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Bifunctional Catalysis by Platinum-Containing Sulfonic Acid Resin

Styrene–divinylbenzene (DVB) co-polymers are available having widely different physical properties, including flexibility of the polymer network, porosity, and internal surface area; resins with surface areas as high as 780 m^2/g have been reported (*1*). Since resin physical properties can be precisely controlled and the networks or surfaces can be functionalized with many chemically different groups, the resins find wide application as adsorbents, ion exchangers, and catalysts. The industrially important catalysts are sulfonated resins, which are used for acid-catalyzed reactions such as esterifications and condensations. Other potentially useful resin catalysts incorporate transition metal complexes [e.g., of rhodium for hydroformylation (*2*)] and metal crystallites (*3*).

The purpose of the experiments reported here was to demonstrate the straightforwardness of rational design of a resin catalyst; chosen for the example was a reaction sequence consisting of propylene hydration [catalyzed industrially by sulfonated styrene-DVB resins (*4*)] followed by dehydrogenation of the resulting isopropanol to give acetone [catalyzed industrially by Zn/Cu alloys (*5*)]. Since the temperature required with Zn/Cu alloys (~400°C) is higher than the acid resin can withstand (~150°C), a more active metal component was preferred; the literature indicates the appropriateness of Pt (*6*), and therefore a Pt-containing sulfonic acid resin was chosen. The results given below, combined with similar patent reports (*7,8*), show the practical value of organic solids, which have catalytic properties much more easily predicted than those of inorganic solid surfaces.

Styrene-DVB catalysts containing Pt crystallites and $-SO_3Na$ groups [prepared and characterized by Hanson *et al.*, samples 2, 4, and 5, Table 1, ref. (*3*)] were acidified with dilute aqueous HNO_3 to convert $-SO_3Na$ groups to $-SO_3H$ groups. One-gram samples were held in a thermostated flow reactor similar to that described previously (*9*), through which was metered a stream of propylene and water at 1 atm and 118°C. Catalysts approached constant activity within 4 hr, and no further change was observed during runs as long as 18 hr. Conversions to isopropanol and acetone were determined from glc analyses of products during steady-state operation. The glc column contained 15% Carbowax 400 on Chromosorb W at 85°C.

Macroporous sulfonic acid resin (~40 m^2/g) in the absence of Pt was an active catalyst for isopropanol formation from propylene and water, as illustrated by the differential conversion data of Fig. 1A. Sulfonic acid resin containing Pt catalyzed formation of both isopropanol and acetone (Fig. 1B, C), and the only side products were traces inferred from their glc retention times to be propylene dimers and trimers.[1] The data show that isopropanol was formed rapidly at the lowest inverse space velocities (contact times), with acetone being formed at negligible rates; at higher inverse space velocities with a catalyst containing 1.2 wt% Pt, the rate of formation of acetone became about 1% of the value for isopropanol, which became sev-

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[1] No other side products were observed, but at high conversions to acetone, the following would be expected: 2,2-diisopropoxypropane [formed by acid-catalyzed condensation of isopropanol and acetone (*10,11*)] and mesityl oxide and phorone [formed by acid-catalyzed self-condensation of acetone (*12,13*)]. Dehydration of isopropanol to give diisopropyl ether would also be expected (*4,14*).

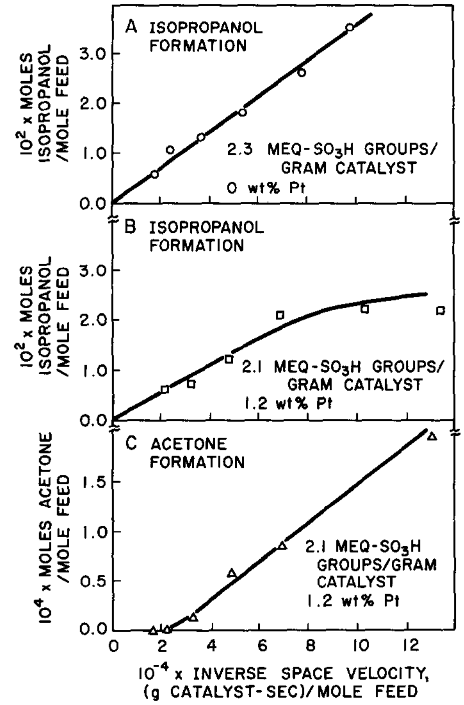
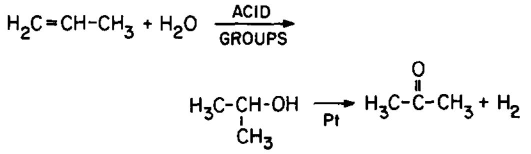


FIG. 1A. Formation of isopropanol from an equimolar mixture of propylene and water catalyzed by sulfonic acid resin at 1 atm and 118°C. (B) and (C) Formation of isopropanol and acetone from an equimolar mixture of propylene and water catalyzed by Pt-containing sulfonic acid resin at 1 atm and 118°C.

eral fold less than its initial value, indicating inhibition of reaction by acetone. These results demonstrate the role of isopropanol as an intermediate in a series reaction network.

The initial rate of isopropanol formation was independent of catalyst Pt content in the range 0.4 to 5.8 wt% and strongly dependent on the concentration of $-SO_3H$ groups (Fig. 2), indicating that hydration occurred independently of platinum. Acetone formation rates (calculated from the higher space velocity portions of the conversion–inverse space velocity plots) were approximately proportional to metal content, confirming the role of Pt as an isopropanol dehydrogenation catalyst. The reaction network is therefore



$$H_2C{=}CH{-}CH_3 + H_2O \xrightarrow[\text{GROUPS}]{\text{ACID}} \underset{\displaystyle CH_3}{H_3C{-}CH{-}OH} \xrightarrow[\text{Pt}]{} H_3C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 + H_2$$

A similar reaction network (propylene hydration to isopropanol followed by oxidative dehydrogenation to acetone) has been inferred previously by Tan *et al.* (*15*) and Moro-oka *et al.* (*16,17*), who found selectivities of 80–85% for acetone formation in the presence of bifunctional mixed oxide catalysts such as SnO_2–MoO_3 in the range 115–200°C.

The relatively high activity and selectivity of the bifunctional resin catalyst suggest that it might be of practical value for the production of acetone and hydrogen from propylene and water, particu-

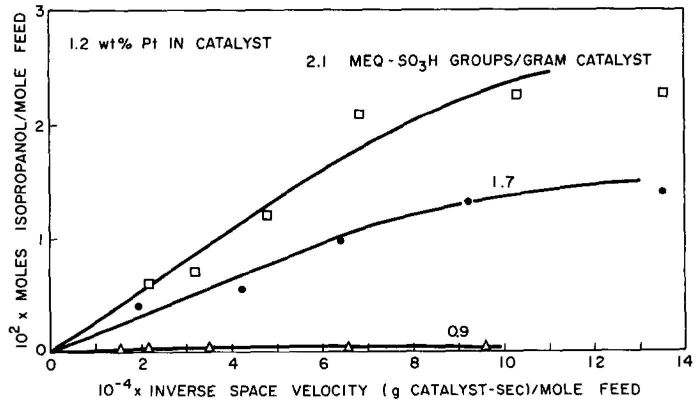


FIG. 2. Propylene hydration at 1 atm and 118°C: dependence of conversion on catalyst $-SO_3H$ group concentration. Feed to the reactor was an equimolar mixture of propylene and water.

larly since in commercial practice the olefin hydration is equilibrium limited (*4*). The nearness of the two catalyst functions could allow the intermediate alcohol to be drained away rapidly, removing the equilibrium limitation. The inhibition of propylene hydration by acetone, however, suggests that bifunctional catalysis might be impractical.

An interpretation of the inhibition by acetone is not evident from the data, but the literature provides the basis for the following speculation: The resin matrix was strongly hydrated, so isopropanol formation was catalyzed by hydrated protons (*18*). Since the hydrated resin network has a strong affinity for acetone (*13,19*), there might have been sufficient acetone present in the matrix to solvate propylene and shield it from catalyst protons. If this interpretation is correct, then an improved catalyst might be prepared from a resin with a larger fraction of its catalytic sites near a surface and therefore readily accessible to propylene; such a catalyst could be prepared from the previously mentioned high-surface-area resin.

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