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Letter

The efficient and selective oxidation of alcohols with zeolite NaY-supported sodium ruthenate

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Abstract

Primary and internal alcohols are efficiently oxidised to their corresponding oxidation products at room temperature by a newly synthesized zeolite NaY-supported sodium ruthenate. Advantages of this system include simple catalyst removal and product isolation, in addition to easy recycling of this catalyst. © 2000 Elsevier Science B.V. All rights reserved.

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The oxidation of alcohols to carbonyl compounds is an important transformation in synthetic organic chemistry, as it is essential for the preparation of many key synthetic intermediates [1,2]. Traditionally, such transformations have been performed with inorganic oxidants, e.g. chromium (VI) compounds in stoichiometric quantities [3]. However, the toxic and corrosive nature of these compounds has severely limited their use, as the quest for effective, 'environmentally friendly' catalytic systems has become the primary aim of 'green chemistry' [4].

With ruthenium catalysts developed thus far, the oxidation of alcohols is the reaction effected with the greatest efficiency. Currently, the scope for zeolite-supported ruthenium complexes for alcohol oxidation has been limited as indicated by the lack of reported literature on this topic. However, related research into the oxidation of alcohols by zeolite-supported chromium trioxide has been recently reported [5]. The oxidation of alcohols with this CrO_3-HZSM-5 zeolite system occurred under microwave irradiation in solvent free conditions. A recently reported 'user-friendly' oxidizing agent known as 'zeofen' (iron (III) nitrate supported on HZSM-5) also oxidized a variety of alcohols to their corresponding carbonyl compounds in good yields under classical heating and microwave irradiation in solventless systems [6]. Disadvantages of the aforementioned systems include extensive metal wastage as these are only stoichiometric oxidants.

We now report on sodium ruthenate supported on zeolite NaY in a series of catalytic alcohol to carbonyl oxidation reactions. NaY was chosen as a support material as this particu-

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lar class of zeolites has large apertures and supercages as well as a high concentration of cationic sites, which enhance their catalytic properties [7].

Zeolite NaY (Si:Al ∼ 2.5) was first dried to remove any water present. Thus, the zeolite was placed in a Schlenk tube and heated under nitrogen overnight at 250°C. The zeolite turned slightly brown during this drying treatment, due to some of the residual organic template being burnt off [8]. A 3.4% metal loading was achieved by stirring 45 mg of sodium ruthenate in 7.0 ml of 1 M NaOH solution with 1 g of dried zeolite NaY for 6 h. The loaded zeolite was then dried under vacuum and stored under nitrogen. Flame emission spectroscopy was used to determine the ruthenium loading on the zeolite as well as the extent of leaching of the sodium ruthenate from the zeolitic support. Negligible leaching of the sodium ruthenate from the support into the solvent was found to occur, thereby indicating an interaction between the ruthenate ion and the cationic sites within the supercages.

Using the loaded zeolite-supported oxidizing agent, benzylic and allylic alcohols were selectively oxidized to their corresponding oxidation products without any over-oxidation products being formed or attack at double bonds or heteroatoms occurring. Geraniol, in particular, is oxidised to geranial only. A high degree of selectivity was therefore exhibited as no allylic isomerization of geraniol to citonellal was evident, as found to occur with perruthenate catalysts [9]. Over-oxidation product was, however, detected for a primary aliphatic alcohol only after long reaction times. The results are shown in Table 1.

The general procedure for the catalytic oxidation of alcohols was as follows.

Activated 4 Å molecular sieves (180 mg), 6 ml of nitrogen saturated solvent (dichloromethane or toluene) and the alcohol (4.78 ×

Table 1
Oxidation of alcohols with the zeolite-supported sodium ruthenate

Alcohol	Product	Cooxidant	Conversion (%)	Time (h)
Cinnamyl alcohol	Cinnamaldehyde	PhIO[a]	77 (5)[b]	24
		T-BAP[c]	100 (8)	24
Cinnamyl chloride	Cinnamaldehyde	PhIO	0 (0)	24
		T-BAP	0 (0)	24
Crotyl alcohol	Crotonaldehyde	PhIO	59 (4)	24
		T-BAP	50 (4)	24
Cyclobutanol	Cyclobutanone	PhIO	84 (6)	24
		T-BAP	100 (8)	3
Cyclohexanol	Cyclohexanone	PhIO	100 (8)	24
		T-BAP	100 (8)	24
Furfuryl alcohol	Furfuraldehyde	PhIO	71 (5)	48
		T-BAP	83 (6)	3
Geraniol	Citral (Geranial)	PhIO	59 (4)	48
		T-BAP	74 (5)	24
1-Hexanol	Hexanal	PhIO	58 (4)	48
		T-BAP	85[d] (6)	24
2-Hexanol	2-Hexanone	PhIO	97 (7)	3
		T-BAP	82 (8)	72
4-Nitobenzyl alcohol	4-Nitrobenzaldehyde	PhIO	58 (4)	24
		T-BAP	96 (7)	24

[a] Iodosylbenzene.
[b] Turnovers in parentheses.
[c] Tetrabutylammonium periodate.
[d] Hexanoic acid detected (15%).

10^{-4} mol) together with 80 μl (5×10^{-4} mol) of isobutyl-methacyralate as the internal standard were added to a nitrogen filled Schlenk tube. 1.5 equivalents (relative to the substrate) of the appropriate co-oxidant, together with 200 mg of the supported oxidant, was added and the resulting mixture was then stirred at room temperature under a nitrogen atmosphere.

The recycling of the zeolite-supported sodium ruthenate was conducted by filtering the supported oxidant from the reaction mixture. It was then used in another oxidation reaction, with a slight decrease in the yields for each subsequent recycle being observed. The advantages of being able to isolate and recycle this oxidant are extremely favourable from an environmental and economical viewpoint.

In conclusion, the zeolite NaY-supported sodium ruthenate was found to be an easily synthesized, recyclable oxidant for the efficient and selective oxidation of benzylic and allylic alcohols to their corresponding oxidation products at room temperature.

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