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Preliminary communication

Hydroformylation of Ethylene Catalysed by Ruthenium Complexes Supported on Zeolite.

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Summary

Hydroformylation of ethylene is catalysed by zeolite-supported ruthenium compounds and gives propan-1-al and propan-1-ol as major products.

The binding of transition metal complexes to many types of support has received considerable attention in recent years (1) and a similar interest in the catalytic activity of transition metal cluster carbonyls has also been apparent (2). Interest in the latter is due to the metal-metal bonded polyhedral structures which may possess some characteristics of the active metal catalysts. The possibility of trapping such clusters in zeolites arises from the observation that metal ions might migrate within the zeolite framework (3), however, it has received scant attention (4).

Faujasite-type zeolite (Na-X) was exchanged with $|Ru(NH_3)_6|^{2+}$ to form the wine coloured ruthenium(III)-containing zeolite, for which the species $|Ru(NH_3)_5OH|^{2+}$ has been proposed (5). This complex (Ru-X) has proved to be an active catalyst for the water gas shift reaction and the resulting carbonyl containing zeolite is equivalent to that produced from the similarly active $|Ru(NH_3)_6|^{3+}$-X (6). Two different batches of catalyst were prepared and were of 3.6% (sample *A*) and 4.7% (sample *B*) ruthenium content respectively. In both cases no appreciable loss of crystallinity was detected by X-ray powder spectra but they exhibited a rather different behaviour in catalytic activity.

Sample *A* was subjected to 100 atms. at 200°C of $H_2/CO/C_2H_4$ (2.5:2.1:1.5) for 46 hours. The pressure fell appreciably and gas-phase mass spectroscopy indicated that while most of the ethylene had been consumed, ethane but not methane had been produced. The liquid phase present in the autoclave was analysed by g.l.c.-mass spectroscopy. The catalyst turm-over was calculated to be at least 20 molecules of C_2H_4 per Ru atom per hour and approximately 60% of the products comprised CH_3CH_2CHO, $CH_3CH_2CH_2OH$ and CH_3-$CH(CHO)CH_2CH_3$ (in the ratio 1:3:1). Other organic products were present but they are not yet completely identified. The formation of aldehydes by hydroformylation was obviously accompanied by side reactions and the main product appears to be propan-1-ol which was presumably produced by the hydrogenation of propan-1-al. Evidence was also observed for the dimerisation of ethylene and subsequent hydroformylation to C_5 products. Higher oligomers were also detected. Sample *A* was then subjected to 100 atms. at 200°C of (1:1) CO/H_2 for 46 hours but no Fischer-Tropsch reaction products were observed and the resulting activated complex also failed to dimerise ethylene at 200°C and 25 atms. pressure. During the hydroformylation reaction, ruthenium was lost from the zeolite as carbonyl compound *C* (ν_{CO} in CH_2Cl_2, 2014s, 1950s cm^{-1}) which in the mass spectrometer gave a parent peak at 406 m/e and the typical monoruthenium isotope pattern. The fragmentation pattern also suggested the presence of a hydrocarbon chain. I.r. spectra of the recovered zeolite *D* revealed the presence of supported ruthenium carbonyl (ν_{CO} 2047m, 1991s, 1958s) and compound *C*, however, the latter was extracted with CH_2Cl_2.

Both the zeolite *D* and a diglyme solution of *C* were reused under the conditions described above. Both were active but although *D* produced a similar product distribution, *C* was more selective and gave CH_3CH_2CHO and $CH_3CH_2CH_2OH$ (about 1:1) with only very small amounts of the other products. Interestingly, only negligible amounts of metal were lost from *D* on reuse.

Catalyst *B* was tested under those conditions used for *A* but although an appreciable fall in pressure was again registered, gas analysis revealed considerable amounts of methane as well as ethane indicating Fischer-Tropsch activity. The liquid phase consisted of several constituents and although no propanaldehyde was detected, a large amount of the hydrogenation product, propan-1-ol was present. The remaining products included hydrocarbons and compounds arising from crossed Fischer-Tropsch and hydroformylation reactions. The resulting black zeolite appeared to contain only metal thus accounting for the formation of CH_4 and higher hydrocarbons (10). In the liquid phase only very small amounts of ruthenium carbonyls were present.

These results indicate that among many other factors the loading of metal complex plays a vital role in such reactions. In the reducing environment, the reduced ruthenium species of the "concentrated" (*B*) zeolite appear to aggregate to form metal particles. At lower loading, metal carbonyls of varying nuclearity are produced but while the mononuclear species are lost from the zeolite, compounds of higher nuclearity may be trapped in the zeolite cages.

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References

1. F. Pinna, C. Candilera, G. Strukul, M. Bonivento and M. Graziani, J. Organometal. Chem., 1978, 159, 91 and references therein.
2. E. L. Muetterties, Bull. Soc. Chim. Belg., 1975, 84, 959.
3. D. R. Plentge, J. H. Lunsford, P. J. Jacobs and J. B. Uytterhoeven, J. Phys. Chem., 1975, 79, 354.
4. E. Mantovani, N. Palladino and A. Zenobi, J. Mol. Catal., 1978, 3, 285.
5. K. Laing, R. Leubner and J. Lunsford, Inorg. Chem., 1975, 14, 1400.
6. J. J. Verdnock, P. J. Jacobs, and J. B. Uytterhoeven, J.C.S. Chem. Comm., 1979, 181.
7. M. J. Doyle, A. P. Kouwenhoven, C. A. Schapp and B. Van Oort, J. Organometal. Chem., 1979, 174, C55.