HOKKAIDO UNIVERSITY

Title	ACTIVATION OF A HETEROGENISED RHODIUM CARBONYLATION CATALYST : INFRARED SPECTROSCOPIC STUDY
Author(s)	SCURRELL, Michael S.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 25(3), 189-191
Issue Date	1978-03
Doc URL	https://hdl.handle.net/2115/25034
Type	departmental bulletin paper
File Information	25(3)_P189-191.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis Hokkaido Univ., Vol. 25, No. 3, pp. 189 to 192 (1978)

—Note—

ACTIVATION OF A HETEROGENISED RHODIUM CARBONYLATION CATALYST: INFRARED SPECTROSCOPIC STUDY

By

Michael S. SCURRELL*)

(Received October 22, 1977)

Abstract

Evidence is presented for the formation of a rhodium acyl complex believed to be responsible for the activity of a heterogenised catalyst in carbonylation of methanol.

Heterogenised versions of homogeneous rhodium catalysts active in the carbonylation of methanol to acetic acid have been reported.[1] A key feature of the process is the necessity for a promotor, usually based on iodine and normally present as methyl iodide.

In homogeneous catalysis the rate determining step is almost certainly[2,3] the oxidative addition of methyl iodide to a Rh (I) complex, resulting in formation of the active rhodium-acetyl species. Spectroscopic evidence for the production of such a species from reaction between rhodium (III) halides, carbon monoxide and methyl iodide has recently been presented.[4] Kinetic studies with supported rhodium complexes have suggested that both types of catalyst operate through similar intermediates[5,6] but no direct evidence for the formation of a rhodium-acyl complex has previously been obtained for heterogenised versions. The present account describes some infrared spectroscopic investigations undertaken to examine this aspect.

The catalyst consisted of rhodium trichloride supported on a Type 13 X zeolite molecular sieve and contained $\sim 1\%$ rhodium by weight. This method of heterogenising the rhodium complex is known to give a particularly active carbonylation catalyst,[1] with conversion of methanol to acetic acid occurring above ~ 373 K.[7,8] Pretreatment of the samples (self-supporting discs) consisted of evacuation at 437 K for 16 h to residual pressures $< 1 \times 10^{-4}$ N m^{-2}. The infrared spectrum**) after such treatment is shown in Figure (A). Following contact of the catalyst with carbon monoxide (initial pressure 13.3 kNm^{-2}) at 373 K for 1 h and subsequent evacuation at 323 K for 5 min spectrum (C) was obtained. Two bands were seen at 2025 (± 5) and 2095 (± 5) cm,$^{-1}$ with no additional changes

*) Instituttet for Kemiindustri, Technical University of Denmark, 2800 Lyngby, Denmark.

**) All spectra were recorded at 323 K.

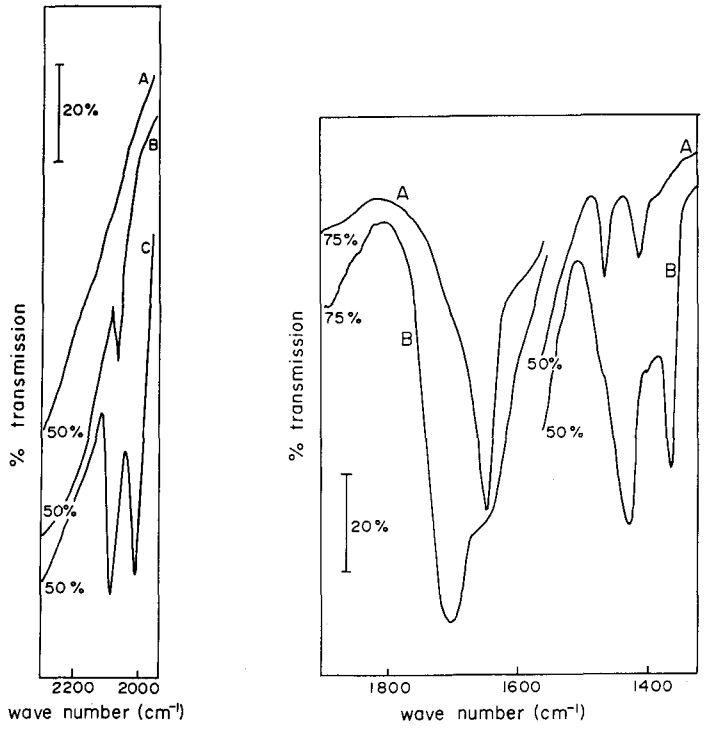

Fig. (A) background spectrum. (B) after exposure to carbon monoxide and methyl iodide at 373 K. (C) after exposure to carbon monoxide alone at 373 K.

n the region below 2000 cm.$^{-1}$ If in place of carbon monoxide a mixture of carbon monoxide and methyl iodide (each at initial pressure 13.3 kN m^{-2}) was used, under the same conditions as before, spectrum (B) resulted. Above 2000 cm^{-1} only one band was present at 2085 ($\pm$5) cm,$^{-1}$ but in the lower energy region intense absorption was found at $\sim$1710 cm,$^{-1}$ with weaker bands at 1440 and 1370 cm.$^{-1}$

In homogeneous media[4] two carbonyl stretching modes were seen at 2064 and 1989 cm^{-1} following reaction between rhodium (III) halides and carbon monoxide, while bands at 2062 and 1711 cm^{-1} were present after additional reaction with methyl iodide. These changes were ascribed to the occurrence of the reaction sequence

$$Rh(CO)_2X_2^- + CH_3I \longrightarrow Rh(CH_3CO)(CO)X_2I^-$$

involving formation of the catalytically active acetyl complex.*)

*) Several recent reports confirm that rhodium acyl complexes may be expected to show a characteristic infrared absorption at $\sim$1700 cm.$^{-1}$ See, for example, D. L. EGGLESTONE, M. C. BAIRD, C. J. L. LOCK and G. TURNER, J.C.S. Dalton, 1977, 1576.

A similar process taking place on the surface of the heterogenised rhodium chloride catalyst would admirably explain the spectral features now reported since the absorption bands are essentially identical in their positions and manner of generation. The observations provide direct evidence for similarities in the development of active centres in homogeneous and heterogenised rhodium carbonylation catalysts and may perhaps serve as a basis for rationalizing parallels in their operational behaviour. The relation of the spectral results to the activity for methanol carbonylation is the subject of a further investigation.

References

1) M. S. SCURRELL, Platinum Metals Rev., **21**, 92 (1977).
2) J. F. ROTH, J. H. CRADDOCK, A. HERSHMAN and F. E. PAULIK, Chem. Technol., 1971, 600.
3) J. HJORTKJÆR and V. W. JENSEN, Ind. Engng. Chem., Prod. Res. Dev., **15**, 46 (1976).
4) D. FORSTER, J. Amer. Chem. Soc., **98**. 846 (1976).
5) K. K. ROBINSON, A. HERSHMAN, J. H. CRADDOCK and J. F. ROTH, J. Catalysis, **27**, 389 (1972).
6) M. S. JARRELL and B. C. GATES, J. Catalysis, **40**, 255 (1975).
7) (a) B. K. NEFEDOV, N. S. SERGEEVA, T. V. ZUEVA, E. M. SHUTKINA and YA. T. EIDUS, Izv. Akad. Nauk. USSR, Ser. Khim., 1976, 582. (b) B. K. NEFEDOV, N. S. SERGEEVA and YA. T. EIDUS, Izv. Akad. Nauk. USSR, Ser. Khim., 1976, 2271.
8) B. CHRISTENSEN and M. S. SCURRELL, J. C. S. Faraday I, **73**, 2036 (1977).