

Ketalization of ketones with diols catalyzed by metal(IV) phosphates as solid acid catalysts

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Abstract

Metal(IV) phosphates of tin, zirconium and titanium in different morphological forms, viz. amorphous, calcined and crystalline, have been used as catalysts for selective ketalization of ketones. A comparative study of the catalysts for the aforementioned reaction has been carried out to understand the effect of the composition and morphology on their catalytic activity.

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1. Introduction

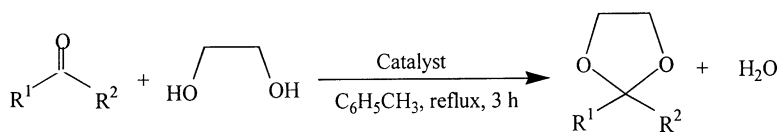
The protection of carbonyl group is sometimes necessary in the manipulation of organic molecules with multiple functional groups. Cyclic acetals and ketals are the most useful protective groups for the carbonyl functionality [1]. Acetals and ketals are generally prepared from carbonyl compounds and alcohols in the presence of acid catalysts. The commonly used catalysts are sulfuric acid, hydrochloric acid, phosphoric acid and *p*-toluenesulfonic acid [1,2]. These catalysts cause corrosion and are not environment-friendly. Therefore, it is desirable to use solid acid catalysts which are free from the previous disadvantages. Recently, diethoxyethane (acetal), which can be used as a diesel additive for the improvement of cetane number, has been prepared from acetaldehyde and ethanol

using a variety of heterogeneous catalysts e.g. montmorillonite, mordenite, sulfonic ion exchange resin and zeolitic and amorphous FCC catalysts [3].

We have applied metal(IV) phosphates as solid acid catalysts for selective ketalization of carbonyl compounds. Metal phosphates have the general formula $M^{IV}(HXO_4)_2 \cdot nH_2O$ where $M^{IV} = Sn, Ti, Zr, Ce, Th$ and $X = P, As, W, Mo$ and possess both, Brønsted and Lewis acid sites. These compounds have been reported as solid acid catalysts for dehydration of alcohols [4], double bond isomerization in alkenes [5] and Friedel Crafts reaction [6]. Earlier, we have applied tetravalent metal phosphates of tin, zirconium and titanium as catalysts for selective cyclodehydration of diols to cyclic ethers [7,8] and hydration of nitriles to amides [9]. Herein, we report, for the first time, application of these catalysts in different morphological forms viz. amorphous, calcined and crystalline for selective ketal formation from the carbonyl compounds and, 1,2- and 1,3-diols.

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2. Experimental

^1H NMR spectra were recorded as CDCl_3 solutions on a Varian FT 200 spectrometer using TMS as an internal standard. Gas chromatographic analysis was performed on Datalab GC 900 series instrument with a flame ionization detector. A 15 m long capillary column, AT-wax (Alltech, USA) and nitrogen as a carrier gas were used.

The amorphous (SnP_{amp} , ZrP_{amp} and TiP_{amp}) and crystalline (SnP_{cry} , ZrP_{cry} and TiP_{cry}) catalysts were prepared by the procedure reported earlier [7,8]. The calcined catalysts (SnP_{cal} , ZrP_{cal} and TiP_{cal}) were prepared by thermal treatment of the corresponding amorphous samples in a muffle furnace at 400°C for 6 h. The catalysts were characterized by elemental analysis, thermogravimetric analysis, XRD, surface area and pore volume determination, and acidity measurement by temperature programmed ammonia desorption as reported in our earlier work [7,8].

A typical procedure for ketalization reaction is as follows: a mixture of cyclohexanone (100 mmol), 1,2-ethanediol (100 mmol), SnP_{amp} catalyst (1.54 mmol, based on tin) and toluene (45 cm^3) were taken in a

round bottom flask fitted with a Dean–Stark apparatus to remove the water continuously from the reaction mixture. The contents were refluxed for the specified periods as shown in the tables. The progress of the reaction was monitored by GC analysis of the small aliquots withdrawn at half an hour intervals.

The ketals were isolated by the following procedure. The reaction mixture was cooled to room temperature and the catalyst filtered off. The filtrate was extracted with water ($3 \times 20\text{ cm}^3$) in a separatory funnel to remove the unchanged diol. The organic layer was dried (MgSO_4) and the solvent removed on a rotary evaporator. The residue was subjected to vacuum distillation to remove the unchanged ketone. The residue after distillation gave nearly pure ketal as shown by thin layer chromatography over silica gel plates. Their structures were confirmed by ^1H NMR spectra.

3. Results and discussion

Ketalization of cyclohexanone with 1,2-ethanediol was studied in order to optimize the reaction conditions and to compare the activity of the catalysts. The results are shown in Table 1. Use of cyclohex-

Table 1
Ketalization of cyclohexanone with 1,2-ethanediol catalysed by metal(IV) phosphates^a

Entry	Catalyst	Mole ratio cyclohexanone:catalyst	Mole ratio cyclohexanone:1,2-ethanediol	Ketal yield ^b (%)
1	SnP_{amp}	65:1	1:1	86
2	SnP_{amp}	130:1	1:1	72
3	SnP_{amp}	35:1	1:1	87
4	SnP_{amp}	65:1	1:1.3	90
5	ZrP_{amp}	65:1	1:1.3	75
6	TiP_{amp}	65:1	1:1.3	69
7	SnP_{cal}	65:1	1:1.3	83
8	ZrP_{cal}	65:1	1:1.3	68
9	TiP_{cal}	65:1	1:1.3	61
10	SnP_{cry}	65:1	1:1.3	74
11	ZrP_{cry}	65:1	1:1.3	60
12	TiP_{cry}	65:1	1:1.3	51

^a Reaction time 3 h.

^b Yield based on ketone taken.

anone to SnP_{amp} catalyst mole ratio of 65:1 gave high yield of the corresponding ketal (entry 1). Lowering the amount of catalyst to half resulted in decrease in the yield of the ketal (entry 2). However, doubling the amount of catalyst has practically no effect on the yield (entry 3). Therefore, ketone to catalyst mole ratio of 65:1 was used in all other reactions. Increase in the mole ratio of cyclohexanone to 1,2-ethanediol from 1:1 to 1:1.3 led to high yield (90%) of the ketal (entry 4). Reactions were complete in 3 h; there was no further increase in the yield on continuing the reaction up to 6 h. These conditions were used for reactions with all the catalysts to compare their catalytic activities. Amongst the three forms, the activity decreased in the following order: SnP > ZrP > TiP (entries 4–12). This is shown graphically in Fig. 1 for the amorphous catalysts. The reason for the higher activity of SnP is its high surface area and higher number of acid sites as compared to ZrP and TiP catalysts. Moreover, SnP_{amp} has more number of stronger acid sites as compared to ZrP_{amp} and TiP_{amp} [7]. Similar trends were observed in the reaction of cyclodehydration of 1,4-butanediol [8].

For a given metal, the amorphous form has the highest activity while the crystalline ones showed the lowest. The calcined samples exhibited activity, which was intermediate between the two (Table 1). This variation of activity among the three forms can be explained on

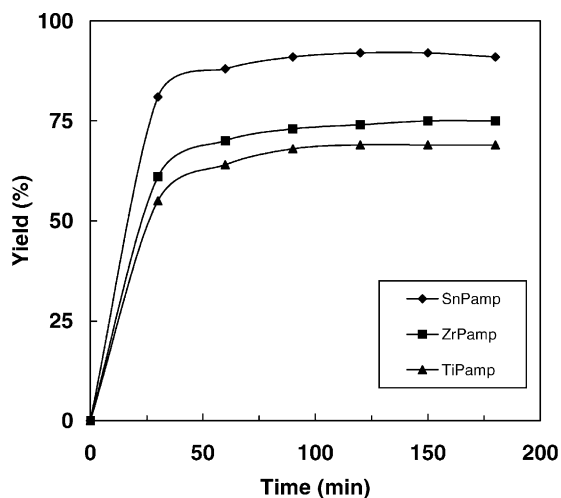


Fig. 1. Ketalization of cyclohexanone with 1,2-ethanediol in the presence of amorphous SnP, ZrP and TiP catalysts.

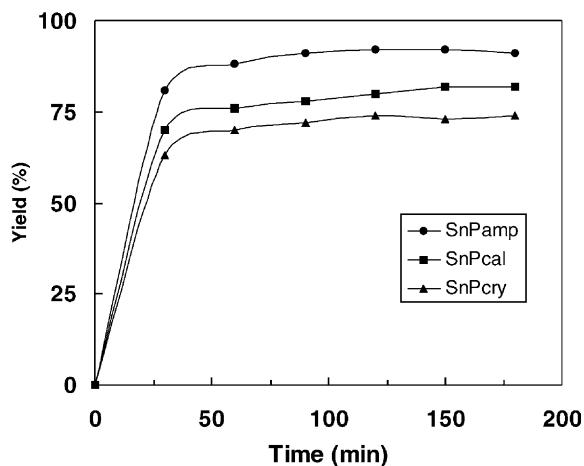


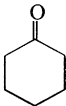

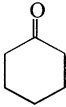
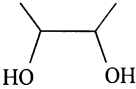
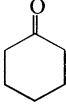
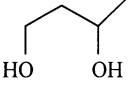
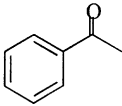

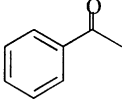

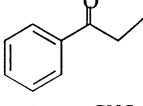

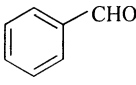

Fig. 2. Ketalization of cyclohexanone with 1,2-ethanediol in the presence of amorphous, calcined and crystalline SnP catalysts.

the basis of their surface area and number of acid sites. Crystalline samples have lower surface area and less number of acid sites as compared to the amorphous form [4,8] and therefore show lower catalytic activity. Calcination of the amorphous catalysts reduces its surface area and also there is a small decrease in the total acidity of the catalyst, which is responsible for relatively lower activity of the calcined catalysts [8]. This comparison is shown in Fig. 2 for SnP catalysts in different forms. Clearly, amorphous catalyst shows higher activity than the corresponding calcined and crystalline catalysts. Similar trends were observed for the corresponding ZrP and TiP catalysts which are not shown graphically.

Since SnP_{amp} showed the highest activity, it was applied as catalyst for the reactions with other substrates (Table 2). To see the effect of the diol variation, 1,2-ethanediol, 2,3-butanediol and 1,3-butanediol were used for the ketalization of cyclohexanone. 1,2-Ethanediol and 2,3-butanediol gave high yield of the corresponding ketals (entries 1 and 2). 1,3-Butanediol which affords six membered ring ketal, gave slightly lower yield (entry 3). Under these conditions, the reaction of acetophenone and 1,2-ethanediol gave moderate yield of the ketal (entry 4). An increase in the reaction time to 6 h has no significant effect on the yield (entry 4). However, increase in the amount of diol led to significant

Table 2

Ketalization of carbonyl compounds with diols catalyzed by amorphous tin(IV) phosphate^a

Entry	Substrate	Diol	Mole ratio of substrate:diol	Yield ^b (%)
1			1:1.3	91
2			1:1.3	78
3			1:1.3	75
4			1:1.3	56 (58) ^c
5			1:2	77
6			1:2	72
7			1:2	62

^a Ketone:catalyst mole ratio 65:1. Reaction time 3 h.^b Yield based on ketone taken.^c Reaction time 6 h.

enhancement in the yields of the ketal (entry 5). Propiophenone, afforded the corresponding ketal in high yield (entry 6). The reaction was extended to benzaldehyde, which gave its acetal in good yield (entry 7). In all the reactions, ketals were obtained as the only products attesting to the high selectivity of the reaction.

4. Conclusion

The tetravalent metal acid salts described herein are novel and selective heterogeneous catalysts for

the preparation of ketals from ketones. Amorphous tin(IV) phosphates, which exhibited the highest activity, shows potential for future development as a practical catalyst for ketalization.

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