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Catalysis Today 114 (2006) 372–376
CATALYSIS TODAY
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Identification, by selective poisoning, of active sites on Ni/Al_2O_3 for hydrogenation and isomerisation of *cis*-2-pentenenitrile

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Abstract

The hydrogenation of *cis*-2-pentenenitrile (C2PN) has been studied over Ni/alumina. Hydrogenation to *n*-pentanenitrile (PN) and subsequent isomerisation to *trans*-2-pentenenitrile (T2PN) and *trans*-3-pentenenitrile (T3PN) was observed. 1-Pentanamine (PA) was also detected in the initial stages of the catalyst life. Use of selective poisoning of metal sites with carbon monoxide and acid sites with ammonia revealed that hydrogenation was a function of the metal, while isomerisation was solely a function of the support. 1-Pentanamine was produced by the support but the site was rapidly deactivated due to carbon laydown.

Keywords: Hydrogenation; *cis*-2-Pentenenitrile; Nickel; Nickel/alumina; Poisoning

1. Introduction

In the synthesis of organic compounds for chemicals manufacturing, catalytic hydrogenation of organic functional groups remains the most common application for heterogeneous catalysis. In particular, a catalyst that shows high activity for the selective hydrogenation of multi-unsaturated hydrocarbons. Selectivity is the key parameter to ensure effective use of raw materials and minimise environmental impact on manufacturing processes.

Studies on multifunctional hydrocarbons can be particularly useful to gain insight into understanding reaction kinetics and surface composition of catalysts. Studies on propenenitrile and cyclohexane hydrogenation have shown that while kinetic data reveals that the nitrile group is more strongly adsorbed than the unsaturated C=C bond, the alkene bond is in fact more reactive than the nitrile group when undergoing hydrogenation [1]. A study on the hydrogenation of 2- and 3-butenenitrile shows the selective hydrogenation of the C=C double bond, while at a reaction temperature of 298–398 K, the nitrile group was unaffected [1].

This paper investigates the heterogeneous gas-phase hydrogenation of multifunctional C-5 alkenes, in particular *cis*-2-pentenenitrile over a Ni/Al_2O_3 catalyst. There has been little work on C-5 hydrogenation [2–4] or on unsaturated nitrile hydrogenation [1,5]. However, in a recent paper a systematic study of unsaturated nitrile hydrogenation has been undertaken in the liquid phase over Raney nickel and cobalt catalysts [6]. They studied *cis*-2-pentenenitrile as one of a number of nitriles. No isomerisation or selectivity to the unsaturated amine was observed. Indeed this system was highly selective to *n*-pentanenitrile. In the study [6], results were presented that indicated that the hydrogenation of the C=C bond in *cis*-2-pentenenitrile was achieved while the molecule is adsorbed by the nitrile functionality.

2. Experimental

2.1. Catalyst

The catalyst used throughout this study was a 16% (w/w) Ni/Al_2O_3, supplied by Johnson Matthey (HTC 400, 1.2RP), that had been pre-reduced and pacified. The catalyst was reactivated by treatment in flowing 5% H_2/N_2 at 523 K for 2 h.

2.2. Characterisation

Carbon monoxide chemisorption was performed on a pulse-flow microreactor system with on-line gas chromatography

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doi:10.1016/j.cattod.2006.02.046

using a thermal conductivity detector. The catalyst (0.25 g) was heated to 523 K at 10 K min^{-1} in flowing 5% H_2/N_2 (BOC high purity, 40 cm^3 min^{-1}). The catalyst was held at 523 K for 2 h before being cooled to room temperature and maintained in a helium flow. Pulses of gas (15 μmol) were introduced to the carrier gas from the sample loop. After passage through the catalyst bed the total contents of the pulse were analysed by GC and mass spectroscopy (ESS MS). Carbon monoxide chemisorption gave a dispersion of 17.8%.

Carbon monoxide temperature programmed desorption (TPD) experiments were performed on an atmospheric glass reactor. A sample of the catalyst was flushed with 100% H_2 (BOC >99.995%) and reduced for 2 h at 523 K, flushed with He (BOC high purity) and cooled to room temperature. Carbon monoxide was passed over the catalyst, in amounts that equated to 1 monolayer coverage of the active metal particles in a flow of helium (50 cm^3 min^{-1}). Once saturated with carbon monoxide the sample was heated at a rate of 10 K min^{-1} from 293 to 873 K in flowing He. The gaseous products were analysed by a Genesys quadrupole multi-ion mass spectrometer, where the TPD trace could be analysed.

2.3. Reactor studies

Prior to reaction, the catalyst (0.25 g) was reduced in 5% H_2/N_2 (BOC high purity) at 523 K for 2 h. Reactions were performed at a temperature of 373 K in an atmospheric glass flow through reactor. In the flow through system the carrier gas was 5% H_2/N_2, which passed through a reagent bubbler containing *cis*-2-pentenenitrile (98%, Aldrich) and through the catalyst bed. The concentration of the *cis*-2-pentenenitrile was controlled with a p-xylene/liquid nitrogen slurry bath that kept the reagent at a constant temperature of 286 K. This gave a *cis*-2-pentenenitrile vapour pressure of 0.0139 atm and hence a H_2:*cis*-2-pentenenitrile ratio of 3.6:1. Vapour samples were taken via a gas sample valve attached to a Varian 3300 gas chromatograph with a TCD detector using a SGE BP20 capillary column (i.d. 0.25 mm, 30 m).

Known quantities of carbon monoxide or ammonia were passed over the catalyst prior to exposure to the reactant *cis*-2-pentenenitrile at 373 K. This was done by filling a gas sample loop of known volume with a predetermined partial pressure of gas and diverting the carrier gas (He, BOC high purity, 50 cm^3 min^{-1}) though the sample loop to transport the gas over the catalyst bed.

3. Results

The θ-alumina support was subjected to the reaction mix under standard reaction conditions. Fig. 1 shows the reaction profile over the support. Surprisingly, θ-alumina was found to be initially active for the formation of 1-pentanamine. With time on stream the production of 1-pentanamine ceased and isomerisation of *cis*-2-pentenenitrile to *trans*-2-pentenenitrile was observed.

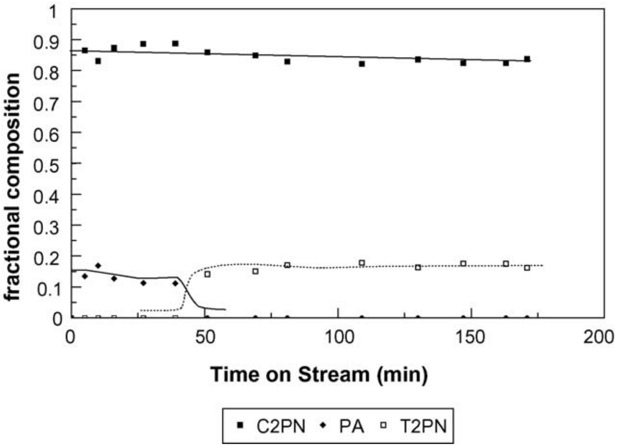

Fig. 1. *cis*-2-Pentenenitrile hydrogenation over θ–alumina at 373 K.

Fig. 2 shows a typical reaction profile of the hydrogenation of *cis*-2-pentenenitrile over Ni/Al_2O_3 at 373 K. Initially, there was a short period of 1-pentanamine formation followed by the production of the saturated nitrile, *n*-pentanenitrile. As the reaction proceeded, isomerisation was observed with the formation of *trans*-2- and *trans*-3-pentenenitrile. It can also be seen that the reactant concentration of *cis*-2-pentenenitrile increased throughout the reaction, implying a deactivation process. Previously, we have reported that there is a two-stage deactivation process for this reaction [7]. Initially there is a rapid deactivation coupled with a loss of mass to the surface due to carbon laydown, followed with a slower deactivation stage, which is coupled with the onset of isomerisation products being detected.

3.1. Selective poisoning with carbon monoxide

At saturation, 2.05×10^{-4} mol of CO were adsorbed per gram of catalyst. This constituted 1 monolayer coverage of the metal sites with CO. No carbon monoxide adsorption was detected over a sample of the support.

Carbon monoxide was adsorbed at 0.25, 0.5 and 1 monolayer coverage onto the reduced catalyst prior to the hydrogenation reaction being initiated. Figs. 3–5 show the resultant reaction profiles for the hydrogenation reaction after

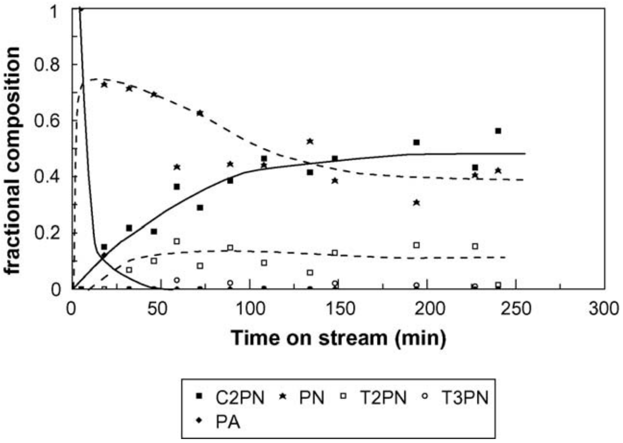

Fig. 2. *cis*-2-Pentenenitrile hydrogenation over Ni/Al_2O_3 at 373 K.

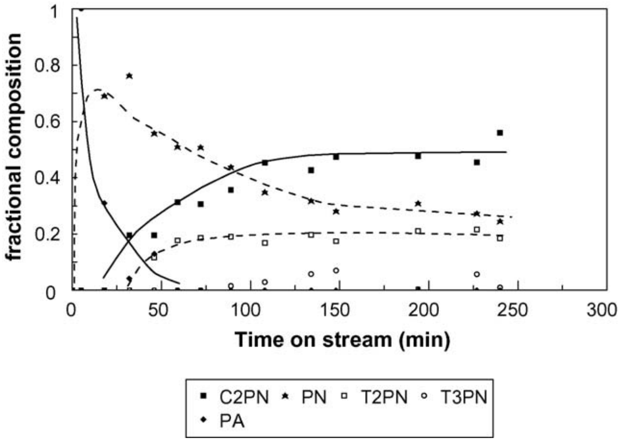

Fig. 3. *cis*-2-Pentenenitrile hydrogenation over Ni/Al_2O_3 at 373 K after exposure to 0.25 monolayer coverage of CO.

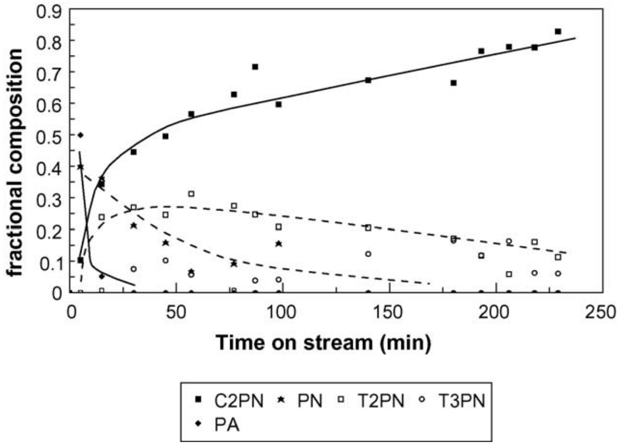

Fig. 4. *cis*-2-Pentenenitrile hydrogenation over Ni/Al_2O_3 at 373 K after exposure to 0.50 monolayer coverage of CO.

the different levels of CO exposure. It can be seen that with increasing CO coverage there was a decrease in overall hydrogenation activity to *n*-pentanenitrile, with no *n*-pentanenitrile being produced at 1 monolayer coverage. Calculation of deactivation rate constants for the initial period of deactivation from the relationship [8], $\ln[(C_{A0}/C_A) - 1] = \ln(kt_w) - k_d t$, where C_{A0} represents the initial reactant concentration, C_A the concentration of the reactant with time, k is the rate constant, t_w represents weight time ($gcat^{-1}$ hl_{fluid}), k_d the deactivation rate constant and t is the time – reveal a linear relationship between CO coverage and deactivation rate constant k_d (Fig. 6).

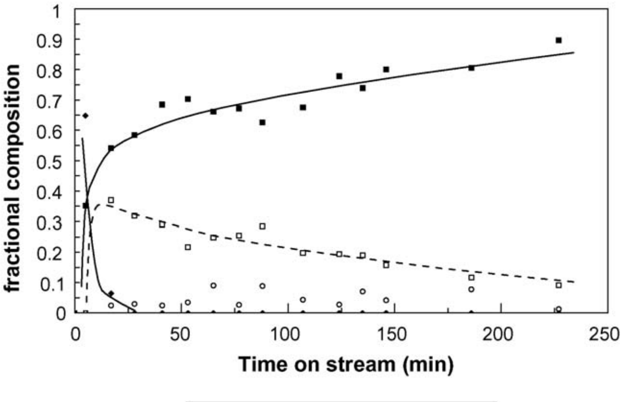

Fig. 5. *cis*-2-Pentenenitrile hydrogenation over Ni/Al_2O_3 at 373 K after exposure to 1 monolayer coverage of CO.

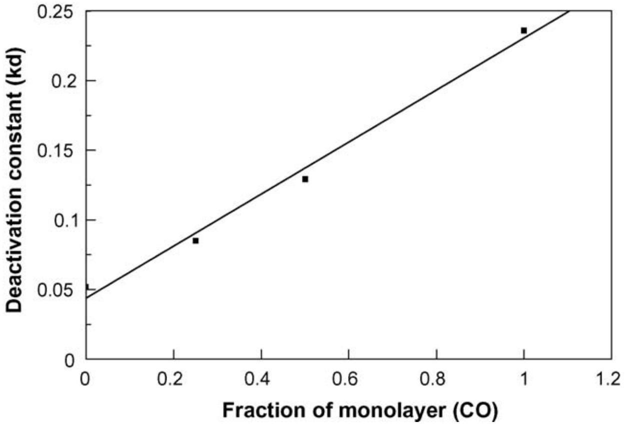

Fig. 6. Deactivation rate constant as a function of CO coverage.

3.2. Selective poisoning with ammonia

At saturation 360 μmol of NH_3 were adsorbed per gram on the alumina support. Over the catalyst, saturation was achieved with 207 μmol g^{-1}. This was taken to constitute 1 monolayer coverage of the acid sites with ammonia.

70.4, 141, and 604 μmol g^{-1} of ammonia were pre-adsorbed onto the reduced Ni/Al_2O_3 catalyst prior to the hydrogenation of *cis*-2-pentenenitrile. Fig. 7 shows the reaction profile after 604 μmol g^{-1} of ammonia was pre-adsorbed and demonstrates that after this amount of systematic poisoning, isomerisation was not observed for the duration of the experiment (215 min). Table 1 reports the time at which each isomer was observed as a function of the extent of ammonia pre-adsorption. In general, as ammonia exposure was increased, there was an increase in the time taken for isomers to be observed in the system. In all cases 1-pentanamine was observed in the early stages of the reaction and was undetectable by 50 min.

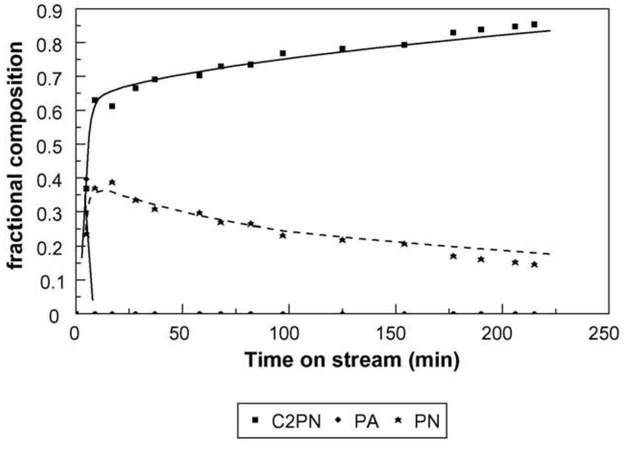

Fig. 7. *cis*-2-Pentenenitrile hydrogenation over Ni/Al_2O_3 at 373 K after exposure to ∼3 monolayer coverage of NH_3.

Table 1
Effect of ammonia exposure on isomer formation during *cis*-2-pentenenitrile hydrogenation

	Breakthrough of isomers	
	trans-2-Pentenenitrile	*trans*-3-Pentenenitrile
Unpoisoned	32	59
0.34 Monolayers	72	89
0.68 Monolayers	45	111
2.92 Monolayers	Not observed after 215 min	

4. Discussion

The hydrogenation of *cis*-2-pentenenitrile over Ni/Al_2O_3 has been investigated and using selective poisoning three reactive centres have been identified: two on the support and one on the metal. The gas-phase reaction also shows considerable differences from the liquid-phase reaction reported in the literature [6], notably the isomerisation reaction.

The alumina support, rather than being inert, plays a significant role in the catalysis. As can be seen in Fig. 1, the alumina catalyses the complete hydrogenation of *cis*-2-pentenenitrile to 1-pentanamine and subsequently the isomerisation to *trans*-2-pentenenitrile. Although some isomerisation activity may have been expected, the total hydrogenation was a surprising result. This initial activity for 1-pentanamine formation appears to occur on a site that deactivates rapidly; no 1-pentanamine was detected after ~45 min on stream. Once this site was deactivated, the major product was *trans*-2-pentenenitrile. The fact that the yield of *trans*-2-pentenenitrile was the same as that of the 1-pentanamine suggests that the hydrogenation site was converted into an isomerisation site. However, we shall re-address this aspect later.

The hydrogenation of *cis*-2-pentenenitrile over Ni/Al_2O_3, shown in Fig. 2, reveals that the principal hydrogenation product is *n*-pentanenitrile. After the initial production of 1-pentanamine, *n*-pentanenitrile is produced and then the isomers. Other studies with low molecular weight unsaturated nitriles, such acrylonitrile [5], butenenitrile [1] and *cis*-2-pentenenitrile [6] over Ni based catalyst reveal that hydrogenation to the corresponding saturated nitrile species is the dominant process. Whereas with higher molecular weight nitriles such as oleonitrile, and non-conjugated unsaturated nitriles such as *trans*-3-pentenenitrile, selective hydrogenation of the nitrile group has been reported as the norm [1,6]. In this study, apart from the initial formation of 1-pentanamine, we observe only the saturated nitrile, *n*-pentanenitrile.

To poison the hydrogenation sites, CO was adsorbed onto the catalyst. No CO adsorption was detected over the support in the absence of metal. Adsorption of CO onto metal particles has been shown to poison hydrogenation activity for a number of systems. Work by Somorjai's group [9] showed that, over Pd(1 1 1) single crystals, no catalytic ethylene hydrogenation was observed at temperatures lower than the desorption temperature of CO, when the surface was pre-adsorbed with CO [9]. In our system, pre-adsorption of CO was performed at 373 K. Fig. 8 shows the TPD of CO over Ni/Al_2O_3 showing two major desorption peaks of CO_2 at 468 and 514 K. CO_2 forms as a result of CO disproportionation on the catalyst. However, these desorption processes occur at temperatures higher than the hydrogenation reaction temperature of 373 K, confirming that CO was adsorbed on the catalyst surface during the hydrogenation. This desorption profile is consistent with other studies on Ni systems [10,11]. The effect of the CO is to reduce the hydrogenation activity to *n*-pentanenitrile. No significant effect is seen on the isomerisation reaction, although the extent of isomerisation is apparently enhanced over the initial stages. The absence of isomerisation of *cis*-2-pentenenitrile over nickel has also been confirmed by Kukula and Koprivova [6] in a study of *cis*-2-pentenenitrile and *trans*-3-pentenenitrile hydrogenation over Raney nickel. These results confirm that hydrogenation to *n*-pentanenitrile is related solely to the metal function of the catalyst and that the metal does not catalyse isomerisation. This result lends credence to the mechanism proposed [1] that the nitrile is adsorbed via the CN functionality even though it is the C=C that is hydrogenated. This mechanism invokes a cyclic intermediate and a concerted hydrogen transfer. If the C=C functionality was adsorbed on the nickel then it would be expected that the carbon backbone would isomerise.

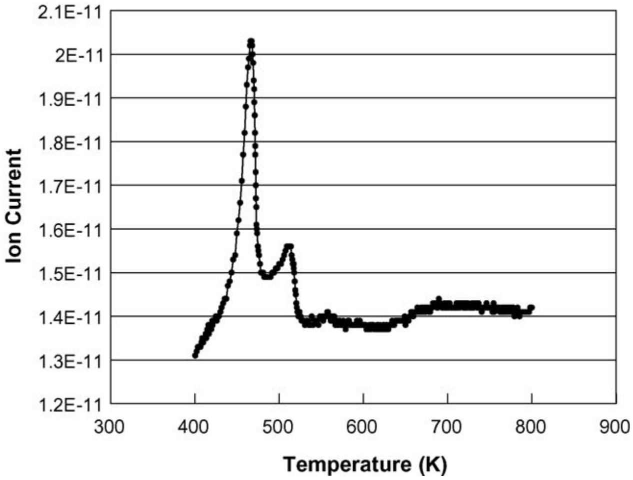

Fig. 8. Temperature programmed desorption of carbon monoxide from Ni/Al_2O_3.

The density of Lewis acid sites on θ-alumina has recently been reported by Kulrsquoko et al. [12] as 5.34 μmol m^{-2}. The surface area of the alumina used in this study was 100 m^2 g^{-1}. Therefore, the number of acid sites calculated in this way corresponds to ~536 μmol g^{-1}, which is slightly higher than found experimentally in this study, for the θ-alumina support, of 360 μmol g^{-1}. When the nickel was added to the alumina, the number of acid sites dropped by 42%. The amounts of ammonia pre-adsorbed were, in relation to the potential number of acid sites, 34%, 68% and 292%. With increasing amounts of ammonia pre-adsorbed an increase in the time taken to observe isomerisation was noted. However, after a certain time (Table 1), the catalyst regains its isomerisation activity. The delayed effect was likely to be a result of desorption of ammonia from the surface species due to the reaction temperature of 373 K. Work by Amenomiya [13] showed that two forms of ammonia could be adsorbed onto alumina depending on the temperature of adsorption, i.e. adsorption at 298 K led to a weakly bound NH_3 species while adsorption at 523 K led to a much more strongly adsorbed species. The isomerisation of 1-butene at 293 K was blocked by the strongly adsorbed species, but only slightly inhibited by the weakly bound ammonia [13]. TPD of ammonia from alumina [14] shows desorption initiating at low temperatures and it is likely that some of the pre-adsorbed ammonia was desorbed during the course of the experiment. Hence, isomerisation on the acid sites was inhibited while there was adsorbed ammonia. As ammonia desorbed, isomerisation activity was resumed. When the highest loading of ammonia was used, the effect was a permanent poisoning of the isomerisation active site on the support within the time-frame of the experiment.

Note that the hydrogenation activity of the nickel particles with respect to formation of *n*-pentanenitrile was relatively unaffected by ammonia exposure.

4.1. Active sites

Through selective poisoning of both metal and support sites, as well as undertaking this reaction on the support in the absence of the metal, we have been able to gain an insight to the nature of the sites responsible for some of the processes associated with the hydrogenation of *cis*-2-pentenenitile. Firstly we can confirm that the olefinic hydrogenation *cis*-2-pentenenitrile occurs on the reduced nickel metal particles, on sites that can be selectively poisoned by pre-adsorption of carbon monoxide. Secondly, the isomerisation reactions of *cis*-2-pentenenitrile to *trans*-2- and *trans*-3-pentenitrile occur on alumina support sites. The sites responsible for this activity are proposed as a Lewis acid–Lewis base pair that upon adsorption with NH_3 poisons the site's ability for isomerisation though the adsorption of NH_2^- and H^+ [13,15].

Less trivial to account for is the complete hydrogenation of *cis*-2-pentenitrile to 1-pentanamine in the early stages of the reaction. It appears to occur on a limited amount of highly active support sites that are rapidly deactivated, in most cases well within the first 20 min on stream. These sites were not deactivated by pre-adsorbed ammonia, suggesting that the sites are not acidic. Hence, the deactivation is more likely due to carbon laydown. In the early stages of *cis*-2-pentenitrile hydrogenation there was a poor mass balance and trace amounts of ammonia were detected during the reaction [7]. It is likely that the delay in isomer production under normal reaction conditions is due to poisoning of the support sites by ammonia formed in situ by hydrogenolysis of 1-pentanamine. No hydrocarbon fragments were detected in the reactor effluent and we suggest that these are retained by the catalyst and are the cause of the rapid deactivation of the 1-pentanamine hydrogenation sites on the support. The nature of this site is unclear; it is present on the support but is not affected by ammonia or carbon monoxide adsorption indicating that it is not acidic or a metallic type site. Further studies are being undertaken to try to determine its nature.

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