

# The Influence of Isomers on Mass Laydown and Catalytic Behaviour in the Hydrogenation of C<sub>5</sub> Hydrocarbons

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## Introduction

Deposition of hydrocarbonaceous material has long been postulated to play a crucial role in the hydrogenation of carbon-carbon multiple bonds. It has been proposed that the reaction itself may occur on top of an adsorbed overlayer [1], that H-transfer from such an overlayer enhances the reaction rate [2] or that deposited carbon forms a new phase with the catalytic metal [3]. The Tapered Element Oscillating Microbalance (TEOM) is a tool capable of recording *in situ* mass changes during a catalytic reaction with a time resolution of 0.1 s and a mass resolution of micrograms. It therefore provides an ideal opportunity to investigate the role of carbon deposition in such reactions. To this end TEOM studies have been conducted on three closely related gas-phase heterogeneous catalytic hydrogenation systems, namely the hydrogenation of pentenes, pentenenitriles and pentyne. In particular the effect, and amount, of carbon laydown over catalysts has been investigated as function of the isomer employed.

## Materials and Methods

Studies on pentene and pentenenitrile hydrogenation have been conducted over a Ni/θ-Al<sub>2</sub>O<sub>3</sub> catalyst, while studies on pentyne hydrogenation have been conducted over Pd/θ-Al<sub>2</sub>O<sub>3</sub> and Pd black. Reactions have been conducted in a TEOM coupled to on-line GC providing the means to record mass changes occurring during reaction and to acquire data on product speciation. Further details on the set-up employed can be found in [3].

## Results and Discussion

### Pentenes

Studies on the hydrogenation of pentenes demonstrate dramatic differences in the behaviour of the internal isomers when interacting with a coked catalyst as compared to their interaction with the fresh material. The individual pent-2-ene isomers are both inactive towards hydrogenation, however in sequential and competitive hydrogenation systems selectivities of ~100 % towards *n*-pentane are observed. Figure 1 shows the mass deposited on the catalyst surface, as recorded by TEOM, after 1 hour pulses of *cis*- and *trans*-pent-2-ene in H<sub>2</sub> in a sequential reaction system. The mass retained after reaction by *trans*-pent-2-ene is seen to be much lower over a catalyst first exposed to *cis*-pent-2-ene than it is over the fresh material. This indicates that the nature of the interaction of the isomer with the catalyst has significantly altered.

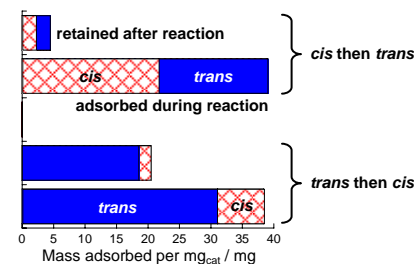
### Pentenenitriles

The hydrogenation of *cis*-2- and *trans*-3-pentenenitrile has also been investigated. For *cis*-2-pentenenitrile over fresh Ni/θ-Al<sub>2</sub>O<sub>3</sub> the fully hydrogenated product, pentylamine, is initially produced with high selectivity at ~100 % conversion. With time-on-stream, and mass build up, selectivity shifts towards pentanenitrile, where the olefin functionality has been selectively hydrogenated, and conversion decreases. On conducting an identical experiment over a catalyst first exposed to *trans*-3-pentenenitrile in H<sub>2</sub> – similar to the sequential pentene studies, *vide supra* – the observed catalytic behaviour is radically different. Over the 7 hour

duration of the experiment the dominant reaction product is pentylamine, however conversion is at all times is significantly lower than over the fresh material. Additionally, the quantity of adsorbed hydrocarbonaceous material is observed to pass through a maximum, after which time conversion of *cis*-2-pentenenitrile increases. Therefore, as was the case for pentene, different isomers of the compound interact differently with the same surface, and the pre-adsorption of one of these isomers alters the behaviour of the catalyst towards the second.

### Pentyne

Finally, TEOM studies have been conducted on the hydrogenation of pentyne. This work has in part led to the creation of a new theory as to the origin of selectivity in this reaction over Pd catalysts [3], namely that a PdC<sub>x</sub> phase is the active site for the selective formation of pentene. Figure 2 shows how mass build-up differs over Pd black between a low hydrogen partial pressure (5 % H<sub>2</sub>/He) system and a high hydrogen partial pressure (100 % H<sub>2</sub>) system. The former of these facilitates the formation of a PdC<sub>x</sub> phase and leads to selective hydrogenation. These studies have been extended to 2-pentyne and to related systems with sequential hydrogenation of both isomers being investigated as has been discussed for pentenes and pentenenitriles.



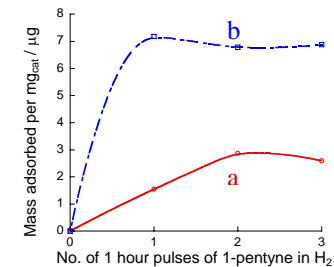
**Figure 1.** Mass retained on Ni/θ-Al<sub>2</sub>O<sub>3</sub> in sequential hydrogenation of *cis*- (hatched) and *trans*-pent-2-ene (solid). Top: retained after reaction, bottom: adsorbed during reaction.

### Significance

The above studies indicate the crucial role played by carbonaceous deposits in the hydrogenation of carbon-carbon multiple bonds. This insight into the number and nature of reaction sites on the catalyst, and their interaction with different isomers of the same chemical species, provides important insights into catalyst design and reactor operation. In particular, alkyne hydrogenation is important in, *e.g.* the removal of trace amount of acetylene from an ethylene rich feed in polyethylene production while pentenes and pentenenitriles provide models for selective olefin hydrogenation with applications in the production of synthetic materials.

### References

1. Thomson, S.J. and Webb, G., *Chem. Comm.* 526 (1976)
2. Jackson, S.J., Hamilton, C.A., Kelly, G.J., *et al.*, *React. Kin. Catal. Lett.* 73, 77 (2001)
3. Teschner, D., Vass, E., Hacecker, M., *et al.*, *J. Catal.* 242, 26 (2006)



**Figure 2.** Mass adsorbed on Pd black in low (a) and high (b) H<sub>2</sub> partial pressure systems after 3 × 1 hour pulses of 1-pentyne in H<sub>2</sub>

