

The Role of Carbon Deposition in the Hydrogenation of Pentenenitriles

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Introduction

The link between mass laydown and catalytic activity and selectivity has been the subject of many investigations. Mass laydown can both improve activity or selectivity [1,2] or lead to catalyst deactivation. Relating mass build-up during reaction to changes in selectivity requires a simultaneous measurement of both phenomena. The Tapered Element Oscillating Microbalance (TEOM), *e.g.* [2], provides a means to measure mass laydown (μg quantities) *in situ* with a time resolution of 0.1 s. The catalytic production of alkenenitriles is important in, *e.g.*, nylon production. However, there have been only limited previous investigations into the hydrogenation of alkenenitriles *e.g.* [3,4]. In this work TEOM-GC has been employed in the study of the hydrogenation of gas-phase pentenenitriles over a Ni/ $\theta\text{-Al}_2\text{O}_3$ catalyst. Additionally, flow-through reactor studies have been conducted providing complementary information. These techniques provide, for the first time, an understanding of the nature of selectivity in such a system based on *in situ* measurements of mass laydown.

Materials and Methods

16 wt.% Ni/ $\theta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ were used as the adsorbents. The adsorbates, *cis*-2- and *trans*-3-pentenenitrile (C2PN and T3PN) were introduced to the catalyst by passing a H_2 carrier gas through a vapouriser and downstream to the TEOM (R&P 1500). The partial pressure of pentenenitrile was 8000 Pa. Additional studies were conducted in a flow-through reactor at atmospheric pressure. In both systems online product analysis was carried out by GC (HP6890) equipped with FID. The reaction temperature in all cases was 373 K.

Results and Discussion

TEOM-GC studies on the hydrogenation of C2PN over Ni/ $\theta\text{-Al}_2\text{O}_3$ show a direct relationship between mass laydown and selectivity (figure 1a). In the initial stages of reaction the principle product observed is the fully hydrogenated product pentylamine (PA). Deactivation towards PA occurs rapidly over the first ~100 minutes of reaction. This occurs concurrently with a period of rapid mass build up ($\sim 0.134 \mu\text{g min}^{-1}$ per mg_{cat}). Simultaneously the product selectivity shifts towards pentanenitrile (PN) formation, *i.e.* selective hydrogenation of the alkene functionality. After the maximum in PN production the catalyst begins to deactivate. This period is characterized by a slower phase of mass accumulation ($0.004 \mu\text{g min}^{-1}$ per mg_{cat}). Studies conducted in the flow-through reactor yield similar selectivity data. The rate of catalyst deactivation, as deduced from these experiments, is shown in figure 1b. The deactivation process shows two distinct stages: an initial, rapid stage coinciding with the rapid mass build up observed by TEOM, and a second, slower stage.

One of the active sites for the formation of PA has been shown, through studies on the pure support, to be located on the $\theta\text{-Al}_2\text{O}_3$ support. Nickel metal was also found to facilitate PA formation by means of a parallel study carried out using a 13 wt.% Ni/SiO₂ catalyst. The pure SiO₂ support showed no evidence of PA formation. However, after impregnation with the

nickel metal, PA was observed in the initial stages of reaction. This confirmed the presence of a second active (Ni) site for PA formation. TEOM-GC studies on the hydrogenation of T3PN over Ni/ $\theta\text{-Al}_2\text{O}_3$ show that, similarly to C2PN, PA is initially the favoured product. Upon deactivation of these sites however no PN is observed indicating that selective Ni sites are inactive towards the hydrogenation of the non-conjugated isomer. That extensive mass laydown occurs over pure $\theta\text{-Al}_2\text{O}_3$ is confirmed by TEOM data. The level of mass laydown recorded over the pure support after 7 hours of reaction is greater than over Ni/ $\theta\text{-Al}_2\text{O}_3$. In addition to hydrogenation activity the support is seen to catalyse hydrogenolysis of C2PN to *cis*-2-pentene and ammonia. The production of NH_3 is likely to poison acid sites present on the support, a conclusion supported by flow-through reactor studies that is also consistent with the widely reported catalytic hydrogenolysis of a similar class of compounds, alkylamines, *e.* [5].

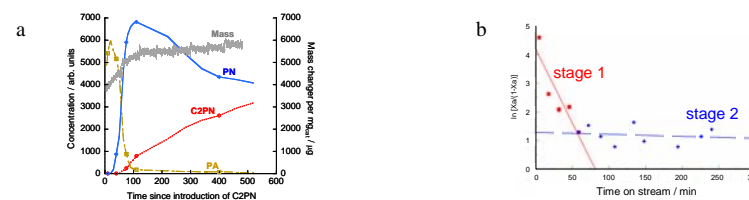


Figure 1. a) TEOM-GC data showing mass laydown and product selectivity during the hydrogenation of C2PN. b) Rate of catalyst deactivation during C2PN hydrogenation.

Deactivation of catalytically active sites has also been achieved by exposing the catalyst to T3PN for a short period prior to use in the hydrogenation of C2PN. The main species observed, throughout the timescale of the reaction, is PA – in contrast to the behaviour of the fresh catalyst where, after an initial period, PN was the dominant product. This indicates that T3PN has selectively poisoned certain active sites and, as was the case for T3PN hydrogenation, the bulk of catalytic activity may be provided by the support.

TEOM-GC experiments have allowed for the development of selectivity in C5N hydrogenation to be followed and directly related to changes in mass laydown, recorded *in situ*, for the first time. Flow-through reactor studies have further allowed for the development of a model of these reactions in terms of the deactivation of groups of active sites present on the catalyst.

Significance

Understanding the relationship between mass laydown and catalyst deactivation and/or selectivity is a key driver in catalysis. This challenge has been tackled in a model selective hydrogenation system with direct relevance to polymer synthesis.

References

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