

Notes

Hydrocarbon formation from alcohols on heteropoly acids: XPS and TES studies

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Conversion of alcohol (isopropyl alcohol) to hydrocarbon on 12-tungstophosphoric acid is shown to proceed by a hydride abstraction route. The formation of polyenylic species as a result of hydride abstraction is identified by transmission electronic spectral measurements and carbon deposition by XPS measurements. The active species appear to be W-O polyhedra as electron emission from phosphorus core levels are not easily discernable.

A number of organic transformations¹ catalysed by heteropoly acids are either promoted by stoichiometrically bound protons or by the redox chemistry these systems are capable of sustaining in oxidation reactions². Recently, we have investigated heteropoly acid catalysed transformation of alcohols to saturated hydrocarbons and proposed that this reaction might involve hydride transfer from the olefinic products formed as a result of initial dehydration reaction³. The unsaturated surface species by successive hydride transfer steps may be expected to yield monoenylic and dienylic species if the alcohol used was a higher alcohol. If this mechanistic sequence were to be true, then we should be able to identify these surface species by transmission electronic spectral (TES) measurements. In addition, the successive hydride transfer steps should lead to carbon deposition on the surface of the spent catalyst. In essence, the molecular level transformation of isopropyl alcohol to propane can be envisaged to proceed by the sequence of steps shown in scheme 1.

The purpose of this investigation is to provide experimental support for the formation of surface

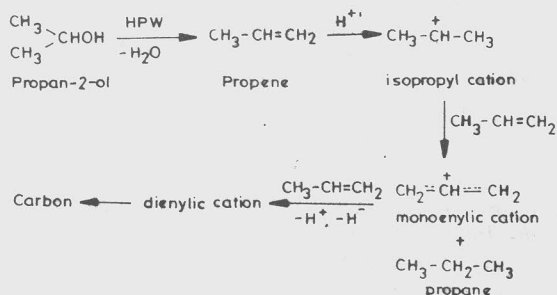
monoenylic and carbon species on a typical heteropoly acid catalyst namely, 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) when isopropyl alcohol is used as the reactant.

Experimental

12-Tungstophosphoric acid was prepared from sodium tungstate and disodium phosphate following the procedure given in literature⁴. The samples obtained were calcined at 573 and 673K for 4 hr in air. Spectroscopic measurements were carried out on thin wafers kept in a glass frame, which served as a sample holder and which in turn was inserted into specially designed cell which could be attached to a high vacuum system for dosing with isopropyl alcohol and degassing at different temperatures. The spectra were recorded on a Cary 2390 spectrophotometer. The XPS measurements were made in an ESCA LAB Mark II spectrometer with MgK_{α} ($h\nu = 1253.6$ eV) radiation.

Results and discussion

Transmission electronic spectra of the solid catalysts after exposure to isopropyl alcohol were recorded and the spectra obtained for the acid and sodium salt are given in Fig.1. It is seen that the exposure of the acid to isopropyl alcohol at room temperature yields bands at 290 and 340 nm. The band at 340-350 nm persists even after 2 hr. However, the spectra of the acid obtained after exposure of the alcohol at 423K displayed absorption band at 340 nm, the intensity of which decreased with increase in contact time. In the case of sodium salt, no clear absorption band was observed even after isopropyl alcohol exposure at 473K. It is known that monoenylic carbocations absorb in the 275-320 nm range⁵ and their band positions are sensitive to the nature of surroundings⁶. LCAO-MO calculations⁷ predict a maximum absorption at 283 nm for the simplest case namely allyl cation. However, on chlorinated alumina⁸ the stabilised form of this species gives a band at 285 nm while on mordenites, the bands are observed at 295-310 nm⁹. The formation of surface monoenylic cations is negligible on the sodium salt indicating that Bronsted acid sites are involved in the process of initial protonation. The first step after absorption of isopropyl alcohol on the heteropoly acid would be the formation of propene by the elimination of water. The propene thus formed undergoes further transformation to give rise to allylic cation by hydride ion abstrac-



Scheme 1

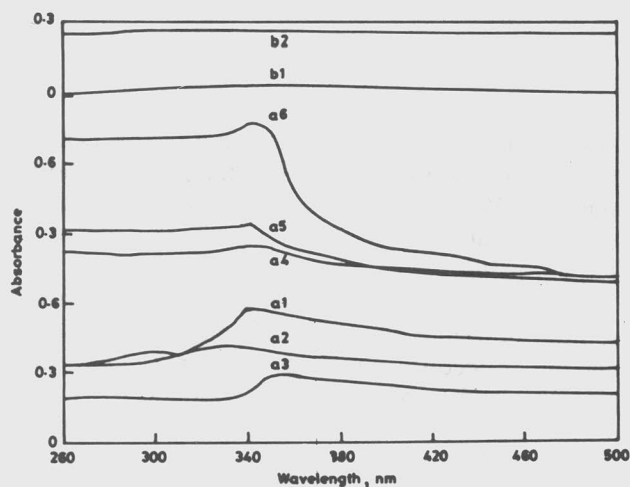


Fig. 1—Transmission electronic spectra of heteropoly compounds exposed to 5 torr of isopropyl alcohol [(a), HPW; (b) NaPW; (a1) 1/2 hr after admission at room temperature (RT); (a2) 2 hr at RT; (a3) 24 hr at RT; (a4) 1/2 hr after admission at 423K; (a5) 2 hr at 423K; (a6) 24 hr at 423K; (b1) 1/2 hr after admission at RT; (b2) 1/2 after admission at 473K.]

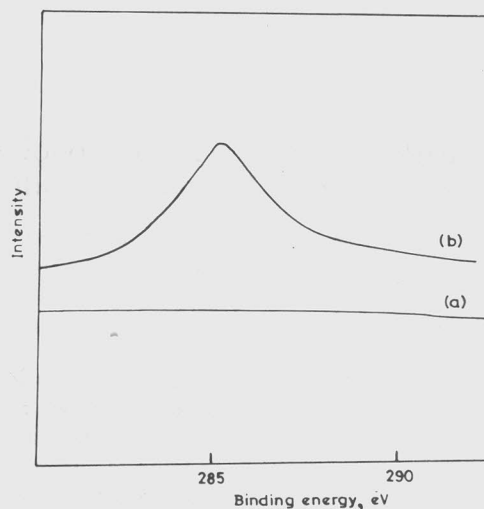


Fig. 2—XP spectra of the heteropoly acid in C (1s) region [(a) Fresh catalyst; and (b) spent catalyst]

tion either effected by a classical isopropyl ion (formed by the protonation of propene in a preceding step¹⁰, thus accounting for the formation of saturated hydrocarbon) or by a Lewis acid centre of the catalyst. In an earlier paper³, we proposed that propane formation could result from disproportionation of propene as well as by nucleophilic attack of the hydride ion on dehydration product or alcohol itself. The present *in situ* absorption spectroscopic measurements seem to clarify the molecular level details of the latter route.

Narrow scan XP spectra of the fresh as well as spent catalysts were also recorded. The only earlier report¹¹ on the XP spectrum of potassium substituted 12-molybdophosphates was aimed at examining the potassium deficiency at the catalyst surface compared to that in the bulk. The XP spectra for W(4f) line of the fresh catalyst and of the spent catalyst show that the surface exposed W ions are in the 6+ state and are predominantly exposed on the surface, while the extent of exposure of phosphorus on the surface seems to be limited. This situation is in conformity with the normal Keggin structure of these substances. Therefore the active centres in the oxidation reactions should be the W-O bonds only. The fresh catalyst does not contain any carbon (Fig.2) even as an impurity, while in the spent catalyst, one can see the large build-up of carbon indicating the validity of the mechanism proposed. The nature of the surface oxygen species of the fresh catalyst seems to be uniform while in the spent catalyst the oxygen (1s) peak is broad indicating that

more than one type of oxide ion species is present. This could have arisen from the formation of hydroxyl groups generated as a result of catalytic reaction. The binding energy of W 4f_{7/2} peak is shifted slightly to the lower value indicating the reduced nature of W 6+ state. Therefore, the redox reactions should involve only W-O bonds. This reduction in the valence state of W could have arisen from the catalytic reaction which would have formed surface OH groups as a result of proton abstraction. In conclusion, it may be stated that XPS and TES studies reveal that the hydrocarbon formation on heteropoly acids could involve hydride abstraction from the olefins formed from alcohol.

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