A Heteropoly Acid Catalyst and its Convenient, Recyclable Application to Liquid-phase Cyclotrimerization of Propionaldehyde

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Heteropoly acids catalyse the cyclotrimerization of propionaldehyde to 2,4,6-triethyl-1,3,5-trioxane; catalyst and product characteristically separate into two phases so the recovered catalyst can be used repeatedly in the reaction.

A heteropoly acid (HPA) is an attractive catalyst material for various types of acid-catalysed reactions, and has been used for the hydration of propylene[1] and isobutene[2,3] and the polymerization of tetrahydrofuran.[4,5] These catalytic features are explained by both the strong Brønsted acidity[6,7] and the softness of the heteropoly anion.[8] In addition to acidity, the HPA has characteristic solubility in various solvents; it is usually insoluble in non-polar but readily soluble in polar solvents. A poor solubility of HPA in a reaction product, however, improves product selectivity, owing to the phase-transfer separation of reactant and product.[4] In this work, the acid-catalysed cyclotrimerization of propionaldehyde using several HPAs, is compared with other acid catalysts.

Keggin-type[9,10] HPA catalysts such as 12-phosphotungstic acid ($H_3PW_{12}O_{40}$), 12-phosphomolybdic acid ($H_3PMo_{12}O_{40}$) and 12-silicotungstic acid ($H_4SiW_{12}O_{40}$), containing *ca.* 30 equiv. of water (Wako) were used in the reactions without further purification. All catalytic runs were carried out in a 50 ml flask using 1 g of catalyst to 10 g of propionaldehyde under the conditions described in Table 1. The major product was isolated on a silica gel column and shown to be 2,4,6-triethyl-1,3,5-trioxane (ETX) by NMR, IR and GC–MS. Small amounts of by-products were assumed to be linear trimers and linear tetramers, evidenced by GC–MS. The conversion and selectivity were calculated by GC analysis using a column of PEG-HT (1 m).

Table 1 Liquid-phase cyclotrimerization of propionaldehyde[a]

Catalyst	Amount /mmol	*t*/h	Conversion (%)	Selectivity[b] (mol%)	TON[c]
$H_3PMo_{12}O_{40}$	0.4	2	87.1	97.2	350
$H_3PMo_{12}O_{40}$[d]	0.4	2	84.7	97.5	340
$H_3PW_{12}O_{40}$	0.3	2	86.3	97.2	490
$H_4SiW_{12}O_{40}$	0.3	2	66.2	97.3	370
SiO_2–Al_2O_3	—	2	2.8	3.1	—
$AlCl_3$	7.5	2	91.5	88.6	19
$ZnCl_2$	7.3	2	87.6	97.5	20
$ZnCl_2$[e]	—	72	69.2	92.5	15
p-TsOH	5.3	2	78.5	48.9	13
p-TsOH[f]	—	2	47.3	97.6	15
H_3PO_4[g]	8.7	4	58.2	97.3	11

[a] Reacted at room temperature, 1 g of catalyst to 10 g of propionaldehyde; [b] selectivity to 2,4,6-triethyl-1,3,5-trioxane; [c] turnover number (molar ratio of aldehyde reacted to trioxane to catalyst); [d] for 12th run; [e] 2nd run; [f] 5th run; [g] contained 15 wt% of water.

Table 1 summarizes typical results of the cyclotrimerization of propionaldehyde catalysed by various acids. An acidic solid such as silica–alumina showed low conversion of propionaldehyde and poor selectivity to ETX even after activation by calcination at 500 °C for 3 h. In contrast, soluble acids selectively catalysed the reaction with high conversions. Lewis acids such as aluminium chloride, iron(III) chloride, and zinc chloride were also active with selectivities higher than 85%.

For $H_3PMo_{12}O_{40}$, the reaction proceeded homogeneously in the initial stages. The reaction mixture became turbid, and began to separate into two liquid phases at about 40% conversion. Ultimately, the product solution of the upper layer changed from acidic to pH ~7, attaining high conversion and selectivity. The catalyst solution of the lower layer can be used repeatedly without isolation of HPA, and its catalytic activity remains unchanged even after the tenth run. $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were also active both exhibited similar phase separation as that for $H_3PMo_{12}O_{40}$.

The composition of the catalyst phase was a molar ratio of *ca.* 1:33:10:11 for $H_3PMo_{12}O_{40}$, H_2O, propionaldehyde, and ETX at a conversion of 80.4%. After the catalyst phase had been evacuated at 60 °C, the residual solid was the same as HPA itself, from IR observation. It has been speculated that the catalyst phase contains a complex of HPA coordinated with the produced ETX. As the complex is insoluble in ETX, but soluble in propionaldehyde, the complex has been gradually removed from the product solution with the increase in conversion. Detailed studies on the active catalyst phase are now in progress.

Although the phase separation was not observed for either aluminum chloride or iron(III) chloride, which both gave gel-like precipitates, a reaction mixture was separated into two liquid phases for zinc chloride, *p*-toluenesulphonic acid and phosphoric acid. The effectiveness of the catalyst decreased with the number of cycles. This is caused by gradual catalyst loss into the product phase, depending upon the partition coefficient of the catalyst to ETX.

HPA catalysts also catalysed the cyclotrimerization of other aliphatic aldehydes, such as butyraldehyde, isobutyraldehyde, hexylaldehyde, octylaldehyde, and decylaldehyde to form 2,4,6-trialkyl-1,3,5-trioxane in yields of 80–100%, also with phase separation between catalyst and product. For acetaldehyde, however, the reaction mixture was homogeneous even at conversions higher than 95%.

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