Evidence for Superacid Sites on the Ammonium Salt of 12-Tungstophosphoric Acid from a Catalytic Test Reaction

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The noticeable activity of the ammonium salt of 12-tungstophosphoric acid for n-hexane conversion at low temperature suggests the presence of superacid sites on the catalyst surface.

Heteropoly acids and their salts are of considerable interest in terms of their activity in acid-catalysed reactions and in oxidation processes. Acid sites with strengths of $H_0 \leqslant -8.2$ and $H_0 \leqslant -5.6$ have been detected by means of an indicator test for 12-tungstophosphoric (HPW) and 12-tungstosilicic (HSiW) acids, respectively.[1] Their ammonium salts show some unexpected features in comparison to the parent acids. They are known to have a high surface area (>100 m^2 g^{-1}) and micropore structure. In spite of fewer acid sites (approximately one-third of those found with the acid), the ammonium salt of HPW (NHPW) shows considerably higher catalytic activity than the parent acid for conversion of methanol to hydrocarbons.[1] It was difficult to estimate the strengths of acid sites in the strong acidity range using the indicator method, since NHPW was grey–bluish after evacuation at 300 °C and the indicators turn yellow in their acidic form. Some information concerning the strength of acidic sites can be found from the results of catalytic tests for reactions requiring sites of different acid strengths. It is well known that strongly acidic centres ($pK_a \leqslant -5.6$) are necessary for cumene cracking,[2,3] and much stronger acidic centres ($pK_a \leqslant -8.2$) are required for disproportionation of toluene. The low temperature transformation of alkanes can be catalysed only by superacids.[4]

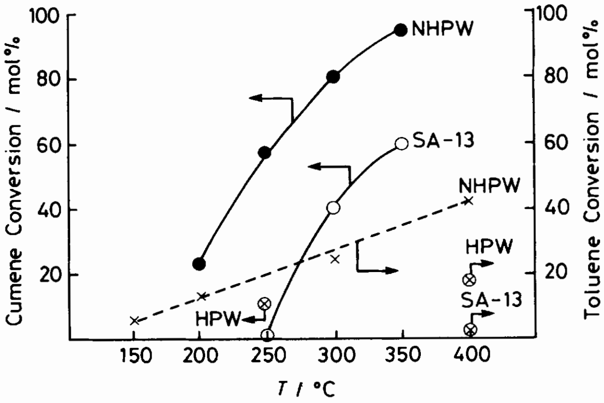

Figure 1. Catalytic activity of HPW, NHPW, and SA-13 for cumene cracking and toluene disproportionation.

The above reactions were chosen for preliminary characterization of the strengths of the acidic sites in NHPW. Commercially available silica–alumina (SA-13) catalyst ($H_0 \leqslant -8.2$) was employed in the tests for comparison, and the tests were performed in a pulse microreactor. It was found that NHPW is more active than SA-13 for all of the reactions studied. Cumene reacted over NHPW at temperatures as low as 200 °C, while SA-13 was completely inactive even at 250 °C. Benzene and propylene were the main products over the temperature range used. It was interesting that in the first pulses of the test performed at 350 °C, only very small amounts of benzene were detected, whereas almost all cumene was converted; the amounts of benzene in the products increased with the pulse number. This suggests that the benzene

Table 1. Activity of NHPW for isomerization of n-hexane.

Reaction temp./°C	n-Hexane conversion/mol%
150	8.6[a]
80	3.5[a]
80	3.0[b]
30	0.2[b]

[a] Microcatalytic pulse reactor, apparent residence time $W/F = 300$ mg min ml^{-1}. [b] Sealed vessels, 300 h.

undergoes further reactions over strongly acidic sites at 350 °C. The presence of very strong acidic centres on the NHPW was confirmed by its high activity for toluene disproportionation. According to Taniguchi *et al.*,[2] acidic centres having an adsorption heat of ammonia higher than *ca.* 100 kJ mol^{-1} (pK_a ~ −8) are effective for toluene disproportionation at 400 °C.

Silica–alumina SA-13 was practically inactive at 400 °C (only about 2%) whereas 42% of toluene was converted to benzene and xylenes under the same conditions over NHPW. NHPW showed activity here at temperatures as low as 150 °C (Figure 1). This very high activity made reasonable an attempt to prove the presence of superacids by means of the catalytic reaction of n-hexane at low temperatures. It is generally believed that the low temperature transformation of n-alkanes can be catalysed only by superacid sites[4,5] and this is often used to confirm the presence of these sites. Activity of NHPW for transformation of n-hexane was measured at 150 and 80 °C using a microcatalytic pulse reactor, and at 80 and 30 °C using sealed glass vessels.

It was found that NHPW is able to catalyse cracking and isomerization of n-hexane over the temperature range used. Although the isomerization of n-hexane is low, there is no doubt that some activity can be found even at room temperature. Hattori *et al.*[5] showed that silica–alumina did not show any catalytic activity for n-butane isomerization at low temperatures and no traces of butane isomers were found at 25 °C after 720 h. On the other hand, generation of superacids by modification with SbF_5 caused a noticeable activity of silica–alumina.

The considerable activity of NHPW for n-hexane transformation at low temperatures undoubtedly results from the action of superacids. The values of the n-hexane conversion found in our experiments (Table 1) are comparable with the results of Becker and Kowalak[6] obtained under similar experimental conditions (conversion of n-hexane over fluorinated H-mordenite was 0.3 and 5% at 60 °C and 90 °C, respectively). The acid strength of fluorinated H-mordenite was $-12.7 \leqslant H_0 \leqslant -13.16$, as estimated by means of an indicator test and calorimetric measurement of the heat of ammonia adsorption.[6] Similar catalytic activity of NHPW and fluorinated mordenite, which was proved to possess superacid sites, gives an additional argument confirming the presence of superacid sites in NHPW.

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