Formation of Size-controlled Micro-pores in Amorphous Mixed Oxides by an Advanced Sol–Gel Method

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Micro-pores in amorphous mixed oxides can be designed by an advanced sol–gel method using various diols as the pore-forming agents.

The size of pores in solid catalysts is an important element for the realization of regioselective reactions. Shape-selective reactions are important in this respect, for example the alkylation of toluene using certain crystalline zeolites.[1] However, in amorphous solids, it is difficult to form size-controlled micropores which can have a molecular sieving effect similar to that of zeolites. This may explain why shape-selective reactions have not so far been achieved with amorphous solid acid catalysts.

We thought that size-controlled micropores could be constructed in amorphous metal oxides by incorporating organic molecules into the metal oxide polymers at the molecular level in their syntheses, or preparing the metal oxide particles using organic compounds as the core molecules, and then burning the organic moieties.

Amorphous mixed oxide particles containing organic moieties were synthesized by an advanced sol–gel method (chemical mixing procedure)[2,3] as follows. A tetraalkoxysilane and an aluminium alkoxide or aluminium–diketone complex were mixed in an ethanol–diol solution containing dimethyl sulphate, and then stirred and warmed (step 1). When the solution appeared homogeneous, water was added to the solution to hydrolyse the various diol–metal complexes formed by ligand exchange reaction at step 1 (step 2). The solution then became viscous and finally coagulated into a transparent gel. The gel was dried under reduced pressure at *ca.* 383 K (step 3). Figure 1 shows the thermogravimetric (TG) analyses of the dry gels prepared by the advanced sol–gel method and a conventional coprecipitation method. Both dry gels (A and B) prepared in diols showed a weight loss at higher

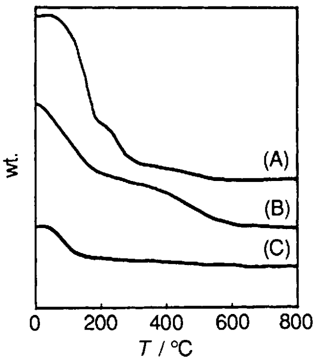

Figure 1. Thermogravimetric analyses of silica–alumina dry gels: (A), advanced sol–gel method (diol = ethylene glycol); (B), advanced sol–gel method (diol = 2-methylpentane-2,4-diol); (C), coprecipitation method.

temperatures (400—600 °C) than the boiling points of water and diols. Corresponding to this, differential thermal analysis of the dry gels in air showed exothermic peaks in this temperature region. Furthermore, it was confirmed by TG–mass spectrometry that both the weight losses result from the decomposition of the diols which were used in the gel preparation and contained in the dry gels. In contrast, the coprecipitation dry gel (C) showed hardly any weight loss at such temperatures. These results suggest that the gels (A) and (B) contain organic residues chemically bonded in the metal oxide frameworks,[4] whereas gel (C) does not have such organic residues.

In the final step, the dry gels obtained by the above sol–gel procedure were finely powdered, and calcined at 823 K for 8 h. Figure 2 shows the micropore distributions of Y-zeolite and the amorphous silica–aluminas prepared by the coprecipitation and the advanced sol–gel methods. The micropore distributions were measured by the Horváth–Kawazoe method[5] from nitrogen isotherms at 77.4 K with an Omnisorp 100 (Omicron Tech. Co.) instrument. The coprecipitated silica–aluminas (specific surface area 369 m^2 g^{-1}) and a commercial silica–alumina (Nikki N-631, specific surface area 358 m^2 g^{-1}) are found to have only a few micropores. The advanced sol–gel silica–aluminas have much bigger pore volumes than the other samples (C) and (D), and the micropore distributions of the sol–gel silica–aluminas are comparable in shape to that of crystalline Y-zeolite, despite their amorphous nature. Furthermore, as the kinetic diameter of the diols becomes bigger, the pore distribution curve of the silica–aluminas shifts to the larger diameter region; in other words, the bulkier diols generally can give silica–aluminas with bigger micropores and also bigger specific surface areas [*e.g.* SiO_2–Al_2O_3 from 2-methylpentane-2,4-diol 486 m^2 g^{-1}; from ethylene glycol 399 m^2 g^{-1}].[3]

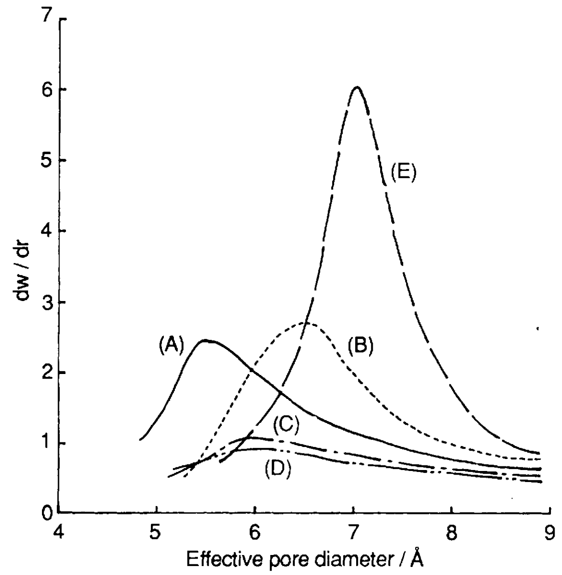

Figure 2. Micropore distributions of silica–alumina: (A)—(C) as in Figure 1; (D), commercial silica–alumina (Nikki N-631); (E), Y-zeolite.

As the amount of organic moieties in the dry gels is determined by the complexing ability of the diols, and the amounts of the diols and water added, we conclude that the micropores in amorphous mixed oxides can be designed by the advanced sol–gel method in which organic ligands such as diols are used as pore-forming agents.

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