

The Nature of the Active Centres in Hydrocarbon Reactions over Platinum Catalysts

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Use of the skeletal rearrangement and the hydrogenolysis of n-hexane as probe reactions, and interaction with titania as a means of modifying catalytic properties, has provided evidence that the active centre in Pt catalysts consists of only a single metal atom in a unique environment.

Reactions catalysed by metals represent an immensely important type of chemical process. Although the subject of extensive research the mechanism of such catalytic reactions and the nature of the active centres are still poorly understood. Evidence is accumulating which supports Taylor's original contention that 'the amount of surface which is catalytically active is determined by the reaction catalysed.'¹ The number of metal atoms which constitute an active centre (the ensemble size) is believed to depend on the type of reaction.^{2,3} Thus, hydrogenolysis reactions (rupture of C-C bonds) are thought to require a larger ensemble than skeletal rearrangement reactions (isomerisation, cyclisation).

We have now obtained evidence that large ensembles may

not be required even for hydrogenolysis reactions. Experiments on Pt/titania catalysts suggest that the active centre for all these different types of reaction may be the same single Pt atom. Table 1 shows how the activity and selectivity of Pt/titania catalysts for the n-hexane reaction vary with pretreatment. When the reduction temperature is increased from 573 (A) to 773 K (B) the H/Pt ratio falls dramatically. This is believed to be due to contamination of the Pt surface by TiO_x moieties.⁴

It is remarkable, therefore, that catalyst B retains about 20% of its activity (the turnover number is about 20 times higher) and the overall selectivity is little changed. Furthermore, the selectivity for the formation of each of the

Table 1. Activity and selectivity of Pt/TiO₂ catalysts in the n-hexane reaction.

Catalyst ^a	H/Pt ^b	Rate ^c	T.O.N. ^d	Selectivity ^e					
				C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
A	0.59	41.4	3.8	8.2	6.5	20.7	7.1	10.3	45.8
B	<0.01	8.9	>50	9.0	7.2	24.7	8.2	9.3	41.5

^a Catalyst A reduced for 1 h at 573 K; catalyst B reduced for 1 h at 773 K. ^b Determined from hydrogen adsorption isotherm. ^c Units are mmol n-hexane converted h⁻¹ g_{Pt}⁻¹. ^d Turnover number, units are 10³ × molecules n-hexane converted s⁻¹ (surface Pt atom)⁻¹. ^e Defined as a percentage of all products; C₁, methane; C₂, ethane; C₃, propane; C₄, butane; C₅, pentane; C₆, 2-methylpentane + 3-methylpentane + methylcyclopentane.

hydrogenolysis products is hardly altered. This is a most significant result. It indicates that even when less than 1% of the surface Pt atoms are accessible the selectivity of these Pt atoms for the hydrogenolysis *versus* the skeletal rearrangement of n-hexane is unchanged. We believe that this demonstrates that for all these reactions the same active centre must be involved. Since statistically the number of ensembles containing two or more Pt atoms must be exceedingly small the active centre most probably consists of a single Pt atom. Rooney and co-workers^{5,6} have presented evidence that skeletal rearrangement requires only a single Pt atom and have suggested that metalocyclobutanes are key intermediates in C–C bond rupture. We believe that our results are consistent with this model and that hydrogenolysis should now be considered to be a reaction which only requires a single Pt atom for the active centre.

Finally, since our catalysts contain Pt particles having an average diameter of about 1.5 nm, a high proportion of the surface atoms will be in edges. TiO_x is expected to absorb most strongly along edges. It seems probable, therefore, that the single Pt atom of the active centre is located in a unique environment in the centre of a planar surface on a Pt crystallite.

Support for this idea comes from the distribution of hydrogenolysis products which shows a low C₁/C₃ ratio (see Table 1). Sachtler and Somorjai⁷ have reported for single crystals of Pt that edges give a high C₁/C₃ ratio and Pt(111) faces give a low C₁/C₃ ratio.

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