Heterogeneous Catalysis of the Friedel-Crafts Alkylation by Doped Natural Phosphate and Tricalcium Phosphate

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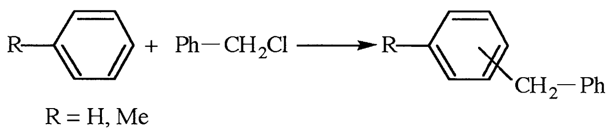
Catatytic behavior has been observed for tricalcium phosphate and either copper or zinc chloride doped natural phosphate for the Friedel-Crafts reaction. Monoalkylation has been quantitatively achieved with high selectivity.

The increasing development of chemical reactions in heterogeneous conditions leads to detection of new performing solid catalysts . Salts and inorganic oxides such a silica, alumina and montmorillonite are some of the most investigated catalysts.[1-5]

The heterogeneous catalysis of the Friedel-Crafts reaction has allowed to bypass the various inconveniences of the homogeneous conditions while improving the reaction yields.[6,7] As an example K10-montmorillonite pure or doped with various transition elements has been used for alkylation of benzene and toluene.[8] It gives rise to a mixture of mono- and dialkylcompounds. A good selectivity for monoalkylation has been carried out by activation at high temperature of doped montmorillonite.[9,10]

We have shown recently [11] that natural phosphate and trisodium phosphate are new basic catalysts for Knoevenagel condensation. Evidence is given here of the influence of phosphate acidic character on hand of the heterogeneous catalysis of benzene and toluene benzylation. Natural phosphate (NP) [13] comes from an ore extracted in the region of Khoribga (Morocco). The fraction of 0.1 - 0.4 mm grain size has been washed, calcined (900 °C in 2 h), washed again and ground. The specific surface area of NP is low (1 $m^2 g^{-1}$) and its density is 3.1. The main constituent is fluorapatite as was shown by the analysis of RX spectra.



The solution of benzyl chloride (9 mmol) in benzene or toluene (15 ml) was refluxed in the presence of the catalyst. High selectivity of the synthesis of the monoalkylcompound has been observed for all catalysts considered. The reactivity of tricalcium phosphate (TCP) [12] is much higher than that of natural phosphate (NP) [13] alone, the activity seems also stronger than that of montmorillonite.[8] The benzylation of benzene using TCP gives the monoalkylation product in 56% (6 h) and 69% (24 h). In the presence of K10-montmorillonite, the monoalkylation product was obtained in 48% (15 h). After deposit of $ZnCl_2$, NP in also more efficient than with $CuCl_2$. The same behavior difference has been observed also when both chlorides are added to K10-montmorillonite.[8] The conversion (100%) of $PhCH_2Cl$ to form diphenylmethane using NP-$ZnCl_2$ (87% in 1,5 h) is more selective than using K10-$ZnCl_2$ (60% in 1,5 h). NP-$ZnCl_2$ is the most efficient catalyst among the phosphates investigated. Table 1 and 2 summarize the best results obtained with the mass of catalyst involved and the minimum reaction times used.

Table 1. Benzene benzylation by Ph-CH_2Cl

Catalyst	Mass / time (g) / (h)	Conversion (%) [a]	Monoalkyl-compound (%) [a]	Dialkyl-compound (%) [a]
TCP [12]	2 / 3.5	57	40	7
NP [13]	4 / 24	42	30	5
NP-$ZnCl_2$ [14]	1.4 / 1.5	100	92 (87) [b]	7
NP-$CuCl_2$ [14]	1.4 / 6	100	80 (74) [b]	7

[a] GC determination. [b] Output in isolated compound after distillation.

Table 2. Toluene benzylation by Ph-CH_2Cl

Catalyst	Mass /time (g) / (mn)	Conversion (%) [a]	Monoalkyl-compound (%) R [a] (R) [b]	O/P [c]	Dialkyl-compound (%) [a]
TCP	1.5 / 30	100	91 (86)	35/65	5
NP	2 / 120	100	91 (87)	42/58	5
NP-$ZnCl_2$	0.6 / 5	100	93 (89)	42/58	3
NP-$CuCl_2$	1 / 15	100	95 (90)	40/60	4

[a] GC determination. [b] Output in isolated compound after distillation.
[c] Ortho / Para ratio determined by proton NMR.

References and Notes

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12 Tricalcium phosphate (TCP) is a commercial product (Prolabo, Ca% ≈ 35.5) previously dried at 150 °C.
13 Chemical analyses of natural phosphate (NP), (%) : CaO (55.94), P_2O_5 (35.07), F^- (4.28), SiO_2 (2.13), SO_3 (1.59), CO_2 (1.10), Na_2O (0.50), MgO (0.39), Al_2O_3 (0.30), Fe_2O_3 (0.17), K_2O (0.03), Cl_2 (300 ppm), Zn (218 ppm), Cr (117 ppm), Cu (31 ppm) and Cd (16 ppm).
14 The doped catalyst has been prepared with a rate of 10 mmol metalic salt (either $ZnCl_2$ or $CuCl_2$) for 10 g natural phosphate.