

The Effect of Halogenated Molecules on the Activity of an Olefin Disproportionation Catalyst

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Summary The activity of an olefin disproportionation catalyst prepared from molybdenum hexacarbonyl supported on γ -alumina may be greatly increased by treating the catalyst with a halogenated olefin prior to admission of the reactants

MOLYBDENUM HEXACARBONYL supported on alumina is known to be a catalyst for the disproportionation of olefins ¹ The method of preparation and activation of such a catalyst, nominally 5% molybdenum hexacarbonyl supported on γ -alumina ($2.4 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$), has been detailed elsewhere ²

Activities for the disproportionation of 0.93 kN m^{-2} of propene at 298 K in a static system ($1.7 \times 10^{-4} \text{ m}^3$) have been measured before and after treatment of the catalyst with various halogenated molecules.

The experimental sequence involved activation² of 0.5 g of supported molybdenum hexacarbonyl at 373 K under vacuum ($1.3 \times 10^{-4} \text{ Nm}^{-2}$) for 1 h. Three runs with propene were then carried out to ensure that the activity of the catalyst was constant, the catalyst being evacuated at 313 K between runs. After exposure to 0.93 kN m^{-2} of the halogenated compound at 298 K for 1 h the catalyst was pumped at 313 K for 2 h and the disproportionation activity for propene was again measured in two successive experiments at 298 K. The initial rates of disproportionation before and after treatment with various halogenated molecules are shown in the Table.

least one, and probably two or more, carbon monoxide ligands. I.r. spectra of catalysts treated with the two most effective olefins in the Table gave three peaks in the carbonyl stretch region and not two as reported³ for a catalyst exposed to propene. This effect, which is being investigated in more detail, provides some evidence that the activating molecules are bonded to the catalyst.

It is reasonable to assume that the activity of a disproportionation catalyst will depend critically on the strengths of bonds formed between the reacting olefins and the metal atom, which will in turn be related to factors such as the electron density on the metal. The increase in activity caused by halogen-containing olefins may thus be attributed to electron-withdrawing substituents reducing the strength of the back bonding from the molybdenum to the other ligands and thus enhancing their reactivity.

Rates of reaction of propene before and after treatment of the catalyst with halogenated species

Compound	Initial rate ($\text{nm}^{-2} \text{ min}^{-1}$)		Factor by which activity increased
	Before treatment	After treatment	
Chloroethylene	0.9	0.9	1
1,1-Dichloroethylene	0.3	6.5	22
<i>cis</i> -1,2-Dichloroethylene	0.7	6.5	9
<i>trans</i> -1,2-Dichloroethylene	0.2	7.4	37
Trichloroethylene	0.9	139.5	155
Tetrachloroethylene	1.4	4.2	3
3,3,3-Trifluoropropene	1.2	93.0	80
Hexafluoropropene	0.2	2.3	11
1-Chloropropane	37.2	27.9	0.8
Hydrogen chloride	4.6	1.9	0.4
Chlorobenzene	1.9	2.1	1.1

The majority of halogenated olefins cause a significant increase in the activity of the catalyst and, in the cases of trichloroethylene and 3,3,3-trifluoropropene, the rise in activity by factors of 155 and 80, respectively, is particularly striking. That no marked increase in activity was caused by exposure of the catalyst to 1-chloropropane, hydrogen chloride, or chlorobenzene would indicate that the presence of a double bond is essential in the activating compound. No disproportionation of the halogenated olefins was detected.

I.r. and other physical measurements have shown^{2,3} that during activation the molybdenum hexacarbonyl loses at

Although no trend is as yet apparent it is obvious that the degree of substitution of the olefins has a marked effect on their efficiency for promoting disproportionation. It is possible that further work in this direction may well indicate how, by suitable choice of ligands, the activity of the catalyst may be 'tailored' as required.

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¹ R. L. Banks and G. C. Bailey, *Ind. and Eng. Chem. (Product Res. and Development)*, 1963, 3, 170.

² E. S. Davie, D. A. Whan, and C. Kemball, *J. Catalysis*, in the press.

³ E. S. Davie, D. A. Whan, and C. Kemball, *Chem. Comm.*, 1969, 1430.