Catalytic Features of Cesium Hydrogen Salts and Triammonium Salt of Heteropoly Acid H₃PW₁₂O₄₀ in the Alkylation of Ammonia with Methanol to Methylamines

Mohammad NASIKIN, Kohei SHINO, Rynichi NAKAMURA*, and Hirono NITAYAMA

Dept. of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology, Otakaya, Meguro-ku, Tokyo 152-8552

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Catalytic features of CsₓHₓ₋ₓPW₁₂O₄₀ (CsₓPW; x = 0 - 3) and (NH₄)ₓPW₁₂O₄₀ (NPW) in the methylation synthesis by sequential alkylations of NH₃ with CH₃OH were investigated by conducting the reaction (NH₃/CH₃OH/He = 2/1/7) at 0.1 MPa by flow method. All the H⁺- or NH₄⁺-containing heteropoly compounds were effective for the methylation synthesis at ca. 573-723 K. In contrast with SiO₂·Al₂O₃, all the heteropoly catalysts exhibited a long induction period in the initial stage of the reaction, during which significant sorption of CH₃OH by the catalysts was observed. For the H⁺-containing heteropoly catalysts, the uptake of NH₃ was also observed in its early stage. The uptakes of CH₃OH by CsₓPW and Cs₂.₅PW were in the range of 2-3 moles per mol-polyanion, while those of NH₃ as NH₄⁺, estimated by TPD analysis, were 1.0 per 1₁⁺ in each fresh sample. These results suggest that both CH₃OH and NH₃ can diffuse into their rigid crystal bulk. After such an induction period, the catalysts showed steady activity. The activity of CsₓPW and the distribution of the amines during the steady state greatly varied with Cs content x. Among the high surface area salts, Cs₂.₅PW, Cs₂.₅PW, NPW, etc. that showed high catalytic activity, Cs₂.₅PW gave almost 100% selectivity to the smaller amines, MMA (monomethylaniline: 0.4 mm) and DMA (dimethylaniline: 0.49 mm), with negligible yield of TMA (trimethylaniline: 0.61 mm) even at high CH₃OH conversions. On the other hand, NPW and CsₓPW with x < ca. 2.9 as well as SiO₂·Al₂O₃ behaved as a non-shape selective catalyst yielding TMA with the smaller amines even at low conversions. It was found, however, that Cs₂.₅PW has almost the same pore distribution (Type IV) as Cs₂.₅PW: both salts have not only small pores (< 1 nm) but also larger pores (> 2 nm) in a significant proportion. This fact implies that the high shape-selective salt, Cs₂.₅PW, has the active sites (H⁺) mostly in its small micropores (probably, < 0.6 nm) where no TMA can be formed or diffuse, while non-shape-selective one, Cs₂.₅PW, has H⁺ throughout its micro- to macropores. In fact, TPD studies suggested that the both salts easily chemisorb MMA and DMA as well as NH₃ (as ammonium ions) even into their bulk or very small pores, but Cs₂.₅PW can hardly chemisorb TMA, while Cs₂.₅PW chemisorbs TMA only onto the surface of its relatively large pores in reasonable amounts.