Metal exchanged layered zirconium hydrogen phosphate as base catalyst of the Michael reaction

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Layered zirconium hydrogen phosphate, exfoliated by intercalation of propylamine and then exchanged with alkali metal ions has proved to be an excellent catalyst for Michael addition of β-dicarbonyl compounds. The reactions occur with high yield, in mild conditions and with ease of work up. The catalyst, recovered from the reaction vessel, may be reused several times.

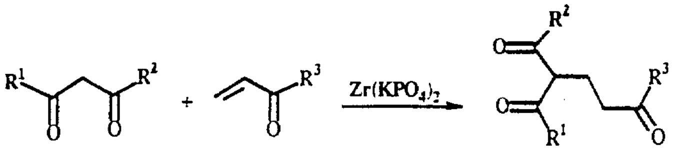
Keywords: Layered zirconium phosphate; heterogeneous base catalysis; Michael addition

Recently much attention has been given to the chemistry of layered phosphates and phosphonates of tetravalent metals, mainly zirconium, for their ion exchange, intercalation, catalytic and ionic conduction properties [1]. Alpha zirconium hydrogen phosphate, $Zr(HPO_4)_2$, is considered the archetype of this class of compounds, its structure [2] arising from the packing of layers each of them consisting of zirconium atoms, lying nearly in a plane and sandwiched between O_3POH groups placed alternately above and below the metal atom plane. The hydrogenphosphates present on each side of the layer are arranged in a hexagonal array at a distance of 5.3 Å from each other; the surface density is 4.12×10^{14} groups per cm^2, equivalent to one POH group every 24 $Å^2$. The layers are so stacked that each POH of one layer is directly above and below the zirconium atom of the adjacent layer, the interlayer distance being 7.6 Å. The protons of the POH groups are easily exchanged with other cations that are accommodated on the surface of the microcrystals and in the interlayer region with a concomitant increase of the interlayer distance. The ion exchange capacity is 6.64 meq/g. Layered α-zirconium hydrogenphosphate may be thus considered a solid acid with regularly spaced surface acidic groups. Moreover the compound is highly insoluble and it has a good thermal stability. Condensation to pyrophosphate of the POH in the interlayer region begins at ca. 450°C, while the condensation of surface POH groups occurs at considerably higher temperatures [3]. Thus α-$Zr(HPO_4)_2$ is a suitable material for acid catalysis at medium temperatures and its catalytic activity has been tested for dehydration, isomerization and hydrogenation reactions [4–6].

To our knowledge no base-catalyzed reactions, using zirconium phosphate as catalyst, have been tested. However, α-$Zr(HPO_4)_2$ contains moderately weak acidic groups that may be converted into moderately strong Brønsted basic sites by exchanging the protons of the POH groups with metal cations.

Alkali metal exchanged forms of zirconium phosphate, that is compounds of formula $Zr(MPO_4)_2$ (M = Li, Na, K, Cs), should thus act as good basic catalysts, able to pull off protons, generating carbanions that may attack an electron-acceptor center.

Preliminary experiments indeed showed that α-$Zr(MPO_4)_2$ microcrystals catalyze Michael reactions, that is:



and it was observed that the rate of a test reaction (i.e. acetylacetone–methylvinylketone) increases with the increasing ionic radius of the exchanged cation. Once the activity of the catalyst was tested, it was decided to perform a series of Michael reactions by using the K^+-form as catalyst.

A large batch of α-$Zr(HPO_4)_2 \cdot H_2O$ was prepared according to the HF-method [7]. The BET specific surface area of the well-formed microcrystals was determined by N_2-adsorption isotherm, at 77 K, of a sample of about 10 g, in order to increase the accuracy of the measurement. The value obtained, 0.5 m^2/g, was similar to those previously reported [8]. In order to increase the surface area, the layered microcrystals were exfoliated by intercalation of *n*-propylamine [9], then washed with HCl 0.2 M up to pH $\approx$ 1 in order to regenerate the hydrogen form. During this latter treatment the dispersion was put under sonication, to prevent the reaggregation of the zirconium phosphate lamellae. As a consequence of this treatment the surface area of the microcrystals rose to 17 m^2/g. The material was then titrated with (KCl + KOH) 0.1 M solution up to pH $\approx$ 10, washed first with 0.02 M K_2HPO_4 to remove the chloride ions, and then with a little water brought to pH 9 with some drops of KOH solution. The microcrystals were finally dried at 200°C for two days in order to remove the crystallization water. The X-ray diffraction pattern of the compound corresponds [10] to that of $Zr(KPO_4)_2$, the surface area being 15.5 m^2/g.

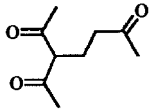
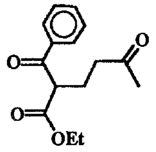
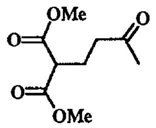
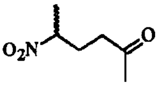
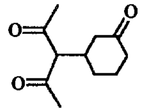
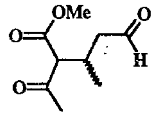
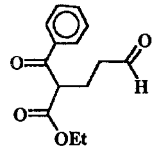
In a typical experiment the Michael donor (1 mmol) was added to 0.180 g of $Zr(KPO_4)_2$ (0.5 mmol) and stirred at 60°C for 20 min. The Michael acceptor

(1 mmol) was then added and the slurry was stirred, at a constant temperature until the disappearance of the reactant, monitored by tlc. Dichloromethane was added to the reaction mixture and the catalyst was filtered off. The solvent was removed under vacuum and the residue chromatographed on a short silica gel column.

Table 1 shows the results obtained by using different Michael donors and acceptors. As may be seen the reactions occur with high yield, in mild conditions, in the absence of solvent and of relevant side reactions. The reaction work up is easy and the catalyst, washed with dichloromethane, may be reused several times.

Table 1

Examples of $Zr(KPO_4)_2$-mediated Michael reactions

Donor	Acceptor	Adduct	Time	Yield [a] (%)
acetylacetone	MVK [b]		30 min	85
ethylbenzoylacetate	MVK		1 h	95
dimethylmalonate	MVK		1 h	95
nitroethane	MVK		3 h	69 [c]
ethylacetoacetate	2-cyclohexen-1-one		10 h	92 [d]
ethylacetoacetate	crotonaldehyde		1 h	89 [d]
ethylbenzoylacetate	acrolein		30 min	98

[a] Yield of isolated pure products, characterised by their IR ^1H NMR, ^{13}C NMR and GC-MS data.

[b] MVK is abbreviation for methylvinylketone.

[c] The reaction was carried out at 25°C.

[d] Diastereoisomeric mixture.

The results are similar and in some cases better than those obtained when the Michael reaction is mediated by potassium fluoride on alumina [11] or transition metal complexes supported on clays [12] or by activated alumina [13,14]. Better results are expected if zirconium phosphate with a higher surface area were used. However, it is noteworthy that the condensation of nitroethane with methylvinylketone occurs easily at 25°C (see table 1).

With these preliminary results we have shown that the catalytical activity of zirconium phosphate is not confined to acid catalysis. Base catalysis may be performed, even at medium and high temperatures (the K-exchanged zirconium phosphate is stable up to 1200°C), by using its alkali metal exchanged forms. Work is in progress to test this base-catalyst for the Michael and other classes of reactions and to study the effect of the nature of the exchanging cation on its catalytical activity.

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