

Temperature-Programmed Desorption of Dimethylpyridine Adsorbed on Silica-Alumina Prepared by Chemical Vapor Deposition

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Synopsis. A temperature-programmed desorption of adsorbed dimethylpyridine clarified the characteristic changes in acid type, acid strength, and acid amount of silica-alumina prepared by depositing silica on an alumina support. Lewis acid sites of the alumina changed into Brønsted acid sites together with a change in the acid strength with increasing silica deposition.

We previously prepared a supported type of silica-alumina by depositing silica on an alumina surface by means of chemical vapor deposition (CVD).^{1,2} Silica was effectively deposited on alumina using tetraethoxysilane in the presence of oxygen at 240 °C, and silica loading was readily controlled by the CVD time. The resulting silica-alumina (CVD SiO₂/Al₂O₃) exhibited high catalytic activities for several types of organic reactions such as 2-butanol dehydration, *m*-xylene isomerization, cumene cracking, and heptane cracking. The catalytic activity for 2-butanol dehydration varied with silica loading, and was correlated to the amount of Brønsted acid determined from the extent of the liberated proton in the phase of an aqueous solution.²⁾

However, the acid property, especially acid strength, in the absence of water has not been clarified. In this work, a temperature-programmed desorption (TPD) of dimethylpyridine (DMP) adsorbed on a CVD SiO₂/Al₂O₃ catalyst using a conductivity cell immersed in a dilute H₂SO₄ solution was carried out in order to evaluate the entire acid property, including acid type (Brønsted or Lewis), acid strength, and acid amount.

Experimental

Alumina supplied by Dia Catalyst & Chemicals Ltd. (DC-2282: specific surface area, 203 m² g⁻¹; pore volume, 0.72 ml g⁻¹; granule size, 24–60 mesh.) was used as a support. A CVD SiO₂/Al₂O₃ catalyst was prepared by contacting tetraethoxysilane vapor with the alumina support in a CVD reactor which comprised a glass column rotating in an electrical furnace inclined at 45° at 240 and 300 °C for a prescribed time in a stream of air and nitrogen, respectively;²⁾ the flow rates of tetraethoxysilane and carrier gas were 2.7 and 400 mmol h⁻¹, respectively. The silica loading was determined by measuring the weight increase of the alumina support after CVD operation followed by calcination at 550 °C for 3 h. K⁺ ion-exchange was performed by immersing a sample in 2 mol dm⁻³ potassium chloride solution at room temperature for 2 h.

After a sample (50 mg) placed in a quartz tube (i.d. 4 mm) with quartz wool had been evacuated at 500 °C for 1 h, excess DMP was injected via a microsyringe at 200 °C, and then evacuated at 200 °C for 1 h. A TPD measurement was carried out from 100 to 600 °C at a heating rate of 5 °C min⁻¹ in a nitrogen flow of 30 ml min⁻¹. The desorbed DMP was

monitored by a conductivity cell immersed in aqueous sulfuric acid (1/2000 mol dm⁻³). A cumulative amount of desorbed DMP as a function of the desorption temperature was recorded, then differentiated to give the acid strength distribution. Independently, desorbed molecules were collected at -196 °C, then analyzed by GLC.

The isomerization of 1-butene was carried out in a closed circulation system (reactor volume, 200 ml; catalyst, 0.05 g) under the conditions of a 1-butene initial pressure of 19 kPa at 0 °C. Prior to the reaction, the catalyst was preheated at 500 °C under reduced pressure (0.1 Pa). The catalytic activity was evaluated in terms of the first-order rate constant during the initial reaction period.

Results and Discussion

Decomposition of DMP was preliminarily examined. In the TPD process above 500 °C, about 30% of the 3,5-DMP desorbed from the alumina was decomposed into 3-methylpyridine and pyridine. The desorbed amines were detected by the change in the conductivity of a cell solution in which protons are neutralized with them. The conductivity detector was sensitive to such amines as pyridine and DMP, but insensitive to desorbed water as well as to such neutral molecules as benzene and ethanol. In addition, the sensitivity for DMP was almost the same as those for methylpyridine and pyridine. The conductivity detector, therefore, is convenient for the TPD measurement of adsorbed DMP.

Figure 1 shows the cumulative amounts of DMP desorbed from the catalysts. For the alumina support, itself, the cumulative amounts of desorbed DMP were 106 and 14 μmol g⁻¹ for 3,5- and 2,6-DMP, respectively. For the CVD SiO₂ (12wt%)/Al₂O₃ prepared at 240 °C

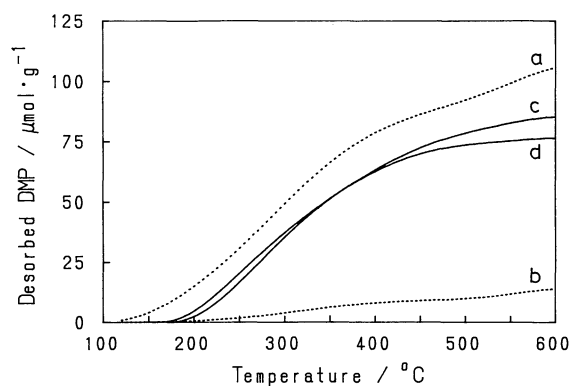


Fig. 1. Cumulative amount of desorbed dimethylpyridine (DMP). Alumina: a, 3,5-DMP; b, 2,6-DMP; CVD SiO₂ (12.4 wt%)/Al₂O₃: c, 3,5-DMP; d, 2,6-DMP.

in air, they were 85 and 77 $\mu\text{mol g}^{-1}$ for 3,5- and 2,6-DMP, respectively. 2,6-DMP is known to selectively adsorb on Brønsted acid sites because of the steric hindrance arising from the two methyl groups, each of which is located adjacent to the nitrogen atom, whereas non-hindered 3,5-DMP is capable of adsorbing on both Lewis and Brønsted acid sites.³⁻⁵ The adsorption of 2,6-DMP on the alumina was seriously restricted, compared to that of 3,5-DMP. The acid amounts measured by 3,5-DMP were also comparable to the amount measured by pyridine.

Figures 2 and 3 show the acid strength distribution of the catalysts. The alumina had a large desorption peak of 3,5-DMP at 300 °C with a shoulder at 570 °C, whereas two small desorption peaks of 2,6-DMP appeared at 300 and 560 °C (Fig. 2). The small peak of 2,6-DMP at 300 °C (Fig. 2b) appears to be caused by desorption from weak Brønsted acid sites. The small peak at 560 °C (Fig. 2b), however, seems to be attributable not to strong Brønsted acid sites, but to strong Lewis acid sites, since alumina has no strong Brønsted acid sites.^{2,6} Additionally, IR spectroscopic observations have revealed that 2,6-di-*t*-butylpyridine is strongly adsorbed on alumina,⁷ and that 2,6-DMP adsorb on Lewis acid sites together with weak Brønsted acid sites,⁸ whereas they have not dealt with the quantitative aspects. Although the TPD of

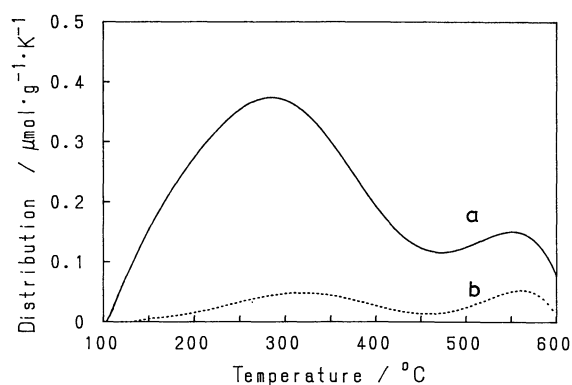


Fig. 2. TPD profiles of alumina. a, 3,5-DMP; b, 2,6-DMP.

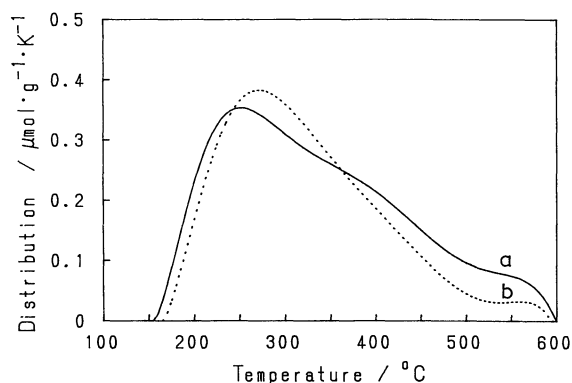


Fig. 3. TPD profiles of CVD SiO₂ (12.4 wt%)/Al₂O₃. a, 3,5-DMP; b, 2,6-DMP.

adsorbed 2,6-DMP tends to overestimate the Brønsted acid sites, the large difference between the distribution curves for 3,5- and 2,6-DMP indicates clearly that the acid sites of the alumina are predominantly composed of the Lewis type. On the other hand, the CVD SiO₂ (12wt%)/Al₂O₃ had a wide distribution at a peak top of 250 and 275 °C for 3,5- and 2,6-DMP, respectively (Fig. 3). Since there is no significant difference between two distribution curves for 3,5- and 2,6-DMP, the CVD SiO₂/Al₂O₃ catalyst has a large amount of Brønsted acid sites together with a small amount of strong Lewis acid sites.

Figure 4 shows the change in the acid strength distribution measured by the desorption of 2,6-DMP for CVD catalysts prepared at 240 °C in air. When a small amount of silica (5 wt%) was deposited on alumina, the amount of 2,6-DMP desorbed near 250 °C was drastically increased (Fig. 4b). A further increase in silica deposition induced an increase in the strong acid sites represented by desorption around 400 °C; both the highest acid strength and the maximum amount of desorbed 2,6-DMP were attained at a silica loading of 12 wt% (Fig. 4c). Above 12 wt%, the amount was decreased with increasing silica loading, together with a small change in the acid strength (Fig. 4d). On the other hand, the desorption behavior of 3,5-DMP was similar to that of alumina, as is shown in Figs. 2 and 3.

Figure 5 shows changes in the amount of desorbed DMP with silica loading. The amount of desorbed 3,5-DMP was almost unchanged up to about 10 wt% of silica; above this loading it slightly decreased with increasing silica loading. In contrast, the amount of desorbed 2,6-DMP exhibited a maximum at a silica loading of 12 wt%. According to a preliminary ³¹P magic-angle spinning NMR experiment of chemisorbed trimethylphosphine, the alumina had predominately Lewis acid sites, and Brønsted acid sites were generated on the CVD SiO₂/Al₂O₃, accompanying the disappearance of the Lewis acid sites.² The TPD results are consistent with the ³¹P NMR results, and are allowed to characterize the strength of Brønsted acid sites of the CVD SiO₂/Al₂O₃ catalysts.

For the isomerization of 1-butene, the catalytic

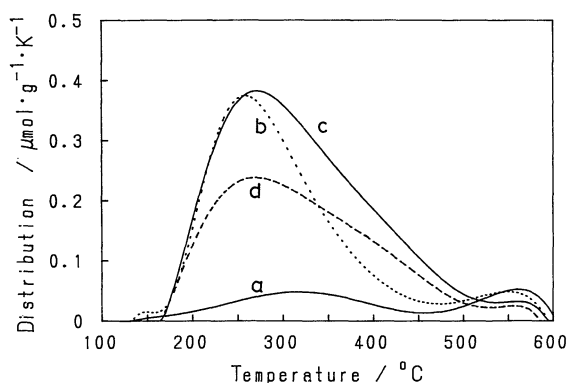


Fig. 4. TPD profiles of 2,6-dimethylpyridine adsorbed on CVD SiO₂/Al₂O₃. Silica loading: a, 0 wt%; b, 5.1 wt%; c, 12.4 wt%; d, 20.3 wt%.

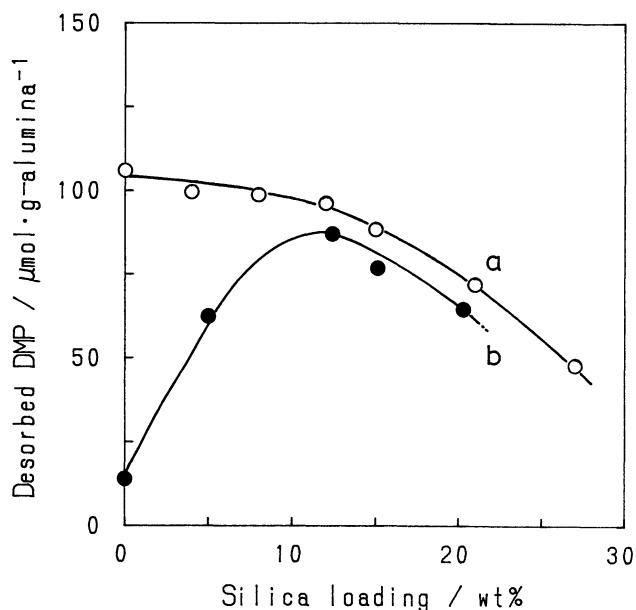


Fig. 5. Change in the total amount of desorbed DMP with silica loading. a, 3,5-DMP; b, 2,6-DMP.

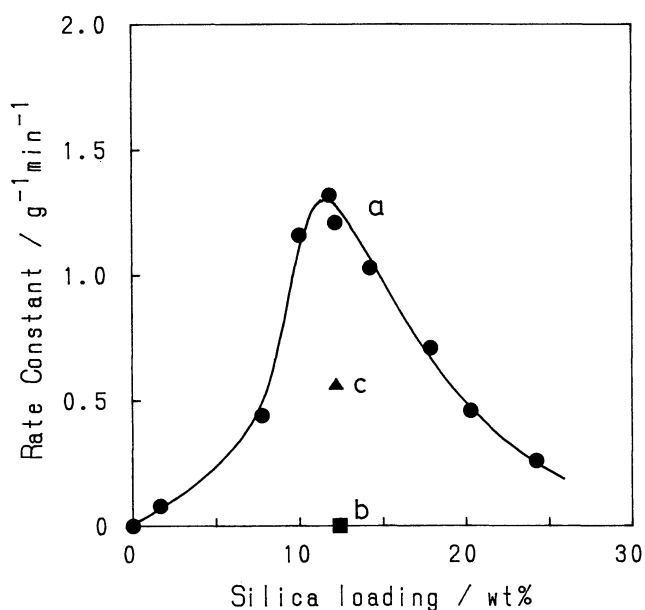


Fig. 6. Change in the initial rate constant for 1-butene isomerization. a, CVD $\text{SiO}_2/\text{Al}_2\text{O}_3$ prepared at 240°C in air; b, CVD SiO_2 (12.4 wt%)/ Al_2O_3 exchanged with 0.11 mmol g^{-1} of K^+ ion; c, CVD SiO_2 (12.2 wt%)/ Al_2O_3 prepared at 300°C in nitrogen.

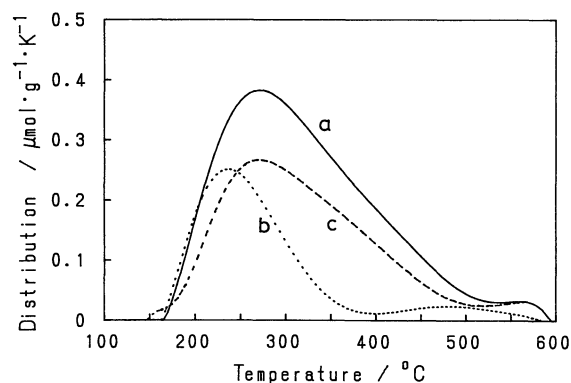


Fig. 7. TPD profiles of 2,6-DMP for various CVD SiO_2 (12 wt%)/ Al_2O_3 catalysts. Symbols as those in Fig. 6.

activity was changed with silica loading (Fig. 6), and was maximized at a silica loading of 12 wt%, at which both the acid strength and amount measured by 2,6-DMP desorption showed maxima. Moreover, the CVD $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst has a cation-exchange ability,² and an exchange of a proton with the K^+ ion suppressed the catalytic activity for 1-butene isomerization (Fig. 6b). The K^+ ion-exchange decreased both the acid strength and the amount (Fig. 7b), and the amount of desorbed 2,6-DMP drastically decreased at temperatures higher than 400°C . In addition, a CVD $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst prepared at 300°C in nitrogen, which had a smaller amount of desorbed 2,6-DMP (Fig. 7c), was less active than that prepared at 240°C in air (Fig. 6c). The catalytic behavior are well correlated with the Brønsted acidity measured by 2,6-DMP desorption.

References

- 1) S. Sato, M. Toita, Y. Q. Yu, T. Sodesawa, and F. Nozaki, *Chem. Lett.*, **1987**, 1535.
- 2) S. Sato, M. Toita, T. Sodesawa, and F. Nozaki, *Appl. Catal.*, **62**, 73 (1990).
- 3) H. A. Benesi, *J. Catal.*, **28**, 176 (1973).
- 4) S. L. Soled, G. B. McVicker, L. L. Murrell, L. G. Sherman, N. C. Dispenziere, Jr., S. L. Hsu, and D. Waldman, *J. Catal.*, **111**, 286 (1988).
- 5) L. L. Murrell and N. C. Dispenziere, Jr., *J. Catal.*, **117**, 275 (1989).
- 6) K. Tanabe, M. Misono, Y. Ono, and H. Hattori, *Stud. Surf. Sci. Catal.*, **51**, 82 (1989).
- 7) J. Dewing, G. T. Monks, and B. Youll, *J. Catal.*, **44**, 226 (1976).
- 8) A. Corma, C. Rodellas, and V. Fornes, *J. Catal.*, **88**, 374 (1984).