Catalytic Properties of Heteropolyacids—Conversion of Isopropyl Alcohol into Saturated Hydrocarbons

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The conversion of isopropyl alcohol into propane on heteropolytungstic acid catalyst occurs mostly by disproportionation of the olefin formed as well as from H transfer carbonization route.

The catalytic properties of heteropolyacids (HPA) of tungsten ($H_3PW_{12}O_{40}$; HPW) and molybdenum ($H_3PMo_{12}O_{40}$; HPMo) and their salts have been examined in detail in recent times with a view to finding out alternatives for zeolites for the conversion of methanol and other alcohols into hydrocarbons. In these studies, HPAs are considered to function similar to zeolites for the production of higher hydrocarbons. Highfield and Moffat observed the formation of C$_3$- and C$_4$-hydrocarbons in the sustained catalysis of isopropyl alcohol (IPA) on HPW at 523 and 623 K. Ohukara et al. observed only propene and water together with a small quantity of ether on copper salts of HPW at 373 K. However, it is expected that saturated hydrocarbons especially propane can be formed on these catalysts as has been observed with methanol. Propane from IPA could be formed by either of the following reactions: (i) hydrogenation of the olefin formed by dehydration; (ii) nucleophilic substitution of OH$^-$ by H$^-$ originating from water; and (iii) disproportionation of propene. The purpose of the title investigation is to examine which one of these three routes (i-iii) is probable on HPW in the conversion of IPA into saturated hydrocarbons.

The surface acidic properties of these systems especially those of HPW and HSiW and their salts have been examined by a number of workers. The acidic properties of these systems are dependent on the temperature of pretreatment as well as the environment employed for calcination. In methanol conversion, heating in air is known to reduce the activity possibly due to extraction of acidic sites by oxygen, while heating in hydrogen/helium is known to enhance the yield of hydrocarbons due to alteration in the distribution of acid sites. In the present work, therefore, the acidity of HPW has been examined using indicator method with a view to (a) evaluating the effect of pretreatment temperature and environments (air, vacuum, flowing argon or hydrogen) on the acidity of the catalyst, (b) correlating acidity with activity for saturated hydrocarbon formation from IPA; and (c) gaining information on the probable route for propane formation.

Materials and Methods

$12\text{-Tungstophosphoric acid was prepared from sodium tungstate and disodium phosphate following the literature procedure. The acid was calcined at 573 K and 673 K for 4 hr under various atmospheres like air, vacuum, argon and hydrogen.}$

Acid strength distribution of the catalyst pretreated under different conditions was determined following the procedure of Benesi$^1$ using Hammett indicators.

The catalytic reactions of IPA were carried out in a fixed bed flow-type reactor working at atmospheric pressure. The products were analysed either gas chromatographically or using Orsat apparatus. The carbon contents on the catalysts were estimated by conversion to carbon dioxide and using baryta solution for estimation.

Results and Discussion

The products of decomposition of IPA in the temperature range of 383-423 K are propene, water, diisopropyl ether and propane. No dehydrogenation product, namely acetone or hydrogen was formed. Direct hydrogenation of propene by hydrogen formed by dehydrogenation, though may be thermodynamically favourable is likely to be kinetically controlled in the above reaction, since dehydrogenation is feasible only at higher temperatures ($> 623 K$). The hydrogen transfer and carbonization reaction is predominant only around 523 K though it is observable even at 423 K (ref. 2). In the light of the observations reported in literature we have carried out the decomposition of IPA at 383 K on the catalyst calcined at 573 K in the presence of various substrates like hydrogen, water, ether and nitrogen. The variation in the amounts of propene and propane formed as a function of partial pressure of IPA is shown in Fig.
The following points emerge from the results presented in Fig. 1.

(i) Similar results obtained for the formation of propane and propene in the presence of nitrogen and hydrogen ruled out direct hydrogenation of olefin by molecular or adsorbed hydrogen.

(ii) In the presence of water, the amount of olefin formed was small while considerable amount of propane was formed indicating that either the olefin formed was converted into propane or the olefin formation was suppressed in presence of water in the feed.

(iii) In the presence of diisopropyl ether propane formation was a favoured reaction.

The extent of carbon formation during IPA decomposition was separately estimated. Propane to carbon ratio was found to be around 1.5 at all temperatures studied. Propene formed disproportionates in accordance with the reaction:

\[ 4 \text{CH}_3\text{CH} = \text{CH} \rightarrow 3 \text{CH}_3\text{-CH}_2 \rightarrow \text{CH}_3 + 3 \text{C} \]

and if this were to be the only route for propane formation then the propane to carbon ratio should have been one instead of 1.5 observed presently. It is therefore considered that propane could also be formed by another route on HPW. The alternate route could involve the nucleophilic attack of the hydride ion on the dehydration product or the alcohol itself.

The acid strength distribution obtained for the catalysts calcined at 573 and 673 K in various atmospheres are given in Table 1. The following points emerge from these results:

(i) In air and argon atmospheres, pretreatment at higher temperatures (673 K) increases the number of highly acidic sites \((H_0 \geq -3.0)\) while moderate acid sites \((-3.0 < H_0 < +3.3)\) predominate in the sample pretreated at 573 K.

(ii) The influence of temperature of pretreatment on the acidity of the catalyst when treated in vacuum or in hydrogen is not significant.

(iii) Samples pretreated in vacuum contain only strong acidic sites \((H_0 < -3.0)\) while samples pretreated in other atmospheres do contain sites with moderate acid strength.

XRD patterns obtained for HPW after pretreatment at various temperatures and atmospheres show that Keggin unit is stable up to 673 K.

In earlier reports on HPAs attempts were made to correlate the surface properties with catalytic activities. Moffat and coworkers have generated data to
show that the formation of C$_4$-hydrocarbons from methanol correlates with the acidic sites of strength $H_a < +3.3$ or $< +1.5$.

Highfield and Moffat have postulated that the activity may be promoted by judicious control of the acid strength distribution, i.e. weaker sites favouring olefin formation while stronger sites may be involved in carbonization route. In order to substantiate the postulate that formation of propane from IPA may involve such a H transfer-carbonization route for propane formation, the relative variation of these plots with temperature may be indicative of the number of such sites participating in the carbonization route.

References