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Friedel-crafts alkylation over Al-incorporated mesoporous honeycomb

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Catalytic activity of Friedel-Crafts alkylation of toluene with benzyl alcohol has been measured over the Al-incorporated mesoporous honeycomb. The honeycomb was fabricated using MCM-48 and pseudobohemite as inorganic binder and the incorporation of aluminum was performed either by direct implementation of $AlCl_3$ or by slurry mixing before the extrusion. Hydrothermal stability and compressive strength can be improved with the increase of the aluminum content. High catalytic activity of Friedel-Crafts alkylation was observed for the honeycomb containing Al initially in the slurry mixture.

1. INTRODUCTION

The catalyst powder should be fabricated into a certain type of structure that can allow a facile diffusion of reactants to catalytically active sites. Honeycomb is the most common commercially available structure that accommodates catalysts at the surface of each small rectangular structure. Recently, the silica-based mesoporous molecular sieves has been investigated extensively as a substrate for catalytic conversion of large molecules inside its uniform pore of which the surface area is ranging from 2 to 30 nm [1]. Their high hydrothermal stability is comparable to those of conventional aluminosilicate zeolites. Ahn et al. showed that the honeycomb can be fabricated from the MCM-48 powder [2]. The integrity of such a mesoporous structure in the honeycomb can be retained during the hydrothermal treatment. Here, we report the results of the catalytic activity of the Friedel-Crafts alkylation over the honeycomb containing aluminum that is incorporated different ways.

2. EXPERIMENTAL

The MCM-48 silica powder was synthesized following the method described in the previous reports using a surfactant mixture of cetyltrimethylammoniumbromide and tetraoxyethylene dodecyl ether. The MCM-48 samples containing the surfactants as synthesized were further treated with an aqueous solution of NaCl, in order to improve the

hydrothermal stability. The samples were then dried in an oven at 100°C, washed with an ethanol-HCl mixture to remove as much surfactant as possible, and finally calcined in air under static conditions at 550°C. The bath composition of the slurry containing the MCM-48 powder was controlled to the 80 wt % of MCM-48, 20 wt % of inorganic binder, 15 ~ 25 wt % of organic binder and the above 100 wt % of water on the basis of the total weight of MCM-48 and inorganic binder. The fabrication of the honeycomb follows a typical procedure consisting of powder mixing, wet mixing, aging, kneading, extruding and final sintering. The test method for the hydrothermal stability, the characterization and the catalytic activity of Friedel-Crafts alkylation of toluene and benzyl alcohol can be found in elsewhere [3].

3. RESULTS AND DISCUSSION

Employing pseudobohemite as inorganic binder increased the mechanical stability of the mesoporous honeycomb. The pseudobohemite contains Al itself, which can also be act as an acid catalyst. Fig. 1 shows the compressive strength and surface area depending on the calcination temperature. The increase of the aluminum incorporation in the honeycomb during the slurry formation decreased the surface area but improved the compressive strength. The incorporated Al may also act as inorganic binder like the pseudobohemite.

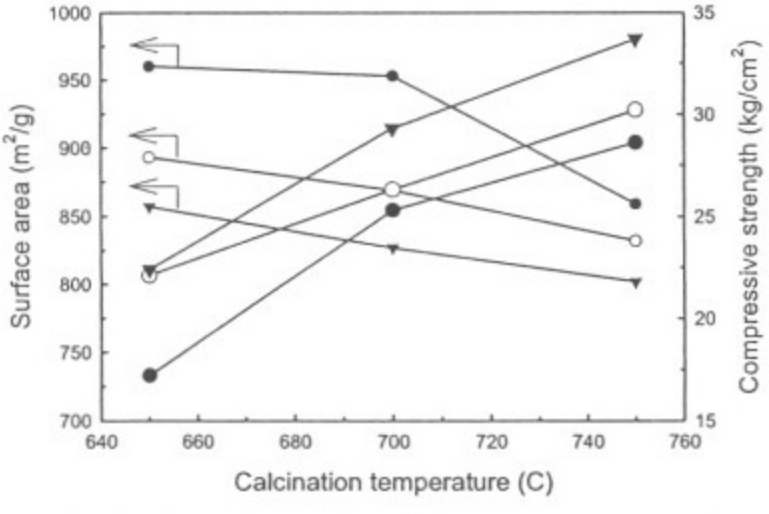

Fig. 1. Change of Surface area and compressive strength as a function of the calcination temperature: (l), 0 wt% $AlCl_3$; (m), 5.6 wt% $AlCl_3$; (t) 11.2 wt% $AlCl_3$.

In addition to the mechanical stability, the hydrothermal stability is a important factor for the design of mesoporous honeycomb. In this work, the hydrothermal stability was measured from the XRD patterns before and after the treatment of the honeycomb in the boiling water for 12 h.

The XRD diffraction patterns indicated that the mesoporous structure was retained after the treatment and the Al incorporation led to more hydrothermally stable mesoporous honeycomb. It was shown that the hydrothermal stability was increased by the incorporation of alkali or alkaline earth ion to the mesoporous material. It seems that the incorporated Al increased the hydrothermal stability in addition to the mechanical stability.

The local environment of Al in the mesoporous honeycomb was probed with ^{27}Al NMR depending on the incorporation methods of Al. Fig. 2 illustrates the NMR spectra of the mesoporous honeycombs. The direct implementation of an acid function to the surface of the mesoporous channel was reported to be another viable method for the catalyst preparation. The spectral intensity of the peak corresponding to the tetrahedral Al site increased for the sample containing the direct implementation of $AlCl_3$. The calcination of the sample at 650 °C resulted in the similar ^{27}Al NMR spectrum to that of the mesoporous honeycomb containing $AlCl_3$ in slurry mixture initially. This suggested that the incorporation method of

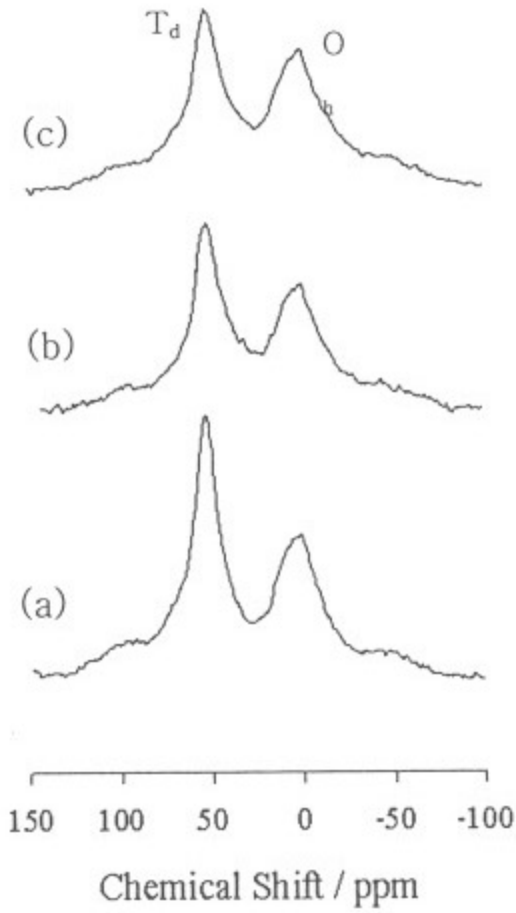

Fig. 2. (a) the Al impregnated mesoporous honeycomb, (b) the sample (a) calcined at 650 °C and (c) the mesoporous honeycomb containing Al in the slurry, after calcination at 700 °C.

Al did not affect the local environment of Al sites, which can be attributed to the large amount of inorganic binder, pseudobohemite.

Fig. 3 shows the microstructure of the mesoporous honeycomb. During the fabrication of the honeycomb, all the components were mixed thoroughly to get homogeneous slurry for the extrusion, which can result in the breaking or destruction of crystalline shape. Indeed, the MCM-48 had a crystalline shape in powder form but the honeycomb had an irregularly tough surface microstructure due to the mixing step as shown in Fig. 3. The increase of Al incorporation led to the increase of mechanical stability and hydrothermal stability. However, in the scanning electron micrograph of the honeycomb sample, there is no significant difference in the surface structure.

The catalytic activity of the Friedel-Crafts alkylation was measured over the honeycomb samples in a similar way reported in the literature. Fig. 4 shows the effect of the Al-incorporation method on the catalytic activity. The honeycomb without Al direct implementation or impregnation gave a comparable catalytic activity for the alkylation of toluene with benzyl alcohol. The conversion of toluene increased up to 40 % for 2.5h.

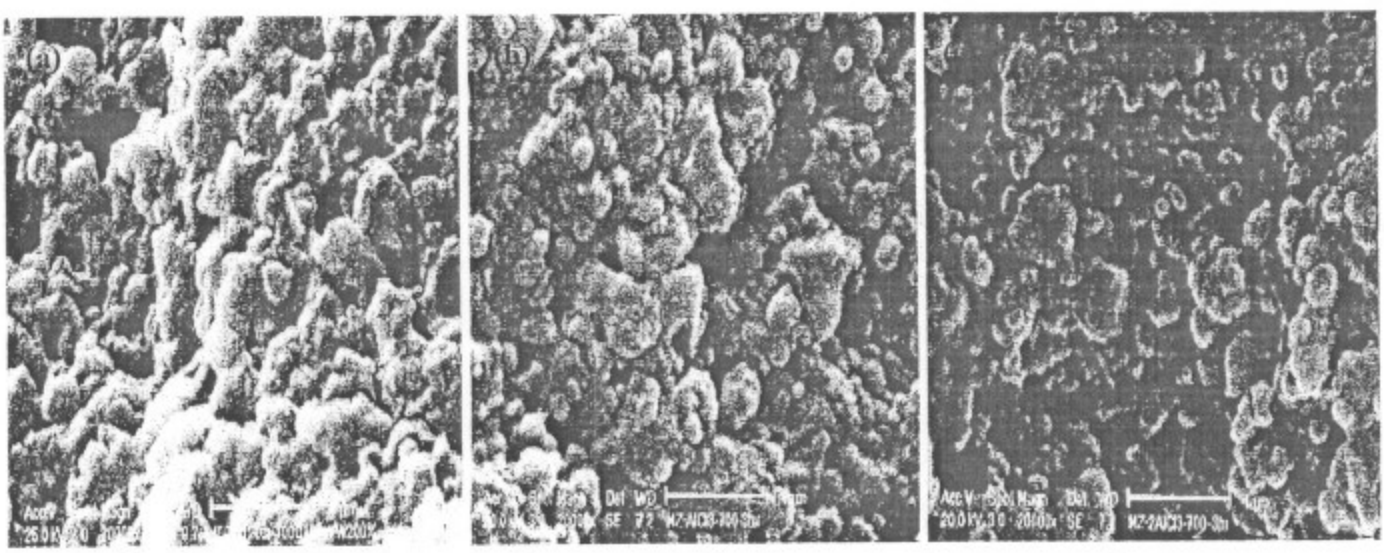

Fig. 3. Scanning electron micrographs of the honeycomb sample calcined at 700 °C: (a), 0 wt% $AlCl_3$; (b), 5.6 wt% $AlCl_3$; (C) 11.2 wt% $AlCl_3$.