Infrared Spectral Studies on an Olefin Dismutation Catalyst

By (MRS.) E. S. DAVIE, D. A. WHAN, and C. KEMBALL*

(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary Correlations between the i.r. spectra and the activity of molybdenum hexacarbonyl on alumina for olefin dismutation when the treatment of the catalyst is varied provide evidence about the nature of the active sites.

MOLYBDENUM HEXACARBONYL supported on alumina is known to be a catalyst for the dismutation of olefins.[1] We have examined the activity of catalysts of this type[2] containing a nominal 5% molybdenum hexacarbonyl on γ-alumina (surface area $1\cdot7 \times 10^4$ m^2 kg^{-1}) for the dismutation of propene to ethylene and butenes at 298 K and we have studied i.r. absorption in the carbonyl stretching region of catalyst samples prepared as Nujol mulls under an inert atmosphere.

Studies were made on catalysts subjected to three different treatments. Type A consisted of catalysts as prepared and without any activation procedure; these had no catalytic activity. Type B had been activated for 1 hr. under vacuum at 373 K and had good activity for dismutation. Typical rates corresponded to a half-life for approach to equilibrium between the propene and the products of some 10—20 min. in a static system using 0·5 g. of catalyst with $1\cdot3 \times 10^3$ Nm^{-2} of propene in a volume of $1\cdot7 \times 10^{-4}$ m^3. Type C had been activated as for Type B and, either directly or after use in one or more catalytic tests, had been exposed to air; these had no catalytic activity. The i.r. spectra for the different types of catalyst are shown in the Figure and the frequencies of the absorption bands corresponding to carbonyl stretching modes are given in the Table together with known values for relevant compounds.

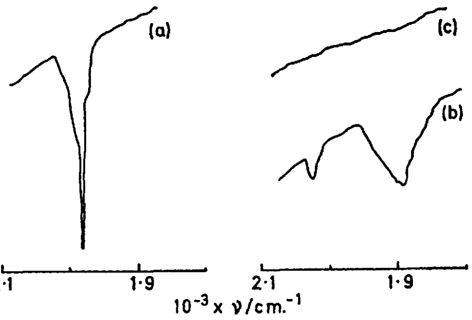

FIGURE. *I.r. spectra of the catalysts*: (a) *Type A*, (b) *Type B*, *and* (c) *Type C.*

The correlations between catalyst treatment, activity, and i.r. spectra are striking. The unactivated catalyst (Type A) with a single sharp carbonyl frequency corresponds to unchanged hexacarbonyl on the support. The activated catalyst (Type B) has lost this sharp band but shows two wider and broader bands. The active catalyst clearly has a lower symmetry than the hexacarbonyl and must have lost one or more of the carbonyl groups. The dead catalyst obtained after exposure to air (Type C) shows no absorption in the carbonyl region.

I.r. absorption frequencies for carbonyl stretching modes

Compound or catalyst	ν/cm.$^{-1}$[a]
Type A	1985
$Mo(CO)_6$ (ref. 3)	2004
Type B	1880, 2020
Type B + cycloheptatriene	1890, 1940, 2020
$Mo(CO)_3$ (C_7H_8) (ref. 4)	1895, 1929, 2000

[a] 1 cm.$^{-1}$ ≡ 29·98 GHz.

Attempts were made to define the nature of the active catalyst more precisely by use of suitable complexing agents. An orange-red cycloheptatriene–$Mo(CO)_3$ complex[4] and a yellow bicycloheptadiene–$Mo(CO)_4$ complex[5] can be formed by interaction of the hexacarbonyl with the respective olefins. It was hoped that the ease of complex formation with these olefins might show whether the active catalyst was essentially $Mo(CO)_3$ or $Mo(CO)_4$ but the results were not conclusive. A type B catalyst exposed to cycloheptatriene changed from pale lemon to orange and gave three weak carbonyl bands of about the expected frequencies as shown in the Table. On the other hand, a deepening of the lemon colour of the type B catalyst occurred on exposure to bicycloheptadiene although no satisfactory spectrum was obtained. The ease of complex formation suggests that in the active catalyst the hexacarbonyl has lost two or more probably three carbonyl groups.

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