catalysts as well. It appears that TOF_0 is smaller for larger *D*, and this trend agrees with previous results obtained for the gas-phase hydrogenation of acetonitrile and benzonitrile over supported nickel catalysts.[8]

TPR and TPD. The TPR was conducted at a heating rate of 10 K min^{-1}. The TPR profile obtained was found to be similar to that measured previously with a sample of platinum tetraamine dichloride supported by ion exchange onto the same silica.[15] The profile indicated a sharp peak of hydrogen consumption at 390 K, and the consumption leveled off below 500 K. In the present work, the reduction temperatures used are 673 K or above, so the reduction of supported platinum species is completed at any temperature used.

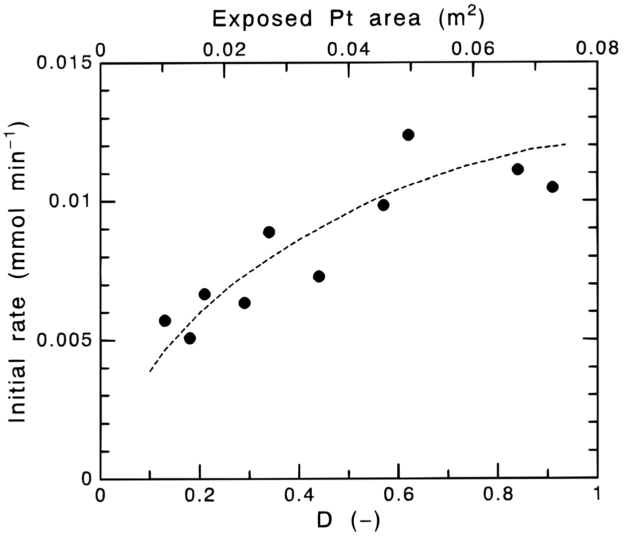

Figure 4. Initial rate of reaction as a function of the exposed platinum area for 1 wt % platinum/silica catalysts reduced at different temperatures. The data were collected using the same sample weight of 0.01 g for all the samples examined. The exposed area is directly proportional to the degree of platinum dispersion, *D*.

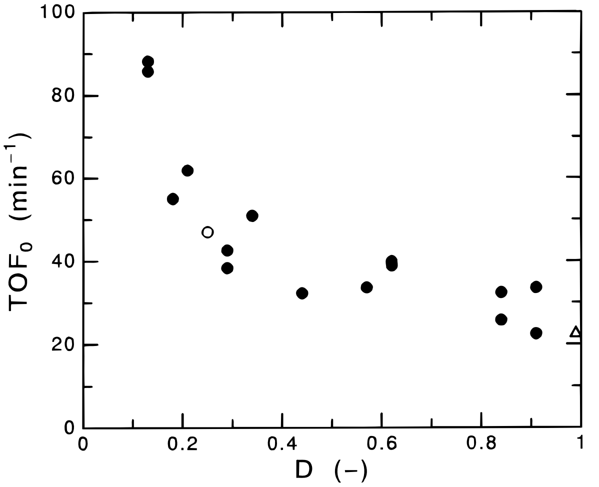

Figure 5. Plot of the initial turnover frequency (TOF_0) against the degree of platinum dispersion (*D*) for various silica-supported platinum catalysts. The amounts of platinum loaded are: 1.0 wt % (●), 0.5 wt % (△), and 2.0 wt % (○).

The TPD was examined with two catalysts reduced at 673 and 973 K. The amounts of hydrogen desorbing during the TPD were found to be very small compared with the total surface area of platinum particles of these samples, being only about 1% of those expected from the surface area. The adsorption of hydrogen by our silica-supported platinum catalysts is weak irrespective of *D*. The hydrogen species adsorbed were mostly swept off by the carrier gas at room temperature.

FTIR. Figure 6 shows FTIR spectra in the range of 2500−2000 cm^{-1} for three catalysts reduced at different temperatures of 673, 923, and 973 K. These data were collected after the evacuation at 370 K for 20 min following the adsorption of acetonitrile at 383 K. It is known in the literature[19−21] that the C≡N stretch of nitriles occurs in the 2210−2260 cm^{-1} region and the C≡N stretching frequency increases with linear coordination to metal centers by about 30 cm^{-1}. In Figure 6 two absorption peaks are found at 2262 cm^{-1} and a larger wavenumber, and they can be both assigned to the C≡N stretching vibration of acetonitrile. The former is due to acetonitrile adsorbed on the support, while the latter on the

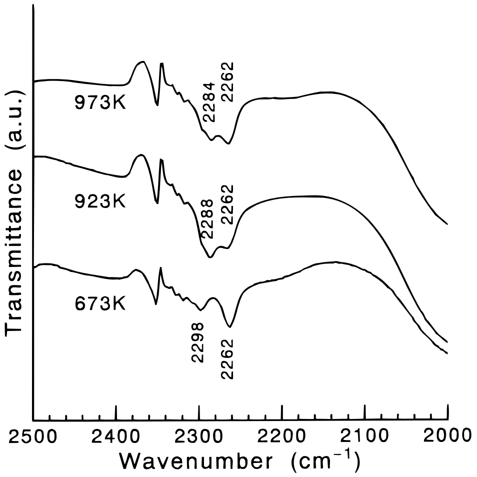

Figure 6. FTIR spectra of acetonitrile adsorbed on 1 wt % platinum/silica catalysts reduced at temperatures given. Increasing reduction temperature decreases the degree of platinum dispersion.

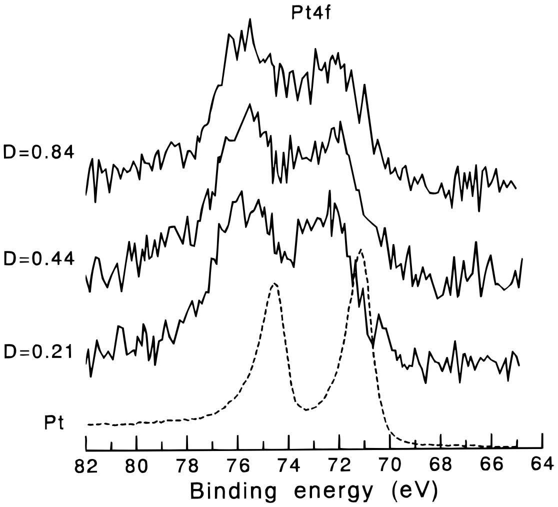

Figure 7. XPS Pt 4f spectra for 1 wt % platinum/silica catalysts reduced at 673 K ($D = 0.84$), 923 K ($D = 0.44$), and 973 K ($D = 0.21$), with a reference spectrum for bulk platinum.

surface of platinum particles, probably through linear coordination, which is the common mode of bonding between nitriles and metals. It should be noted from Figure 6 that the stretching frequency of acetonitrile adsorbed on platinum particles depends on the reduction temperature, i.e., the degree of metal dispersion. The stretching frequency tends to red-shift with a decrease in *D* (on increasing reduction temperature). This implies that the C≡N bond of acetonitrile adsorbed on larger platinum particles is weaker than that on smaller ones, and so it should be easier to be hydrogenated. Further discussion will be given in the following section.

XPS. Figure 7 shows Pt 4f spectra for three catalysts different in *D* with a reference spectrum of platinum foil. For the catalysts, we can see two peaks, which are present at higher binding energies, around 76 and 72 eV, and are broader compared with the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks of the foil. When *D* is smaller, the two peaks shift to lower binding energies. Similar changes with particle sizes are reported for supported platinum samples in the literature.[22−26] It can be said that we have observed a lower TOF_0 value for higher Pt 4f binding energy.

Figure 7 also indicates that the ratio of intensities of the two peaks changes with *D*. This may be ascribable to the size distribution of platinum particles, which should be different depending on *D*. Another possibility to consider is that some incompletely reduced platinum species ($Pt^{\delta+}$) are present at the metal/support interface. However, this is unlikely because our TPR result showed that the reduction was completed in our catalysts.

4. Discussion

The present results demonstrate that the gas-phase hydrogenation of acetonitrile over silica-supported platinum catalysts is structure-sensitive and the initial specific activity, TOF_0, increases with a decrease in the degree of platinum dispersion, *D*. This trend is the same dependence as found for nickel catalysts using several supports[8] and alumina- and silica-supported platinum catalysts.[9] For magnesia-supported iron catalysts, in contrast, Bond and Stone showed that the rate of acetonitrile hydrogenation correlated to the number of exposed metallic iron atoms.[7] From the results of Figure 1 and few other data for long reaction periods of time up to 120 min, the deactivated steady activities seemed to less significantly depend on *D* compared with the initial activities. The study of the influence of *D* on the deactivation and the resultant steady activity is now in progress in our laboratory. The following discussion is given to suggest causes for the dependence of TOF_0 on *D* observed.

Initial Activities. The variation of TOF_0 with *D* may be explained by invoking the difference in the electronic state of the surface layer of platinum particles and in the adsorption of reactants on them between the catalysts. Several XPS studies with supported platinum catalysts showed that the binding energies of Pt $4f_{7/2}$ and Pt $4d_{5/2}$ increased with an increase in *D*.[22−26] Huizinga et al. reported, for example, that the binding energies of Pt $4d_{5/2}$ were 314.0 and 314.4 eV for $D = 0.2$ and $D = 0.9$, respectively, for their alumina-supported platinum samples.[23] Our XPS results agree with those previous data. The difference in the electronic state may influence the adsorption of reactants on the surface of platinum particles. Since the adsorption of hydrogen by our catalysts is very weak irrespective of *D*, our attention should be given to acetonitrile.

The adsorption of acetonitrile was studied so far for a few metals by vibrational spectroscopies, and the limited data indicated that the bonding modes were similar to those found in metal complexes, as reviewed by Albert and Yates.[20] The adsorption of acetonitrile mostly occurs by an end-on interaction with the nitrogen lone pair; in only a few cases, it is adsorbed by an side-on interaction with the π system of the C≡N group. Vibrational spectroscopy studies indicate that the acetonitrile adsorbed by the end-on interaction has a higher C≡N stretching frequency compared with free gaseous acetonitrile, while the acetonitrile adsorbed by the side-on interaction has a smaller frequency. For the end-on case, the donor electron pair is C≡N antibonding and little back-donation should occur into the π^* level of the CN group, increasing the strength of the C≡N bond. For the side-on, however, the back-donation should occur, weakening the C≡N bond.

The present FTIR results indicate that the C≡N stretch occurs at higher frequency for the higher *D* value. The surface layer of smaller platinum particles is more favorable to the adsorption of acetonitrile and increases the strength of the C≡N bond of the adsorbed species. As a result, the C≡N bond of acetonitrile adsorbed by smaller platinum particles should be more difficult to hydrogenate. Thus, the specific activity of larger platinum particles is higher than that of smaller ones, as shown in Figure 5.

In previous work,[9] we examined the activities of silica- and alumina-supported platinum catalysts, which were prepared in different ways. The activity of the latter was higher compared with the former. The size of platinum particles may be important to explain this result as well, for which the present result is informative. In addition, we should consider the oxidation state of platinum species and/or some metal–support interactions. The reduction of platinum precursors was difficult to complete and the adsorption of hydrogen was very weak in the case of alumina support as indicated by TPR and TPD measurements. So, it is likely that there are incompletely reduced $Pt^{\delta+}$ species and/or there occurs the formation of an alloy between platinum and aluminum. However, the roles of these species other than metallic platinum are not clear at present.

Cabello et al. have recently studied gas-phase hydrogenation of acetonitrile on nickel-based catalysts prepared from hydrotalcite-like precursors.[10] They have reported that the hydrogenation of the nitrile to the imine takes place on nickel sites and the rate of this process determines the overall rate of reaction. According to reaction scheme proposed by Verhaak et al.,[6] Cabello et al. assume that the subsequent hydrogenation occurs on acid sites and nickel sites and the selectivity depends on the nature of those sites. The state of reduction of nickel was shown to be modified by addition of magnesium species. However, this does not affect the adsorption of acetonitrile and hydrogen as examined by the heats of adsorption, little influencing the rate of reaction.

In the present hydrogenation, triethylamine is the main product irrespective of *D*. As mentioned above, the electronic state of platinum particles depends on *D*, and it affects the reactivity of the CN group of adsorbed acetonitrile. However, this does not influence the selectivity, suggesting that the hydrogenation of the nitrile to the imine is the rate-determining step, as in the case of Cabello et al.,[10] and the following hydrogenation and condensation producing the tertiary amine are faster steps. Since the silica gel used is an inert support, it is less likely to play a role in the formation of triethylamine, and it should also occur on the surface of platinum particles. The role of support in the hydrogenation of nitriles has been given different opinions, and it is still a matter of argument. Volf and Pasek stated that the activity of supported nickel catalysts was influenced by the nature of support but the selectivity was not.[1] This agrees with our previous observations with nickel catalysts.[8] In contrast, Verhaak et al. indicated the significance of the acid–base properties of supports in determining the activity and selectivity of supported nickel catalysts.[6]

In a previous work, we found that diethylamine was produced with a selectivity higher than that of triethylamine by gas-phase hydrogenation of acetonitrile over supported platinum catalysts.[9] This is different from the present result that triethylamine is selectively formed. The previous catalysts were prepared from different metal precursor and support materials, platinum tetraamine dichloride and Silbead-N silica gel including Al_2O_3 in 2 wt % (Mizusawa Industrial Chemicals, Ltd.), through ion-exchange adsorption. The present results demonstrate that the high selectivity of triethylamine does not change with the size of metallic platinum particles. The previous catalysts should have other $Pt^{\delta+}$ species due to the incompleteness of reduction and/or the formation of an alloy with aluminum, as mentioned above. This may influence the selectivity as well as the activity. In addition, the acid/base properties of previous catalysts should be different, a probable reason being high pH value on the loading of platinum precursors, and this would also influence the selectivity. As pointed out by Nonneman et al., impurities present in the supports would be also important; wet impregnation can leach out the impurities, and they can end up on the surface of metal particles, modifying their catalytic activities.[27] Further work is needed to clarify the effects of the oxidation state of platinum and the supports.

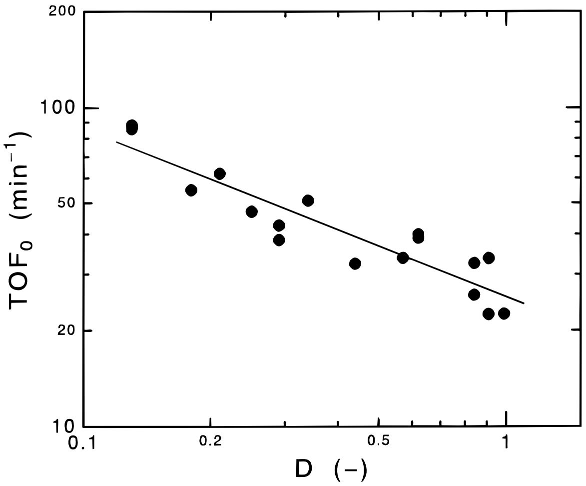

Figure 8. Logarithmic plot of TOF_0 against D for the data given in Figure 5, using the same symbol for all the catalysts different in the amount of platinum loaded.

Similar correlations between the specific activity and the degree of metal dispersion as observed in the present work are reported in the literature.[11] An example is the work of Boitiaux et al., who studied the liquid-phase hydrogenation of unsaturated hydrocarbons including 1-butyne, 1,3-butadiene, and isoprene over supported palladium catalysts.[28] It was observed that the turnover frequency decreased with an increase in the palladium dispersion. They explained that the low activities of very small particles were due to the formation of a strong complex of these hydrocarbons.

Structure Sensitivity. We should like to note a few aspects concerning the structure-sensitivity of supported metal catalysts. The results of Figure 5 are plotted in the logarithmic form in Figure 8, and one can see a good linear correlation. Similar correlations are reported for several catalytic reactions in the literature.[11] Farin and Avnir gave a phenomenological expression for those correlations and proposed a parameter to measure the structure sensitivity.[29] Recently we have proposed to use the slope itself of such a linear correlation as a measure of the degree of structure sensitivity.[30] In the present case, we can say that the reaction is negatively structure-sensitive and the degree of structure sensitivity is 0.53 ± 0.13 (95% confidence limits), which corresponds to a Farin and Avnir reaction dimension of 2.53. In addition, we have noted that TOF at $D = 1$ is more useful to examine the influence of support than TOF at $D < 1$ because the metal is in the form of two-dimensional islands at $D = 1$ and the influence of support should be the strongest in this extreme case. Those concepts have been applied to a few catalytic reactions in a recent work and are being used to examine the effects of various supports on the gas-phase hydrogenation of nitriles as well. Further, it is demonstrated in a few cases that the structure sensitivity depends on reaction conditions.[31–33] We should also pay attention to this respect in our cases by using different reaction conditions in future work.

In closing, we briefly deal with the deactivation during the course of hydrogenation. As described above, a possible explanation is that the main product, triethylamine, accumulates on the surface of catalysts, covering the active sites to cause the deactivation. The triethylamine is basic and its adsorption would be promoted by smaller platinum particles (larger *D*), similar to acetonitrile. In addition, triethylamine is a large molecule, so its adsorption would be easier for smaller particles (large curvature) owing to less steric effects.

5. Conclusion

It has been demonstrated that the gas-phase hydrogenation of acetonitrile over silica-supported platinum catalysts is sensitive with respect to the degree of platinum dispersion. The initial specific activity, TOF_0, decreases with an increase in the degree of platinum dispersion, while the product distribution little depends on it, tertiary amine being the main product. It is believed that the overall rate of reaction is determined by a step of hydrogenation of the adsorbed nitrile into the imine. The adsorption of acetonitrile is influenced by the size of platinum particles. The surface of smaller particles is more favorable for the adsorption of acetonitrile by its antibonding lone electron pair. This should increase the strength of the $C\equiv N$ bond, making it more difficult to hydrogenate the acetonitrile adsorbed by smaller particles.

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