

Baeyer-Villiger oxidations with ionic liquids intercalation compounds into layered zirconium phosphates

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Introduction

To the best knowledge of the authors of this abstract, there is a lack of results concerning the use of ionic liquids intercalation compounds into layered zirconium phosphates on Baeyer-Villiger oxidations.

The oxidation of *p*-methoxybenzaldehyde and 2,4,6-trimethylbenzaldehyde is a very useful reaction from the industrial point of view, since its products are important starting materials for the production of fine chemicals used in medicine, cosmetics and perfumery.

In the last decades, the use of metal phosphates as catalysts in various reactions received considerable attention [1,2]. These materials exhibit important characteristics for intercalation chemistry because their interlayer gallery can be expanded and modified to accommodate almost any size entity from small ions to macromolecules. More recently, ionic liquids (ILs), a class of organic compounds with extraordinarily low melting temperatures, also received significant attention. They are considered as “green” or “designer” solvents and are used in various catalysis and extraction reactions worldwide. However, in general, their separation from the reactants and products is a difficult process. This disadvantage may well be avoided if the ionic liquids are intercalated into suitable materials.

Recently, a series of ionic liquids have been intercalated into α and γ -zirconium phosphates [3]. Having in mind a comparative study with other types of catalysts previously tested with *p*-methoxybenzaldehyde and 2,4,6-trimethylbenzaldehyde, in our laboratory, their oxidation was performed using 1-ethyl-3-methylimidazolium chloride and 1-hexyl-3-methylimidazolium chloride intercalated into α and γ -zirconium phosphates, hydrogen peroxide as oxidant and acetic acid as solvent.

Experimental

α -ZrP[C₂mim]Cl, γ -ZrP[C₂mim]Cl and α -ZrP[C₆mim]Cl were prepared from α -ZrP and γ -ZrP, previously intercalated with *n*-butylamine, and 1-ethyl-3-methylimidazolium chloride and 1-hexyl-3-methylimidazolium chloride, respectively. These solids were characterized by XRD and Raman spectroscopy. The oxidation reactions of 2,4,6-trimethylbenzaldehyde and *p*-methoxybenzaldehyde were carried out in acetic acid at 60°C using hydrogen peroxide as oxidant. The molar ratio between the substrate and the oxidant was 1:4. The reaction mixtures were analysed after 6 and 24 hours of reaction by GC and GC/MS chromatography.

Results/Discussion

Table 1. Oxidation of 2,4,6-trimethylbenzaldehyde with H₂O₂ (1:4) in acetic acid at 60°C, after 6 hours of reaction

| Products (%) | Blank | α -ZrP | α -ZrP[C ₂ mim] | α -ZrP[C ₆ mim] | γ -ZrP | γ -ZrP[C ₂ mim] |
|--|-------|---------------|-----------------------------------|-----------------------------------|---------------|-----------------------------------|
| Selectivity of 2,4,6-trimethylphenol | 10.2 | 12.0 | 14.0 | 17.1 | 11.2 | 15.0 |
| Selectivity of 2,4,6-trimethylphenyl formate | 89.8 | 88.0 | 86.0 | 82.9 | 88.8 | 85.0 |
| Conversion of 2,4,6-trimethylbenzaldehyde | 100 | 100 | 100 | 100 | 100 | 100 |

Table 2. Oxidation of 2,4,6-trimethylbenzaldehyde with H₂O₂ (1:4) in acetic acid at 60°C, after 24 hours of reaction

| Products (%) | Blank | α -ZrP | α -ZrP[C ₂ mim] | α -ZrP[C ₆ mim] | γ -ZrP | γ -ZrP[C ₂ mim] |
|--|-------|---------------|-----------------------------------|-----------------------------------|---------------|-----------------------------------|
| Selectivity of 2,4,6-trimethylphenol | 7.2 | 9.7 | 18.6 | 22.2 | 8.3 | 38.6 |
| Selectivity of 2,4,6-trimethylphenyl formate | 92.8 | 90.3 | 81.4 | 77.8 | 91.7 | 61.4 |
| Conversion of 2,4,6-trimethylbenzaldehyde | 100 | 100 | 100 | 100 | 100 | 100 |

Table 3. Oxidation of *p*-methoxybenzaldehyde with H₂O₂ (1:4) in acetic acid at 60°C, after 6 hours of reaction

| Products (%) | Blank | α -ZrP | α -ZrP[C ₂ mim] | α -ZrP[C ₆ mim] | γ -ZrP | γ -ZrP[C ₂ mim] |
|--|-------|---------------|-----------------------------------|-----------------------------------|---------------|-----------------------------------|
| Selectivity of <i>p</i> -methoxyphenol | 45.8 | 52.1 | 73.0 | 74.0 | 55.7 | 74.0 |
| Selectivity of <i>p</i> -methoxyphenyl formate | 54.2 | 47.9 | 27.0 | 26.0 | 44.3 | 26.0 |
| Conversion of <i>p</i> -methoxybenzaldehyde | 100 | 100 | 100 | 100 | 100 | 100 |

Good results have been obtained in the oxidation reactions of 2,4,6-trimethylbenzaldehyde and *p*-methoxybenzaldehyde. The best results were found with the catalysts α -ZrP[C₆mim]Cl and γ -ZrP[C₂mim]Cl. Good results were also obtained with α -ZrP[C₂mim]Cl. These catalysts have basic properties, so, we suggest that their structure can play a decisive role in the conversion of the 2,4,6-trimethyl and *p*-methoxyphenyl formates into the respective phenols since the hydrolysis of formates in basic media is irreversible.

References

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