A Silica Monolayer on Alumina and Evidence of Lack of Acidity of Silanol Attached to Alumina

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A silica monolayer on alumina was formed by chemical vapour deposition of silicon methoxide; almost all the silanol attached to the alumina did not form a Brønsted acid site.

Silica–alumina catalysts are typical and well-known solid acids, and the formation of the acid site in the binary mixture has been investigated. The model proposed by Thomas,[1] *i.e.*, isomorphous replacement of aluminium within the silica matrix, seems to be well accepted, since this structure is in good agreement with the accepted one of decationized zeolites. The problem has also been investigated by quantum chemical calculations, and a few cluster models have been proposed.[2—4] However, the exact structure of the acid site has not been determined yet, because appropriate methods for experimental confirmation of the generation of acid sites are not available. One promising method relies on study of well-defined surfaces. Based upon these considerations, we applied the CVD (chemical vapour deposition) method which is currently used for control of zeolite pore size[5] and formation of thin layers on oxides.[6,7] Our intention was to prepare a silica monolayer on alumina in order to check whether the silanol attached to the alumina possesses acidity or not.

A silica monolayer was prepared by CVD of silicon methoxide vapour (1.5 Torr at 273 K) on Al_2O_3 (JRC-ALO 4, 176 m^2 g^{-1}, a reference catalyst supplied from the Catalysis Society of Japan) at 593 K. The deposition was readily terminated owing to inhibition of mass-transfer of alkoxide in the vessel; the exhaust gas was evacuated, and then alkoxide admitted again to continue the deposition. Finally, hydrolysis by water vapour removed the methoxide residue completely. Discrimination between the silica-covered surface and the exposed surface of alumina was made by benzaldehyde–

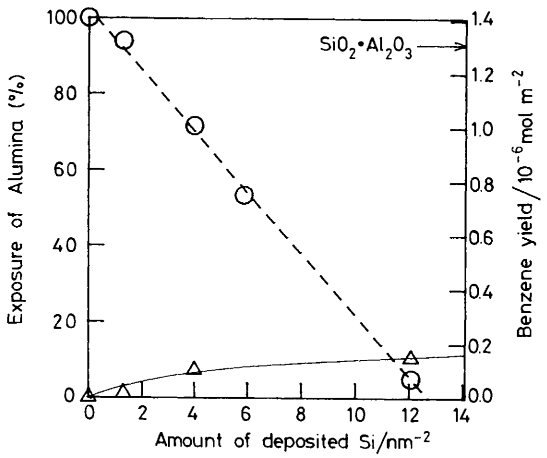

Figure 1. Relationship between the exposure of alumina (○) and the catalytic activity in the cracking of isopropylbenzene (△) and the concentration of Si deposited.

ammonia titration (a method which was derived from the principle of selective adsorption of benzoate species on alumina, see details in ref. 8). The acidic profile was determined by cracking of isopropylbenzene at 623 K, a test reaction studied by pulse techniques, and the i.r. spectra of adsorbed pyridine.

Figure 1 shows the relationship between concentration of deposited silicon and the exposure of the alumina surface, defined as the alumina surface area divided by the total surface area. The exposure of alumina decreased linearly with the surface concentration of deposited silicon, and became zero at 13 Si nm^{-2}. Because the cation site density on the surface of Al_2O_3 is 14.5 nm^{-2},[9] this relationship indicates that silicon is deposited with a 1:1 bonding to aluminium (Si–O–Al), and a silica monolayer with a simple structure can be obtained. I.r. spectra of the full-coverage silica monolayer showed a silanol absorption at 3745 cm^{-1}, and absorptions due to four types of hydroxide on alumina at 3768, 3730, 3674, and 3585 cm^{-1} were no longer present. This adds support to the above conclusion.

Catalytic activity in the cracking of isopropylbenzene (cumene) on these silica-covered alumina surfaces increased with the amount of deposited silicon, but activities were very small compared to that on a silica–alumina catalyst (1.31×10^{-6} mol m^{-2} on silica–alumina, Nikki N-631 L), as shown in Figure 1. Because the active sites on the silica–alumina catalyst do not seem to be dispersed completely, the activity would be lower than the experimentally obtained value. Because cracking of cumene was observed on silica–alumina, but not on alumina, it occurs on the Brønsted acidic sites. Therefore, the small catalytic activity on the silica-coated alumina indicates that almost all the deposited silicon does not form Brønsted acid sites. I.r. spectra of pyridine adsorbed on the silica monolayer showed only a small peak at 1545 cm^{-1} which may be ascribed to the Brønsted acid site. Therefore, the silanol attached to the alumina (Al–O–Si–OH) is not a species which shows Brønsted acidity in the binary mixture of the silica–alumina catalyst.

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