Disproportionation of Propene by a Heterogeneous Catalyst Derived from Hexamethyltungsten

By Walter Mowat, John Smith, and David A. Whan*

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

Summary Treatment of silica or γ-alumina supports with a solution of hexamethyltungsten, followed by activation at temperatures of 373 K or above, yields alkene disproportionation catalysts with activities comparable to catalysts derived from molybdenum hexacarbonyl.

Heterogeneous disproportionation of olefins[1] occurs over catalysts prepared from supported molybdenum or tungsten oxides.[2] It is known that much more active catalysts, which will readily disproportionate propene at room temperature, can be prepared from supported molybdenum hexacarbonyl.[3] Although tungsten hexacarbonyl interacts with silica and γ-alumina in a fashion similar to molybdenum hexacarbonyl,[4] the resulting catalysts are more than an order of magnitude less active than their molybdenum analogues. In contrast, catalysts for the homogeneous room temperature disproportionation of olefin normally contain tungsten[5] in preference to molybdenum.

Table

Disproportionation of propene

Catalyst activation temperature /K	Catalyst activity[a]			
	Measured rate/% min^{-1}		Rate per 0·001 g of tungsten or molybdenum/% min^{-1}	
	WMe_6	$Mo(CO)_6$	WMe_6	$Mo(CO)_6$
373	5·2	4·0	0·7	2·6
473	9·0	5·8	1·2	3·8
573	9·0	1·3	1·2	0·9

[a] Initial rates of disappearance of propene at 3·33 kN m^{-2} and 298 K. It is likely that the higher rates will be diffusion limited Surface area of support = 4·71 × 10^{5} m^{2} kg^{-1}.

Results obtained in these laboratories[6] have suggested that molybdenum hexacarbonyl is merely a convenient source of molybdenum as catalytic activity is in no way associated with the carbon monoxide ligands. From this conclusion it was postulated that the relatively low activity of catalysts prepared from tungsten hexacarbonyl might simply be a reflection of the poor ability of the hexacarbonyl to yield tungsten in an active form and the activities of catalysts based on a variety of tungsten compounds were measured.

Hexamethyltungsten[7] is rather more reactive and thermally less stable than tungsten hexacarbonyl and might thus be expected to interact with the support more readily. When silica or γ-alumina supports are impregnated with hexamethyltungsten, and activated at or above 373 K, a catalyst is obtained which converts propene into ethylene and butenes at room temperature. In a typical experiment 0·017 g of hexamethyltungsten {estimated as WM_4-[ON(Me)NO]$_2$}[7] in 1 ml of cyclohexane was introduced to 0·1 g of silica, previously evacuated for 1 h at 298 K, in an inert atmosphere and allowed to stand in the dark for 45 min before removal of the solvent. After thermal activation in vacuum for 1 h and cooling to 298 K, 3·33 kN m^{-2} of propene was admitted to the reaction vessel. Ethylene and butenes were produced at once and equilibrium was approached in 15—20 minutes. Catalyst activities, expressed as initial rates of disappearance of propene calculated from second-order rate plots, are given in the Table along with comparable data for a molybdenum hexacarbonyl on silica catalyst. Analysis of the catalysts after use showed that those prepared from $Mo(CO)_6$ contained 1·5% molybdenum and those from WMe_4 7·8% tungsten.

The results reported confirm that a heterogeneous olefin disproportionation catalyst with an activity at room temperature comparable to that of the known molybdenum based catalysts can be made if an appropriate tungsten precursor is chosen.

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