The Ru-Cu-Al-Hydrotalcite-Catalysed Oxidation of Alcohols to Aldehydes or Ketones

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Received 21 March 2001

Abstract: A new heterogeneous ruthenium-copper-hydrotalcite catalyst for the efficient and selective conversion of a variety of aliphatic, allylic and aromatic alcohols to either aldehydes or ketones is described. Suitable co-oxidants include iodosylbenzene, tetrabutyl ammonium periodate and, depending on substrate, oxygen.

Key words: alcohol, oxidation, ruthenium, hydrotalcite, XPS

Heteronuclear catalysts have often been found to be more active than their individual mononuclear components.¹ A classical example is the Pd/Cu/O₂-based Wacker process for the industrial preparation of acetaldehyde.² To our knowledge there has been a single prior report of a bimetallic Ru/Cu system for the partial oxidation of alcohols. The report describes a mixture of mononuclear ruthenium and copper containing compounds which shows fairly low rates of conversion and selectivity - possibly because the Ru and Cu are not in close proximity.³ This prompted us to investigate a new Ru/Cu-containing hydrotalcite system as a catalyst for the oxidation of alcohols - a process of key importance in synthetic organic chemistry. The hydrotalcite permits the bringing together of different metals within the same compound, whilst it also contains interlayer spaces which are reactive environments. Some previous applications of hydrotalcite-type anionic clays include uses as catalysts for the polymerisation of alkene oxides, aldol condensation, reforming, alcohol synthesis, methanation, Baeyer-Villiger oxidations and the photoxidation of isopropyl alcohol to acetone.4,5 An advantage of the hydrotalcite catalysts is that they are heterogeneous catalytic systems, thus permitting the easy removal of the catalysts from the reaction medium. Whilst a number of efficient homogeneous ruthenium catalysts for the mild oxidation of alcohols are known,67 difficulties with product separation remain and often the expensive catalyst cannot be re-used after workup.

The Ru-Cu-Al-hydrotalcite (Ru-Cu-HT) was prepared by adding a solution of RuCl₃.3H₂O (0.40 g, 1.53 mmol), CuCl₂·6H₂O (2.61 g, 15.3 mmol) and AlCl₃·6H₂O (1.23 g, 5.1 mmol) in water (10 mL) to a solution of Na₂CO₃ (1.10 g) in 46.4 mL 1 M NaOH. The mixture was stirred at 65 °C for 18 h, after which the green product was filtered off, washed with water and dried at 110 °C for 12 h. The product was ground into a powder before use. EDS confirmed the presence of Ru, Cu and Al and flame emission spectroscopy showed the ruthenium content to be 6.4%.



Scheme 1 Proposed redox behaviour of the cations in the Brucite sheet

Typical oxidation procedures involved adding activated 4 Å molecular sieves and toluene (6 mL) to a Schlenk tube, after which the substrate (0.478 mmol) and isobutyl-methacrylate (80 μ L) as internal standard were added. For the reactions using O₂ as co-oxidant, the reactions were carried out at 60 °C in O₂ saturated toluene under an atmosphere of oxygen. Alternatively, either iodosylbenzene (PhIO) or tetrabutylammonium periodate (TBAP) (0.717 mmol) was added as co-oxidant and the reactions carried out in N₂ saturated toluene at 60 °C under nitrogen. The hydrotalcite (250 mg) was added last in all cases. The reactions were followed by gas chromatography. Product isolation involved filtering off the hydrotalcite and molecular sieves, which could then be reused, followed by chromatography and/or fractional distillation, as required.

The results of the oxidation reactions are shown in Table 1. As can be seen, the Ru-Cu-HT was found to be a very efficient and selective oxidant for the variety of alcohols investigated when either PhIO or TBAP were used as cooxidants. The efficiency of oxygen as co-oxidant depends on the alcohol substrate, with conversions ranging from 20% to 100%. Low activity with oxygen has been observed for some other hydrotalcite catalysts.⁸ No over-oxidation products, namely carboxylic acids, were detected in any of the reactions. Similarly, no attack of sensitive functional groups, e.g. double bonds, nitro groups or heteroatoms was detected, with the inertness of cinnamyl chloride indicating that organohalides are not attacked. Also no evidence of allylic rearrangement of double bonds, as would e.g. be seen by the formation of citronellal from geraniol,⁹ was observed. The mildness of these oxidants is also emphasised by the selective conversion

Co-oxidant	Substrate	Product	Yield (%)	Time (hrs)
TBAP PhIO O ₂	1-hexanol	hexanal	100 62 26	24 24 24
TBAP PhIO O ₂	2-hexanol	2-hexanone	100 100 30	3 48 24
TBAP PhIO O ₂	CH=CHCH ₂ OH	CH=CHCHO	100 100 100	3 48 24
TBAP PHIO O2	CH ₂ OH	СНО	100 51 45	3 24 48
TBAP PHIO O ₂	CH ₂ OH	CHO NO ₂	88 71 58	24 24 24
TBAP PHIO O ₂	OH	°	100 70 30	24 24 48
TBAP PHIO O2	ОН	0	92 90 78	24 24 24
TBAP H ₃ C PHIO O ₂ H ₃ C	C= CHCH2CH2C(CH3)=CH2CH2OH	H ₃ C , C= CHCH ₂ CH2Q(CH ₃)=CH2CH0 H ₃ C	100 94 78	24 48 24
TBAP PHIO O ₂	СН₃СН—СНСН₂ОН	СН ₃ СН—СНСНО	47 43 42	24 24 24

Table 1 The oxidation of alcohols to aldehydes or ketones with various co-oxidants

42 24

of furfuryl alcohol to furfuraldehyde, since furfuryl alcohol reacts explosively with more vigorous oxidants.¹⁰

In the absence of co-oxidants, the catalyst shows low activity in air. The recyclability of the catalyst was investigated in detail on the oxidation of cinnamyl alcohol (Table 2). Storing the catalyst under nitrogen between recycles results in a steady decrease in the activity of the catalyst. However, storing the catalyst in air greatly increases the catalysts lifetime, with quantitative yields of cinnamaldehyde still being obtained after each recycle, albeit after slightly longer reaction times. A similar effect has been observed for a supported osmium *cis*-hydroxylation catalyst.¹¹ The Ru-Cu-HT catalyst with the above co-oxidants is less efficient for large electron rich molecules. Thus cholesterol is oxidised to 5-cholesten-3-one by the Ru-Cu-HT-O₂ system in low yield. Use of TBAP or PhIO as co-oxidant results in a number of products. A similar effect was observed for the RuCl₂(PPh₃)₃-PhIO catalysed oxidation of cholesterol where the substrate was reported to have decomposed during the attempted oxidation.¹² No reaction with cholesterol occurs with 4-methylmorpholine N-oxide as co-oxidant.

XRD analysis of the Ru-Cu-HT catalyst shows features that are typical of all hydrotalcites, namely sharp and intense lines at low values of the 2θ angle and less intense and generally asymmetric lines at the higher angular

Table 2	Oxidation	of cinnamayl	alcohol to	cinnamal	dehyde with
the recycle	ed Ru-Cu h	ydrotalcite sto	ored under	different e	nvironments

Recycle	Atmosphere (storage)	Time (hrs)	Yield (%)
1 st recycle	N ₂	24	100
2 nd recycle	N ₂	24	90
3 rd recycle	N ₂	24 48	32 65
1 st recycle	Air	24	100
2 nd recycle	Air	24	88
3 rd recycle	Air	24 48	98 100

values. The presence of both sharp and diffuse non-basal reflections indicates a partially disordered structure. The basal spacing was determined to be 7.56 Å vs. 7.92 Å reported for a Ru-Mg hydrotalcite.⁸

XPS measurements on a newly prepared catalyst showed binding energies of 282.1 eV and 932.8 eV due to Ru(VI) and Cu(II), respectively. Measurements on a recycled catalyst showed a binding energy of 282.1 eV due to Ru(VI), whilst XPS measurements on a spent catalyst (after a stoichiometric reaction with cinnamyl alcohol to give cinnamaldehyde in 100% yield) showed binding energies of 282.2 eV, 933.0 eV and 935.3 eV, corresponding to Ru(VI), Cu(II) and Cu(0).¹³ This suggests that copper is involved in the oxidation of Ru(III) to Ru(VI) in the synthesis of the hydrotalcite and in the regeneration of the active catalytic species, Ru(VI), as shown in the scheme. The scheme is further supported by the observation that the catalyst acts as a two electron oxidant, since it converts cyclobutanol to cyclobutanone.¹⁴

In conclusion, the Ru-Cu-HT catalyst was found to be easy to synthesise, stable, recyclable and to oxidise efficiently and selectively aliphatic, allylic and aromatic alcohols to their corresponding oxidation products under mild conditions. The catalyst compares well to recently reported supported oxidants^{15,16} and Ru-Co-HT catalysts,⁸ with the advantage over the latter that aliphatic primary alcohols are also oxidised in very high yield. Advantages over clayfen¹⁷ include a more general applicability, easier synthesis and indefinite stability.

Acknowledgement

We thank the NRF, URF and NMT Electrodes for support and Martin Onani for helping to prepare this manuscript.

References and Notes

- (1) Adams, R. D. Polyhedron 1988, 7, 2251-2252.
- (2) Miessler, G. L.; Tarr, D. A. Inorganic Chemistry, Prentice-Hall: New Jersey, 1999; p 504.
- Minmoun, H.; Malmaison, R.; de-Seine, H. German patent (3)1979, 29 20 678.
- (4) Cavani, C.; Trifiro, F.; Vaccari, A. Catal. Today 1991, 11, 173-301.
- (5) Kaneda, K.; Ueno, S.; Imanaka, T. J. Chem. Soc., Chem. Commun. 1994, 797-798.
- (6) Friedrich, H. B. Platinum Metals Rev. 1999, 43, 94-102.
- (7) Dijksman, A.; Arends, I.W.C.E.; Shelden, R.A. Chem. Commun. 1999, 1591-1592.
- (8) Matsushita, T.; Ebitani, K.; Kaneda, K. Chem. Commun. 1999, 265-266.
- (9) Markó, I.E.; Gautier, A.; Tsukazaki, M.; Llobet, A.; Mir-Plantalech, E.; Urch, C.; Brown, S.M. Angew. Chem., Int. Ed. 1999, 38, 1960-1962.
- (10) Hazards in the chemical laboratory, 5th Edn., Luxon, S. G. Ed.; Royal Society of Chemistry: Cambridge, 1992; p 407.
- (11) Herrmann, W. A.; Kratzer, R. M.; Blümel, J.; Friedrich, H. B.; Fischer, R. W.; Apperley, D. C.; Mink, J.; Berkesi, O. J. Mol. Catal. A 1997, 120, 197-205.
- (12) Müller, P.; Godoy, J. Tetrahedron Lett. 1981, 22, 2361-2364.
- (13) Moulder, J.; Stickle, W.S.; Sobol, P.E.; Bomben K.D. in Handbook of X-Ray Photoelectron Spectroscopy, Perkin Elmer Corp., 1992.
- (14) Lee, D.G.; Congson, L.N.; Spitzer, U.A.; Olson, M.E. Can. J. Chem. 1984, 62, 1835-1839
- (15) Friedrich, H. B.; Singh, N. Tetrahedron Lett. 2000, 41, 3971-3974.
- (16) Hinzen, B.; Ley, S. V. J. Chem. Soc., Perkin Trans. 1 1997, 1907-1908.
- (17) Cornelis, A; Laszlo, R. Synthesis 1985, 909-919.

Article Identifier: 1437-2096,E;2001,0,06,0869,0871,ftx,en;D07501ST.pdf