Catalytic Property of Silica-Supported 12-Tungstophosphoric Acid Modified with Organosilanes

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Environment around active centers in homogeneous catalysts such as metal complexes and organocatalysts was well organized by precise design of ligands and molecular structures. However, controlling the reaction environment around active sites on heterogeneous catalysts has not been intensively investigated so far.

In this study, we investigated modification of SiO_2-supported heteropoly acid $H_3PW_{12}O_{40}$ (HPW/SiO_2) with three types of organosilanes and the effect of the modification on the catalytic performance in a Friedel-Crafts (FC) reaction.

First, SiO_2 (Aerosil 300, 285 m^2g^{-1}) was modified with organosilanes by stirring it in toluene under reflux conditions. Here, R-Si(OEt)$_3$ (R = ethyl, octyl, and phenyl) was used as organosilanes. The modified samples were designated as C2-, C8-, and Ph-SiO_2, respectively. Then, 5 wt.% HPW was supported on the pristine and modified SiO_2 by incipient wetness method. Liquid-phase FC reaction of benzene with benzyl chloride was conducted at 80 °C.

The modification with organosilanes did not cause significant changes in the surface area and pore structure of SiO_2. Density of grafted organosilane was increased along with the increase in the dose amount and then reached constant at around 0.4 nm^{-2}. Since density of silanol groups on SiO_2 was 1.5~2.0 nm^{-2}, the maximum density of organosilane, bound with three silanol groups, could be calculated to be 0.5~0.7 nm^{-2}. The remaining silanol groups reacted with HPW molecules. X-ray diffraction did not show any diffraction peak assigned to bulk HPW, indicating that HPW was highly dispersed. Based on the surface density of organosilanes and HPA, it is speculated that one HPW molecule is surrounded by approximately ten organosilanes at the maximum, as depicted in Fig. 1.

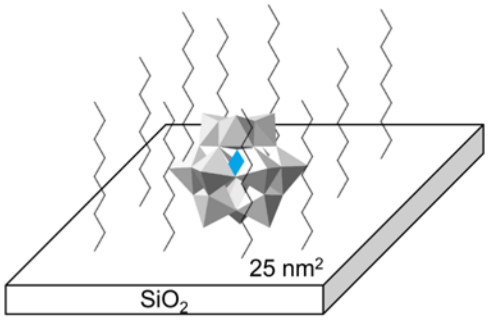

Fig. 1 Structure model of HPW/C8-SiO_2

Fig. 2 shows yield of diphenylmethane in the FC benzylation at 2 h. HPW/SiO_2 showed a slight yield of diphenylmethane. In contrast, organosilane-modified catalysts were highly active for the reaction, especially HPW/C8-SiO_2, showing the highest yield (20%). Acid properties of these catalysts were examined by benzonitrile (BN)-TPD study. The amount of BN adsorbed on HPW/SiO_2 was 25 µmol/g-cat, which decreased to 15 µmol/g-cat for HPW/C8-SiO_2. Nevertheless, the desorption peak shifted to higher temperature. It is speculated that benzyl chloride and/or benzene may be strongly adsorbed on the organosilane-modified catalysts, leading to the high catalytic activity for the FC reaction.

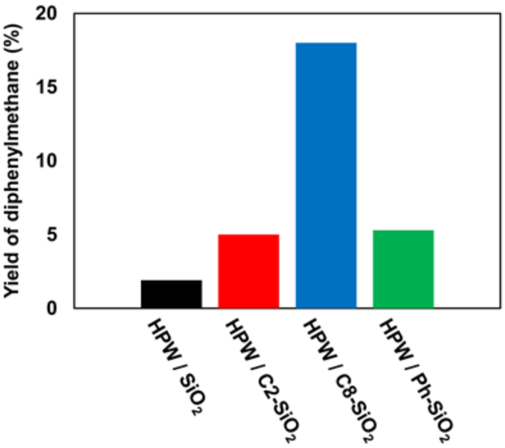

Fig. 2 FC benzylation of benzene over pristine and modified HPW/SiO_2 catalysts. Reaction conditions; catalyst 0.1 g, Benzene 30 mmol, Benzyl chloride 10 mmol, 353 K, 2 h.