CHAPTER 4

HYDRODENITROGENATION OF QUINOLINE AND 1,2,3,4-TETRAHYDROQUINOLINE

4.1 INTRODUCTION

In this and the next chapter, studies carried out on different hydrotreating reactions using model compounds over different supported Ni-Mo-catalysts are presented. The HDN of quinoline (Q) and 1,2,3,4-tetrahydroquinoline (1THQ) over Ni-Mo-catalysts is presented in this chapter. Detailed characterization of these catalysts was reported in Chapter 3.

Catalytic hydrodenitrogenation (HDN) is an important reaction associated with the hydrotreatment of petroleum fractions. Enhanced removal of nitrogen compounds from petroleum fractions, especially from middle distillates has become important due to decreasing NOx specification in vehicle exhausts. Though the most commonly used and HDN catalysts are Co-Mo and Ni-Mo/γ-Al2O3, numerous improvements in the formulation of these catalysts have been reported over the years. These include the use of supports like silica, silica-alumina, carbon, zeolites and ordered siliceous mesoporous materials (Harvey and Pratt 1989, Rajagopal et al 1992, Eijsbouts et al 1991 and Lu et al 2007), and novel active supported species like nitrides and phosphides (Schlatter et al 1988). Though many reports on the use of ordered mesoporous silicas, such as MCM-41, SBA-15 and HMS, as supports for HDS catalysts (Linares et al 2008, Montesinos-Castellanos and Zepeda 2008, Klimova et al 2008) are available in the literature including a recent
study on the influence of pH of impregnating solution on the characteristics and activity of Ni-Mo/SBA-15 catalysts in the HDS of thiophene (Rayo et al. 2008), investigations on their use in HDN of model N-compounds is scarce (Sundaramurthy et al. 2008).

Quinoline and its derivatives are suitable model compounds for investigating HDN reactions as these compounds are present in the middle distillate fraction, which is widely used in transportation (diesel and jet fuel). HDN of quinoline and its hydrogenated derivatives has been investigated for many years over numerous catalysts in order to understand the mechanistic aspects of the reaction (Brunet and Perot 1985, Jian and Prins 1998). Though many reaction sequences for the HDN of quinoline have been discussed in the literature, it is generally believed to proceed mainly through hydrogenation of the aromatic ring (containing the N-atom) and cracking / hydrogenolysis of the -C-N- bond to produce o-propyl aniline and subsequently, the hydrocarbon, propylbenzene.

Ni-Mo-catalysts with the same composition of the supported oxides (NiO (4 wt%) and MoO₃ (15 wt%)) were prepared using supports with different characteristics and evaluated in the HDN of quinoline (Q) and 1,2,3,4-tetrahydroquinoline (1THQ) at different process conditions. The catalysts used in these studies are listed in Table 4.1. The reactions were carried out in a high-pressure fixed-bed (down-flow) reactor, which has been described in Chapter 2. The general operating conditions were in the range: temperature, 553-613 K; pressure, 20-70 bar; WHSV (h⁻¹), 0.5-2; H₂/oil (v/v), 200-800 STP and catalyst loading, 3 g. The catalyst was always presulfided prior to carrying out the HDN reaction. The composition of the feed was usually about 5000 ppm of the N-compound in decalin. To prevent stripping off of the S from the sulfided catalysts and to prevent its deactivation, the feed was spiked with dimethyldisulfide (DMDS; 6800 ppm of S). The products of
the reaction were analysed in a gas chromatograph. Details of the experimental method used in catalyst sulphidation, carrying out the reactions and analysis of the products have been presented in Chapter 2.

Table 4.1 Details of the catalysts used in hydrodenitrogenation studies

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<thead>
<tr>
<th>Composition, wt%</th>
<th>Catalyst code (designation)</th>
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<tr>
<td>Metals</td>
<td>Support components</td>
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<tr>
<td>NiO</td>
<td>MoO₃</td>
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| 4.2 HYDRODENITROGENATION OF QUINOLINE

The sequence of reactions taking place during the HDN of Quinoline (Q) has been identified and reported by many workers (Jian and Prins 1998); the reaction pathways are shown in Scheme 1. Quinoline is first hydrogenated to 1,2,3,4-tetrahydroquinoline (1THQ) or 5,6,7,8-tetrahydroquinoline (5THQ) according to the reaction conditions. In one route
(1THQ pathway), the 1THQ undergoes cracking to yield o-propylaniline (OPA). It may then undergo hydrogenolysis to give the denitrogenated product, namely propyl benzene (PB). Further, PB may also undergo hydrogenation via the propyl cyclohexene (PCHE) intermediate into propyl cyclohexane (PCH). In another route (5THQ pathway), 5THQ undergoes a hydrogenation to form decahydroquinoline (DHQ), which then undergoes hydrocracking to produce NH₃ and PCHE, the latter molecule subsequently undergoing hydrogenation into PCH. The different products reported in this work are identifiable in the scheme.

![Scheme 4.1 Network of reactions during HDN of quinoline](image)

**4.2.1 Influence of Temperature**

The HDN of Q was investigated in the temperature range of 553-613 K at 50 bar total pressure, WHSV (h⁻¹) of 1.0 and H₂/Q ratio (mole) of 48 (H₂/liquid feed (v/v) = 400 STP). The feed was made up of Q in decalin and contained 5420 ppm of N. All the catalysts were sulfided prior to use.
Conversion and product distribution obtained at different temperatures over the different catalysts are presented in Figure 4.1. Over all the catalysts, quinoline conversion is 100% in the range of temperatures investigated. The major product of the conversion is 1THQ. The next important one is the end product, n-propyl benzene (PB). The expected intermediates, \( o \)-propyl aniline (OPA), decahydroquinoline (DHQ) and 5,6,7,8-tetrahydroquinoline (5THQ) are also found in the product in different amounts. Over NiMo(S)/SBA (containing the least acidic support), the yield of 1THQ is nearly 100% at 553 K. The yield of 1THQ is 96% at the same temperature over NiMo(S)/MCM, prepared from the next weakly acidic support. This suggests that the transformation of Q into 1THQ occurs rapidly over the hydrogenation sites present in all the catalysts, but the further transformation of 1THQ into OPA requires acid sites (Scheme 4.1). It is noticed that larger amounts of OPA are present in the products from catalysts containing \( \text{Al}_2\text{O}_3 \) (NiMo(S)/AL, NiMo(S)/MCM-AL and NiMo(S)/AlMCM-AL) than in the products from the other catalysts. This could be due to the rapid cracking of 1THQ at the \(-\text{C—N—}\) bond to produce OPA, and the relatively slower conversion of OPA into PB. Over the weakly acidic NiMo(S)/SBA and NiMo(S)/MCM, the formation of PB starts only after 593 K, while over NiMo(S)/AL, the formation of PB starts after 553 K. In the case of the more acidic NiMo(S)/AlMCM and the BEA containing, NiMo(S)/15BEA-AL, NiMo(S)/30BEA-AL and NiMo(S)/15DA1BEA-AL, the formation of PB is significant even at 553 K, the yields being 5, 18, 10 and 25%, respectively, over the catalysts in the same order.
Figure 4.1 Influence of temperature on conversion of quinoline and product distribution over Ni-Mo(S)-catalysts prepared from different supports
(conditions: WHSV (h⁻¹), = 1; press. = 50 bar; H₂/liquid feed (v/v) = 400 STP)
The temperature of onset for PB formation does not appear to be directly related to the amount of acidity as measured by the TPD studies. As DAIBEA and AlMCM-41 are known to possess Bronsted acid sites and the cumene cracking activity of the corresponding sulfided catalysts, NiMo(S)/15DAIBEA-AL and NiMo(S)/AlMCM, is large (Chapter 3, Figure 3.19), it is likely that the cracking of the –C-N– bond in the aromatic amine (cracking of OPA into PB) is facilitated by Brønsted acidity. Earlier workers have reported that the cracking of OPA into PB is greater over SiO₂-Al₂O₃ (mainly Brønsted acidity) than over Al₂O₃ (mainly Lewis acidity) (Ramirez et al 2000). The presence of larger amounts of OPA in the products of catalysts containing Al₂O₃ (NiMo(S)/AL, NiMo(S)/MCM-AL and NiMo(S)/AlMCM-AL) suggests that the cracking of the alicyclic –C—N– bond in 1THQ occurs easily over Lewis acid sites present in the alumina component.

Comparing the BEA containing catalysts, the yield of PB increases sharply in the case of NiMo(S)/15DAIBEA-AL, goes through a maximum in the case of NiMo(S)/15BEA-AL, and increases steadily in the case of NiMo(S)/30BEA-AL. The reason for the appearance of a maximum in the case of the 15BEA-AL supported catalyst is the formation of PCH at higher temperatures. The rapid increase in PB formation up to about 95% yield at 613 K is probably because of lower diffusion constraints due to the presence of mesopores created during dealumination. The slower increase in PB formation in the case of NiMo(S)/15BEA-AL and NiMo(S)/30BEA-AL catalysts is probably due to larger diffusion constraints inside the zeolite pores. Interestingly, NiMo(S)/30BEA-AL, expected to be highly acidic due to the presence of substantial amount of BEA, also produces more PCH than the other catalysts. The other important product is DHQ, whose yield is less than 20% over all the catalysts; its yield increases up to 573-593 K and decreases at higher temperatures. The amount of propylcyclohexane (PCH) in
the products from all the catalysts except the BEA-containing catalysts is very small (<1%). The presence of larger amounts of PCH in the BEA-containing catalysts especially at higher temperatures is probably due to their strong acidity and ability to crack the –C-N- bond in decahydroquinoline (DHQ); the yield of PCH increases with temperature in the case of both NiMo(S)/15BEA-AL and NiMo(S)/30BEA-AL.

Figure 4.2 Influence of temperature on HDN of quinoline over Ni-Mo(S)-catalysts prepared from different supports (conditions: Temperature = 533-613K; WHSV (h⁻¹), = 1; press. = 50 bar; H₂/liquid feed (v/v) = 400 STP)

The activity of all the catalysts for HDN of quinoline at different temperatures is compared in Figure 4.2. The HDN activity reported in the figure is the sum of the yields of PB and PCH. It is found that the HDN activity is highest for NiMo(S)/15DAlBEA-AL followed by NiMo(S)/15BEA-AL. The order of HDN activity of the catalysts at 613 K is: NiMo(S)/15BEA-AL > NiMo(S)/15DAlBEA-AL > NiMo(S)/AlMCM-AL > NiMo(S)/Al > NiMo(S)/MCM-AL > NiMo(S)/MCM > NiMo(S)/SBA > NiMo(S)/AlMCM > NiMo(S)/30BEA-AL.
4.2.2 Influence of Feed rate

Change of feed rate was carried out by changing the liquid flow rate keeping the catalyst loading constant (~3 g). Correspondingly, the H₂ flow rate was also changed to keep the H₂ partial pressure constant. The activity profiles and product selectivity as a function of space velocity (WHSV, h⁻¹) are presented in Figure 4.3. The studies were carried out in a limited range of space velocity, 0.5 to 2.0 h⁻¹. It is found that the conversion is nearly 100% over all the catalysts except NiMo(S)/MCM-41, which exhibits a slightly lower conversion of 96% at a space velocity of 2.0 h⁻¹. Over all the catalysts, the yield of PB decreases rapidly with WHSV, while 1THQ increases.

At the temperature (613 K) used in the studies, the major product over NiMo(S)/15DAI/BEA-AL, NiMo(S)/15BEA-AL, NiMo(S)/AL and NiMo(S)/MCM-AL is PB even at WHSV (h⁻¹) of 2, while it is 1THQ in the case of the other catalysts. As the former catalysts are generally more acidic than the others, it appears that acidity is an important factor in PB formation. It is noticed that the yield of PB decreases rapidly with WHSV over all the catalysts except NiMo(S)/15DAI/BEA-AL. Thus NiMo(S)/15DAI/BEA-AL appear to be the most active catalyst for HDN of quinoline. DHQ, OPA and PCH are formed in much smaller amounts over all the catalysts. The yield of DHQ is substantial over NiMo(S)/MCM, NiMo(S)/AlMCM and NiMo(S)/MCM-AL suggesting that these catalysts possess good hydrogenation activities. The Al containing catalysts, in general, are found to produce more OPA as already pointed out in the earlier section.
Figure 4.3 Influence of feed rate on conversion of quinoline and product distribution over Ni-Mo(S) on different supports (conditions: Temperature = 613K; press. = 50 bar; H₂/liquid feed (v/v) = 200-800 STP)
4.2.3 Influence of Pressure

The influence of pressure on the HDN of Q has been carried out in the total pressure range between 20 to 50 bar over NiMo(S)/MCM, NiMo(S)/SBA, NiMo(S)/AlMCM, NiMo(S)/15DAiBEA-AL and NiMo(S)/BEA-AL and between 30 to 70 bar over NiMo(S)/AL, NiMo(S)/MCM-AL and NiMo(S)/AlMCM-AL. The studies were done by changing the total pressure keeping the feed rate constant. As the HDN of quinoline proceeds through a ring hydrogenation (aromatic hydrogenation) step (Scheme 4.1), the influence of H₂ partial pressure is important.

As expected, therefore, both conversion and HDN activity increase with pressure for nearly all the catalysts, with a few exceptions. In the case of NiMo(S)/15DAiBEA-AL, there is a small decrease in PB yield at the highest pressure (50 bar) studied. This is accompanied by a corresponding increase in yield of PCH (an HDN product). Hence, the HDN activity is not decreased at this pressure. In the case of NiMo(S)/AlMCM-AL, there is a suppression of HDN activity (PB + PCH yield) at 70 bar pressure. However, a corresponding increase in the yield of the intermediate 1THQ is noticed. This suggests that at the high pressure, the cracking of 1THQ is suppressed. This is also confirmed by a decrease in the yield of OPA at the higher pressure. The small dip in the yield of PB observed at the intermediate pressure of 50 bar in the case of NiMo(S)/AL is also difficult to explain. The only explanation is that the reaction network is a complex one and the active sites (hydrogenation and cracking) are likely to be affected by changes in H₂ and H₂S partial pressures. For example, under certain conditions both H₂ and H₂S could either suppress the reaction or enhance it (Sundramurthy et al 2008, Montesinos-Castellanos and Zepeda 2008).

Though there is a general trend of increasing conversion of Q with pressure, the extent of the pressure effects are different for the different
catalysts. While the activity of NiMo(S)/MCM, NiMo(S)/SBA, NiMo(S)/AlMCM and NiMo(S)/30BEA-AL increase by about 10 to 20% on increasing pressure from 20 to 50 bar, the increase is very small for NiMo(S)/15DAIBEAL (less than 5% increase) and very large for NiMo(S)/15BEA-AL (~55% increase). In the case of NiMo(S)/AL, the conversion is being already 100% at 30 bar. Both, NiMo(S)/MCM-AL and NiMo(S)/AlMCM-AL exhibit 93-94% conversion at the lowest pressure (30 bar) and 100 % conversion at 50 bar.

Regarding the effect of pressure on the other products, the observations are quite complex, and difficult to explain. A small decrease in the yield of PCH is noticed in the case of NiMo(S)/MCM and NiMo(S)/AlMCM, while it goes through a maximum along with OPA in the case of NiMo(S)/15BEA-AL. Over the other catalysts, PCH yield is smaller and generally remains constant or increases marginally with pressure. The yield of OPA generally decreases with pressure in the case of many of the catalysts.
Figure 4.4 Influence of pressure on conversion of quinoline and product distribution over Ni-Mo(S) on different supports (conditions: Temperature = 613 K; WHSV (h⁻¹), = 1 H₂/liquid feed (v/v) = 400 STP).
4.3 HYDRODENITROGENATION OF 1,2,3,4-TETRAHYDROQUINOLINE

1,2,3,4-tetrahydroquinoline is the primary intermediate in the HDN of quinoline. During the HDN of Q, it was found that nearly all the catalysts converted Q into 1THQ rapidly and it was the HDN of 1THQ that was the difficult reaction. It was therefore decided to investigate the HDN of 1THQ. The other tetrahydro intermediate, 5,6,7,8-tetrahydroquinoline (5THQ) was formed in much smaller amounts.

4.3.1 Influence of Temperature

The HDN of 1THQ was investigated in the temperature range of 553-613 K at 50 bar total pressure, WHSV (h^{-1}) of 1.0 and H_{2}/1THQ ratio (mole) of 48. The feed was made up of 1THQ in decalin and contained 5260 ppm of N. Conversion and product distribution obtained at different temperatures over the different catalysts are presented in Figure 4.5. Over all the catalysts, conversion of 1THQ increases with temperature, conversion at 613 K (highest temperature investigated) being nearly 100% in the case of NiMo(S)/AL. The lowest activity at this temperature is that of NiMo(S)/SBA, being 45%. The catalysts can be arranged in the following decreasing order of activity (conversion) at 613 K (Figure 4.6): NiMo(S)/15BEA-AL > NiMo(S)/15DAIBEA-AL > NiMo(S)/AlMCM > NiMo(S)/AlMCM-AL > NiMo(S)/MCM > NiMo(S)/AL > NiMo(S)/MCM-AL > NiMo(S)/30BEA-AL > NiMo(S)/SBA. However, conversion of 1THQ itself does not relate to HDN activity; it is the yield of PB + PCH that relates directly to HDN activity. The yield of PCH is mostly small over all the catalysts except in the case of NiMo(S)/AL and NiMo(S)/AlMCM-AL.
Figure 4.5  Influence of temperature on conversion of 1,2,3,4-tetrahydroquinoline and product distribution over Ni-Mo(S) on different supports
(conditions: WHSV (h⁻¹) = 1; press. = 50 bar; H₂/liquid feed (v/v) = 400 STP)
The yield of PB (HDN activity) increases with temperature, the most active catalyst being NiMo(S)/AL with 90% yield of PB + PCH, followed by NiMo(S)/AlMCM-AL with ~80% yield of PB and the least active catalyst being NiMo(S)/SBA-15 with ~20% of PB (all at 613 K). The decreasing order of activity (at 613 K) of the catalysts for HDN is (Figure 4.7): NiMo(S)/15BEA-AL > NiMo(S)/15DAIBEA-AL > NiMo(S)/AlMCM > NiMo(S)/MCM-AL > NiMo(S)/AlMCM-AL > NiMo(S)/AL > NiMo(S)/MCM > NiMo(S)/30BEA-AL > NiMo(S)/SBA. Both conversion and HDN activity orders are nearly the same because the major product at 613 K is PB (and PCH in the case of AL). At lower temperatures, the intermediate OPA is also found in the products. Similarly, substantial amount of DHQ is also found in the products obtained at lower temperatures. Generally, the yields of OPA and DHQ decrease or go through a maximum with temperature.

![Figure 4.6](image.png)

**Figure 4.6** Influence of temperature on conversion of 1,2,3,4-tetrahydroquinoline over Ni-Mo(S) on different supports (conditions: WHSV (h⁻¹), = 1; press. = 50 bar; H₂/liquid feed (v/v) = 400 STP)
4.3.2 Effect of Feed Rate

The activity profiles and product selectivity as a function of space velocity (WHSV, h\(^{-1}\)) are presented in Figure 4.8. Increasing the feed rate decreases both conversion and yield of PB for all the catalysts. The most active catalysts (based on 1THQ conversion) at the highest space velocity investigated (WHSV, 2.0 h\(^{-1}\)) are NiMo(S)/15DAiBEA-AL and NiMo(S)/15BEA-AL, both exhibiting a conversion of ~83%. The least active catalysts are NiMo(S)/SBA and NiMo(S)/30BEA-AL, both possessing activity of ~37%. As at this feed rate, PCH yield is very small (~1-2%) over all the catalysts, HDN activity is best represented by yield of PB.
Figure 4.8 Influence of feed rate on conversion of 1,2,3,4-tetrahydroquinoline and product distribution over Ni-Mo(S) on different supports
(conditions: Temperature = 613K; press. = 50 bar)
The highest HDN activity is noticed in the case of, again, NiMo(S)/15DAIBEA-AL and NiMo(S)/15BEA-AL, exhibiting 66 and 61% yields for PB. The lowest HDN activity is, again, exhibited by NiMo(S)/30BEA-AL and NiMo(S)/SBA, having conversions of ~20 and 17%, respectively. The similarity in conversion and HDN activity of the two catalysts is a bit surprising because, NiMo(S)/30BEA-AL is expected to be the most acidic catalyst, in that 30% of the support is zeolite BEA and SBA-15 has little or no acidity. In fact, cumene cracking activity of NiMo(S)/30BEA-AL is much more than that of NiMo(S)/SBA (Figure 4.10). However, the acidity of the sulfided catalysts estimated from TPD of NH$_3$ points to a different picture, total acidity of NiMo(S)/30BEA-AL and NiMo(S)/SBA are, respectively, 0.91 and 0.81 mmol/g, and the strong acidity (NH$_3$ desorbed beyond 673 K) of the two catalysts, in the same order, are 0.11 and 0.02 mmol/g. The most active catalysts, NiMo(S)/15DAIBEA-AL and NiMo(S)/15BEA-AL, possess total acidity of 0.77 and 0.83 and strong acidity of 0.14 and 0.02 meq/g. Cumene cracking activities of both the catalysts are large, NiMo(S)/15DAIBEA-AL being slightly more active. Thus, acidity alone cannot explain the relative activity of the different catalysts. Other factors such as dispersion of the Ni-Mo-S phase and diffusion effects (pore size distribution) are also likely to be important.

4.3.3 Effect of Pressure

The influence of pressure on the HDN of 1THQ was investigated in the total pressure range between 20 to 50 bar for Ni-Mo(S) supported on MCM, SBA, AlMCM, 15DAIBEA-AL and BEA and between 30 to 70 bar for NiMo(S) supported on AL, MCM-AL and AlMCM-AL. There are two routes to HDN of 1THQ, viz. i) hydrogenolysis/hydrocracking of the –C–N– bond and ii) hydrogenation to DHQ and subsequent breaking of the –C–N– bond.
Figure 4.9 Influence of pressure on conversion of 1,2,3,4-tetrahydroquinoline over Ni-Mo(S) on different supports (conditions: Temperature = 613K; WHSV (h⁻¹), = 1; press. = 20-50 bar; H₂/liquid feed (v/v) = 400 STP)
The first route is expected to yield PB while the second one is expected to produce PCH. As PCH was not found to any significant amount in the product even at the highest pressures used, it appears that the first route is the major one. Both conversion and PB yield (HDN activity) increase with pressure for all the catalysts, except NiMo(S)/AL. In the case of this catalyst, no effect of pressure on conversion is noticed, though the yield of PB increases with pressure. Surprisingly, the yield of DHQ is substantial at lower pressures in the case MCM and AlMCM supported catalysts. The reason for this is not clear, but is probably due to the rapid hydrogenation of 1THQ to DHQ and the slower hydrogenolysis of DHQ to the products at lower pressures. In the case of NiMo(S)/SBA, NiMo(S)/AL, NiMo(S)/MCM-AL and NiMo(S)/AlMCM-AL, the yield of DHQ goes through a maximum with pressure. The other important component in the product is OPA, which is found to generally decrease with pressure, increases in the case of NiMo(S)/AlMCM.

4.4 COMPARATIVE ANALYSIS OF THE ACTIVITY RESULTS

Cumene cracking activity of the sulfided catalysts was carried out to find out their acidity in the sulfided state at temperatures similar to those used in the HDN reactions. The activity results obtained at three temperatures over all the sulfided catalysts were reported in Figure 3.19 in Chapter 3. The order of activity for cumene cracking at 623 K is: NiMo/15DAIBEA-AL > NiMo/AlMCM > NiMo/15BEA-AL > NiMo/MCM-AL > NiMo/30BEA-AL > NiMo/AlMCM-AL > NiMo/MCM > NiMo/SBA ~ NiMo/Al2O3 ~ 0.
Figure 4.10 Cumene cracking activity of the catalysts: (A) bar chart presenting activity at different temperatures 623, 673, 723 K: the points represent the TPD acidity of supports (○), oxide catalysts (●) and sulphide catalysts (★); (B) relationship between cracking activity and TPD acidity of the supports (Cumene cracking conditions: Temp. = 623 K; WHSV (h⁻¹), = 1; press. = 1 atm.; H₂/liquid feed (v/v) = 400)
A bar chart of the cracking activity of the sulfided catalysts at different temperatures is presented in Figure 4.10 A. Super imposed on this plot are the acidities measured by TPD for the support, oxide and sulphide catalysts. It is noticed that no relationship can be made out between cracking activity and acidity of the oxide and sulphide catalysts. However, a weak relationship between cracking activity at 623 K and acidity of some of the supports is apparent.

A plot of cumene cracking activity vs. TPD-acidity of the support is presented in Figure 4.10 B. The data obtained at 623 K is used as conversions are lower at this temperature and complications due to diffusion effects are less likely to be dominant. Further, data from other HT-reactions were obtained mostly at temperatures below 623 K. The plot shows substantial scatter and some of the supports do not fall in the trend. The cumene cracking activity of the catalysts is a measure of their Brønsted acidity, while the TPD-method measures total acidity (Lewis and Brønsted) from both the support and the supported oxide/sulphide phases. Based on the absence of correlation with the acidity of the catalysts, and the presence of a marginal trend (Figure 4.10 B) with support acidity, one may surmise that the acid sites belonging to the supported oxide and sulphide phases of the catalysts are not able to crack cumene, either because they possess mainly Lewis sites or the Brønsted sites are too weak. However, the acid sites available on the exposed portions of the sulphide catalysts are sufficiently active to crack cumene.

Examining Figure 4.10 B, at least three supports are considerably away from the trend line. The explanations for the deviation have already been presented (Section 3.3.2.2). The negligible cracking activity of NiMo(S)/AL is, as already pointed out, due to the absence of Brønsted acidity. The lower cracking activity of NiMo(S)/30BEA-AL, inspite
of its large Brønsted acidity, is probably due to diffusion constraints arising from the zeolitic microporosity and the presence of substantial amount of inactive Lewis sites in the AL and BEA components. At the same time, the catalyst containing a lower amount of zeolite (NiMo(S)/15BEA-AL) is more active suggesting that this is an optimum or near optimum amount of loading. Earlier workers have reported that the commercial BEA sample itself contained substantial amount of Lewis acid sites (Marques et al 2003). The lower acidity of NiMo(S)/15DA1BEA-AL compared to NiMo(S)/15BEA-AL is attributable to the decrease in Brønsted acidity due to removal of framework Al-ions, and the removal of the Lewis acidity in the zeolite during dealumination.

\(^{27}\)Al-MASNMR of DA1BEA (Chapter 3, Figure 3.7a) revealed the removal of extra framework Al-ions that are likely to be Lewis acid sites, from the sample. At the same time, the slightly larger activity of NiMo(S)/15DA1BEA-AL compared to NiMo(S)/15BEA-AL is due to the greater accessibility of its acid sites because of an increase in mesoporosity of the zeolite on dealumination. The slightly lower activity observed in the case of AlMCM-AL is again probably due to the presence of a substantial amount of Lewis sites, a portion of these sites arising from the Al component. Moreover, during the deposition of the metal oxides, it is possible that some of the Brønsted acid sites became less-accessible due to pore blockage, though such an effect is not readily apparent from N\(_2\)-adsorption studies. The general scatter in the plot (Figure 4.10 B) is mainly due to the presence of different amounts of Lewis and Brønsted acidity in the catalysts.
Figure 4.11 HDN activity (at 613 K) and cumene cracking activity (at 623 K) of different sulfide catalysts: the points represent the TPD acidity of supports (○), oxide catalysts (●) and sulphide catalysts (★); (Conditions: HDN - temp. = 613 K; WHSV (h⁻¹), = 1; press. = 50 bar; H₂/liquid feed (v/v) = 400 STP; Cumene cracking - conditions: Temp. = 623 K; WHSV (h⁻¹), = 1; press. = 1 atm.; H₂/liquid feed (v/v) = 400)
Figure 4.12  Relationship between HDN activity for Q and 1THQ and TPD acidity of the supports (conditions for HDN: same as in Figure 4.11)

Bar charts of the HDN activity of the catalysts (at 613 K) for Q and 1THQ are presented in Figure 4.11 A and B. The acidities measured by TPD and cumene cracking (at 623 K) are also presented in the same figure. An important observation is that the HDN activity of the catalysts is not
apparently related to the TPD acidity of the oxide or sulphide catalysts. However, some relationship appears to exist between the acidity of the supports and HDN activity (Figure 4.12 A and B).

The plot for 1THQ reveals a linear relationship of activity with acidity (Figure 4.12 B); but this is not so in the case of Q (Figure 4.12 A). This is mainly because of the higher than expected activity of MCM-41 and SBA-15 supported catalysts, in spite of their low acidities. The reason is not clear, though it is probably related to the good dispersion and nature of the Ni-Mo(S) phase and may be some mechanistic reason involving stronger adsorption of the flat quinoline molecule on the active centres in these catalysts. The higher activity of these catalysts causes the trend line becoming a curve instead of a straight line (see dotted line in figure) as in the case of 1THQ. The second observation to be noted is that the trend line itself could be a different one with a negligible slope that includes the points of the catalysts supported on AlMCM-AL and 30BEA-AL, as shown in the figure in broken lines. This trend does not appear to be likely considering the cumene cracking activity and 1THQ plots. In these plots also, the deviating points are those of NiMo(S)/AlMCM-AL and NiMo(S)/30BEA-AL. The poor activity of NiMo(S)/30BEA-AL is due to its microporosity and presence of diffusion constraints. In the case of AlMCM-AL, as already mentioned, the reason may be that its Lewis acid content is large and the active sites are less accessible for the reactants.

Plots of HDN activity of the catalysts for the two feeds vs. cumene cracking activity of the catalysts are presented in Figure 4.13 A and B. The relationship between cumene cracking activity (Brønsted acidity) and HDN activity is not good, though a weak trend is noticed. The absence of a good relationship between cumene cracking and HDN activity of the catalysts suggests that Brønsted acidity is not critically needed for the HDN of Q and
ITHQ, though total acidity (including Lewis acidity), of the supports, may be important. However, the two most active catalysts are NiMo(S)/15DAIBEA-AL and NiMo(S)/15BEA-AL, which are expected to contain substantial amounts of Brønsted acid sites.

Many types of acid sites are expected to be present in sulfided Ni-Mo catalysts: Lewis and Brønsted acid sites on the exposed portion of the support and coordinatively unsaturated Mo-sites (CUS) in Ni-Mo(S) slabs. Weak Brønsted acidity has also been suggested to be present in the supported sulphide-phase arising from –SH groups attached to Mo (Duchet et al 1988).

Another observation is that NiMo/AL is more active than NiMo/MCM and NiMo/AlMCM for the HDN of Q, while the reverse is true for 1THQ. The reason for this difference is not clear. It is possible that fission of the –C—N- bonds (in Q, 1THQ and OPA) can also occur through hydrogenolysis over the metal (sulphide) sites without assistance from the acid sites. Therefore, it appears that acidity characteristics (of the catalysts or supports) alone cannot explain the relative activity of the catalysts, observations and other factors related to the Ni-Mo(S) specie (such as dispersion, number and location of the CUS sites and -SH groups) and diffusion effects need to be considered.
Figure 4.13 Relationship between HDN activity and cumene cracking activity of the sulfided catalysts (Conditions: same as in Figure 4.11)
4.5 CONCLUSIONS

i) The HDN of quinoline (Q) takes place through the hydrogenation of its heterocyclic ring into 1THQ. All the expected products in the predicted sequence of steps leading to its HDN are present in the reaction products. The hydrogenation of Q into 1THQ is nearly 100% over all the catalysts.

ii) The addition of BEA or its dealuminated form enhances the HDN activity of Ni-Mo(S) supported on alumina in the HDN of Q and 1THQ.

iii) The order of decreasing activity of the different catalysts for the HDN of the two substrates at similar conditions (temperature, 613 K; pressure, 50 bar; WHSV (h⁻¹), 1) are slightly different.

Q: NiMo(S)/15BEA-AL > NiMo(S)/15DAIBEA-AL > NiMo(S)/AlMCM-AL > NiMo(S)/Al > NiMo(S)/MCM-AL > NiMo(S)/MCM > NiMo(S)/SBA > NiMo(S)/AlMCM > NiMo(S)/30BEA-AL

1THQ: NiMo(S)/15BEA-AL > NiMo(S)/15DAIBEA-AL > NiMo(S)/AlMCM > NiMo(S)/MCM-AL > NiMo(S)/AlMCM-AL > NiMo(S)/AL > NiMo(S)/MCM > NiMo(S)/30BEA-AL > NiMo(S)/SBA.

iv) HDN of 1-THQ into the final products, propyl benzene and propyl cyclohexane requires the intervention of acid sites. Both Lewis and Brønsted acid sites seem to be active, though the more active catalysts are the ones possessing strong Brønsted acidity.
v) The cumene cracking activity of the sulfide catalysts is related somewhat to the TPD acidity of many of the supports. It is not related to the acidity of the oxide or sulfide catalysts.

vi) Again, activity of the catalysts for the HDN of Q and 1THQ is not related to the acidity of the oxide or sulfide catalysts. It appears to be related to the TPD acidity of the supports.