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Potassium Exchanged Layered Zirconium Phosphate as Base Catalyst in the Synthesis of 2-Nitroalkanols

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The synthesis of 2-nitroalkanols from nitroalkanes and aldehydes occurs efficiently, in mild conditions without solvent, when mediated by layered $Zr(KOPO_3)_2$. The reaction has been tested in the preparation of ten different nitroalkanols and the data obtained seem to indicate that not only the surface but also the interlayer $\equiv P\text{-}O^-K^+$ groups are involved in the catalytic process.

In recent years many inorganic solids have been used as catalysts or supports of catalysts in liquid phase organic synthesis for fine chemicals.[1,2] Among them, special attention has been given to layered materials (clays and modified clays, metal (IV) phosphates and phosphonates, layered double hydroxides, and so on) since the lamellar surface seems more effective than porous or spongy surface in many catalyzed reactions.[3] Furthermore, these layered compounds may also offer the inner layer surfaces to the reactants, as a result of intercalation processes.[4,5]

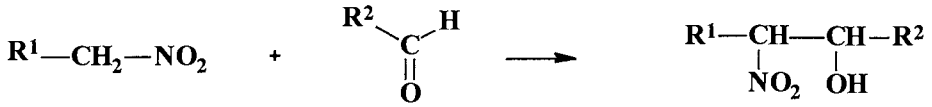
Layered metal (IV) phosphates and phosphonates of the α-type have the formula $M(IV)(RPO_3)_2$ (M = Ti, Zr, Sn, Ce; R = OH or organic groups) and their structure arises from the packing of layers each of which is constituted of a plane of metal atoms capped by tetrahedral PO_3R groups. The P-R bond points toward the interlayer space.[6-8] These compounds show remarkable structural and chemical analogies with smectite clays and compare well with them in terms of the degree of crystallinity, chemical stability and ion exchange capacity.[9] Like the smectite clays,[10] the layered phosphates and particularly $\alpha\text{-}Zr(HOPO_3)_2$, have been and are being investigated as catalysts specially in acid- catalyzed reactions.[11,12] In a recent communication[13] we have shown that the catalytic activity of zirconium phosphate is not confined to acid catalysis, base-catalyzed reactions, such as the Michael addition, being efficiently performed in the presence of the potassium exchanged form of the compound, i.e. $Zr(KOPO_3)_2$. It is likely that the surface $\equiv P\text{-}O^-$ group acts as a strong Bronsted base able to extract a proton from a Michael donor, store it while the potassium ion stabilizes the carboanion that attacks the acceptor. In that paper we noted that the reaction of nitroethane with methylvinylketone occurs easily at 25 °C in 3 h with a 69% yield. Thus it seemed of interest to test this base-catalyst in the nitroaldol condensation (Henry reaction) for the preparation of 2-nitroalkanols which are a useful intermediate to obtain fine chemicals such as nitroalkenes, aminoalcohols, nitroketones.

The classical methods of preparation of 2-nitroalkanols[14] (use of NaOH solution, triethylamine, powdered KOH or KF) are often disadvantageous, since the yield is not high and mixtures of undesiderable products are sometimes obtained. Good result are obtained with trialkylsilyl chlorides, but the procedure is

laborious.[15] The reaction has been improved by the use of heterogeneous catalysts such as alumina[16] or alumina supported potassium fluoride.[17]

We report here a mild, simple and efficient synthesis of 2-nitroalkanols from nitroalkanes and aldehydes in the presence of Zr $(KOPO_3)_2$ without any solvent (Table 1).

Table 1.



1 2 3

3	R^1	R^2	Reaction time/ h	Yield [a] /%
a)	CH_3—	C_2H_5—	24	62
b)	CH_3—	i-C_3H_7—	14	72
c)	CH_3—	C_5H_{11}—	23[b]	85
d)	CH_3—	c-C_6H_{11}—	24[b]	75
e)	HO—CH_2—	C_2H_5—	6	89
f)	HO—CH_2—	i-C_3H_7—	8	88
g)	HO—CH_2—	C_5H_{11}—	8	66
h)	C_5H_{11}—	C_2H_5—	24[b]	67
i)	CH_3—		23[b]	83[c]
l)	C_5H_{11}—		25[b]	71[c]

a) Yield of isolated product; all products were obtained as a diasteroisomeric mixture.

b) The reaction was carried out at 40 °C.

c) The product cannot be purified because of its instability.

The catalyst was obtained by titrating α-zirconium phosphate, previously exfoliated by intercalation of propylamine, with a (KCl +KOH) 0.1 M solution up to pH 9-10, as described in reference 13. The N_2 adsorption specific surface area of the catalyst, previously outgassed at 200 °C, turned out to be 8.5 m^2/g. In a typical experiment 1.5 g of catalyst (4.2 mmol) was added to the mixture of 9 mmol of each reactant, held under stirring at room temperature, under a N_2 flow. The formation of the product was monitored by TLC; at the end of the reaction, dichloromethane was added to the mixture, the catalyst was filtered off and the solvent removed

under reduced pressure. The purification of the product was performed by chromatography and the product was identified by I.R. and ^{1}H-N.M.R. spectral data.[18]

Most of the tested reactions take place with a good yields in much shorter times than when alumina is used as a catalyst[16] and are comparable with those obtained in the presence of alumina-supported potassium fluoride.[17] In the case of more bulky substrates (c, d, h, i, l) the reaction time, at room temperature, is several days while at 40 °C the reactions take place in less than one day.

Some experiments have been performed on a test reaction (i.e. nitroethanol and propionaldehyde) to check the effect of the ratio substrate/catalyst on the reaction time. As may be seen in Fig. 1, the change of this ratio from 1 to about 8 does not affect considerably the reaction time.

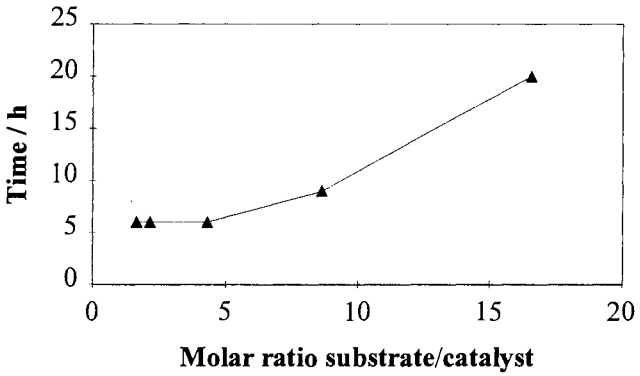


Fig. 1. Reaction times of 2-nitroethanol and propionaldehyde condensation as a function of substrate/catalyst molar ratio. The reactions were performed at room temperature and the times refer to yields higher than 85%.

K^+-exchanged zirconium phosphate thus shows a good catalytical activity in spite of its low surface area, as if the interlayer regions of this layered compound were also involved in the catalytic process. To obtain experimental evidence for this assumption, the test reaction was carried out using as catalyst a layered zirconium phosphate having the interlayer regions inactivated after condensation of the inner ≡P-OH groups into P-O-P groups. The original zirconium phosphate was heated at 650 °C for 12 h, to obtain layered zirconium pyrophosphate with an interlayer distance of 6.1 Å.[19] This compound still possesses surface P-OH groups as shown by the uptake of cations and by its catalytic activity in isopropanol dehydration.[20] The surface ≡P-OH groups were converted into ≡P-O$^-$K$^+$ by titration with (KCl + KOH) 0.1 M solution up to pH 9; the surface ion exchange capacity was 75 μeq/g. 1.5 g of this catalyst was heated at 200 °C for 12 h, and subsequently added to the reaction mixture as previously described. A strong decrease of the catalytic activity was observed, the yield of the product being less than 10% after two days at room temperature. This result seems to support the hypothesis that the nitroaldol condensation mediated by $Zr(KOPO_3)_2$ in some manner involves the interlayer catalytic sites.

Studies of the reaction mechanisms as well as the investigation of other Zr $(KOPO_3)_2$ mediated reactions, are underway. The Authors wish to thank CNR and MURST, Italy, for financial support.

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17) J. M. Melot, F. Texier-Boullet, and A. Foucaud, *Tetrahedron Lett.* , **27**, 493 (1986).
18) **3a**: data quoted in Ref.16. **3b**: data quoted in Ref.17. **3c**: oil; ^{1}H-NMR 200 MHz ($CDCl_3$) δ = 0.91 (3H, t, J = 7 Hz, $C\underline{H}_3$-CH_2); 1.20-1.52 (8H, m, methylenes); 1.54, 1.57 (3H, each d, J = 7 Hz, $C\underline{H}_3$-CH-NO_2); 3.82-4.25 (1H, m, C<u>H</u>-OH); 4.44-4.62 (1H, m, C<u>H</u>-NO_2); IR (CH_2Cl_2) 3614, 1556 cm^{-1}. **3d**: data quoted in Ref.16. **3e**: oil, ^{1}H-NMR 200 MHz ($CDCl_3$) δ = 1.03, 1.05 (3H, each t, J = 7 Hz, methyls); 1.50-1.70 (2H, m, CH_3-$C\underline{H}_2$); 3.94-4.30 (3H, m, C<u>H</u>-OH and $C\underline{H}_2$-OH); 4.45-4.68 (1H, m, C<u>H</u>-NO_2); IR (CH_2Cl_2) 3610, 1560 cm^{-1}. **3f**: oil, ^{1}H-NMR 200 MHz ($CDCl_3$) δ = 0.98-1.10 (6H, m, methyls); 1.70-1.88 (1H, m, $(CH_3)_2$-C<u>H</u>); 3.70-4.30 (3H, m, C<u>H</u>-OH and $C\underline{H}_2$-OH); 4.58-4.82 (1H, m, C<u>H</u>-NO_2); IR (CH_2Cl_2) 3612, 1560 cm^{-1}. **3g**: oil, ^{1}H-NMR 200 MHz ($CDCl_3$) δ = 0.90 (3H, t, J = 7 Hz, methyl); 1.20-1.63 (8H, m, methylenes); 4.00-4.36 (3H, m, C<u>H</u>-OH and $C\underline{H}_2$-OH); 4.43-4.66 (1H, m, C<u>H</u>-NO_2); IR (CH_2Cl_2) 3618, 1558 cm^{-1}. **3h**: oil, ^{1}H-NMR 200 MHz ($CDCl_3$) δ = 0.88 (3H, t, J = 7 Hz, ($C\underline{H}_3$-CH_2); 1.01, 1.03 (3H, each t, J = 7 Hz,$C\underline{H}_3$-CH_2-CH-OH); 1.22-1.90 (10H, m, methylenes); 3.73-3.98 (1H, m, C<u>H</u>-OH); 4.38-4.52 (1H, m, C<u>H</u>-NO_2); IR (CH_2Cl_2) 3612, 1552 cm^{-1}. **3i**: data quoted in Ref.17. **3l**: oil, ^{1}H-NMR 200 MHz ($CDCl_3$) δ = 0.88 (3H, t, $C\underline{H}_3$-CH_2); 1.10-2.10 (8H, m, methylenes); 4.80-4.98 (1H, m, C<u>H</u>-NO_2); 5.03-5.20 (1H, m, C<u>H</u>-OH); 6.40, 7.40 (3H, each m, aromatic); IR (CH_2Cl_2) 3600, 1560 cm^{-1}.
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