

Non-First-Order Hydrodenitrogenation Kinetics of Quinoline

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Received April 14, 1983; revised July 11, 1983

Two sulfided cobalt-molybdenum catalysts have been used to study the hydrodenitrogenation process of quinoline. One catalyst was supported on alumina, and one catalyst was supported on 50% alumina, 50% ultrastable faujasite zeolite. The denitrogenation products were identical for both catalysts. At low temperature, the CoMo/Al₂O₃ catalyst was more effective for nitrogen removal than the CoMo/USY-Al₂O₃ catalyst; at higher temperature, the reverse was true. Non-first-order kinetics were observed for feeds of high nitrogen concentration. At low feed nitrogen concentration, however, first-order denitrogenation kinetics were observed. A Langmuir-Hinshelwood expression in which ammonia is weakly adsorbed on the catalyst was used to interpret the data. From the analysis of the denitrogenation kinetics for two catalysts, evidence is presented for the direct participation of the catalyst support in the denitrogenation process. At elevated temperatures, the acid sites of the support appear to be capable of breaking the secondary carbon-nitrogen bond improving denitrogenation performance. The kinetic response to support acidity is discussed in terms of the various contributions to the Langmuir-Hinshelwood model.

INTRODUCTION

The kinetics (1-11) and mechanism (12-18) of hydrodenitrogenation have been extensively studied for both commercial, multi-nitrogen component, and laboratory or single nitrogen compound, feedstocks. For oils containing a single-nitrogen compound, a more complete analysis has been possible. Mechanistically, hydrodenitrogenation of unsaturated-nitrogen compounds proceeds stepwise. For heterocyclic nitrogen compounds, ring saturation occurs prior to nitrogen removal with the rate determining step, breakage of the secondary carbon-nitrogen bond. Likely reaction intermediates for the bond breaking step are carbonium ions (2).

Kinetically, most studies find that nitrogen removal is pseudo-first order with respect to total nitrogen concentration (1-10). The denitrogenation kinetics of pyridine (1) dissolved in xylene has been determined over a wide range of initial pyridine concentrations. Although nitrogen removal was first order with respect to nitrogen, the pseudo-first-order rate constant

was observed to decrease with increasing initial nitrogen concentration. A Langmuir-Hinshelwood-type model was proposed with inhibition terms due to nitrogen compounds. Since the observed kinetics were first order, it was assumed that only nitrogen compounds are strongly adsorbed on the catalyst surface and that the adsorption coefficients for all nitrogen compounds, including ammonia, are nearly equal. According to the kinetic model the pseudo-rate constant was inversely proportional to the initial nitrogen concentration. For other, pure compound denitrogenation studies, similar kinetic expressions have been proposed (2, 3, 7).

Previously, kinetic data obtained for hydrotreating of shale oil with experimental catalysts incorporating strongly acidic zeolites has given non-first-order denitrogenation kinetics (9) with respect to nitrogen concentration. Since there are few examples of systems displaying non-first-order denitrogenation kinetics for nitrogen removal, this study was undertaken to determine under what conditions non-first-order kinetics can be observed for denitrogena-

tion of quinoline and how the experimental conditions influence the observed kinetic order.

EXPERIMENTAL METHODS

Equipment. All runs were made in a fixed-bed, bench scale, flow system of conventional design. The reactor is a 80-cm stainless-steel vertical reactor of 1.0 cm i.d. equipped with an internal thermowell and traveling thermocouple. Reactor temperature control was maintained by four electrical heaters. Hydrogen was used on a once-through basis and was metered from the unit. The hydrogen flow rate was measured by a wet test meter and maintained at a constant $155 \text{ m}^3/\text{m}^3$ of oil. Liquid feed was fed to the reactor by a Ruska pump and mixed with hydrogen prior to the reactor. The top of the reactor bed, containing 25 cm of α -alumina, was used to preheat the feed. The liquid product was composited for 24 h in a sample receiver.

Materials. A white oil (boiling range 350 to 450°C) with a nitrogen and sulfur content of less than 1 ppm was used as a carrier for quinoline. Quinoline (Aldrich) of 96% purity was used as received. Catalyst supports were prepared by the following procedure using American Cyanamid alumina sol and Davison ultrastable faujasite molecular sieve. Appropriate amounts of alumina sol, 10.3 wt% solid Al_2O_3 , and ultrastable molecular sieve were thoroughly mixed in a blender. After mixing, the alumina was rapidly precipitated by a basic NH_4OH solution and dried at 250°F. The resulting solid was ground to pass 100 mesh, milled with water and extruded to 0.2 cm. The extrudate was dried at 120°C and calcined in air at 535°C for 1 h. The composition of the zeolite/alumina support was 50 wt% zeolite and 50 wt% Al_2O_3 .

Finished catalysts were prepared by adding 18.41 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 14.55 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 72 ml H_2O to 131.25 g of calcined support. After 1 h at room temperature, the catalyst was dried at 120°C and calcined for 1 h in air at

535°C. Nominal composition of both catalysts was 3.0 wt% CoO, 10.0 wt% MoO_3 , and 87.0 wt% support. Surface properties for the alumina supported catalyst are surface area, 215 m^2/g ; pore volume, 0.56 cm^3/g ; and an average pore diameter, 4V/A, 104 Å. Surface properties for the zeolite/alumina catalyst are surface area, 304 m^2/g ; pore volume, 0.34 cm^3/g ; and an average pore diameter, 4V/A, 45 Å.

Procedure. Finished catalysts were crushed and screened to 14/20 mesh and packed in the reactor. All catalysts were presulfided at approximately 2.0×10^3 kPa by passing a mixture of 8% hydrogen sulfide in hydrogen over the catalyst at a flow rate of approximately one standard cubic foot of gas per hour. Sulfiding was conducted for 1 h each at 150, 200, and 315°C.

Following pretreatment, the unit was pressurized to 6.89×10^3 kPas hydrogen pressure. The temperature of the catalyst bed was raised to either 330 or 375°C.

In order to obtain both high and low nitrogen conversion, two catalyst loadings at each temperature were required for each catalyst. After each catalyst loading, the feed was run for 6 days in order to obtain a steady state condition before any samples were taken for analysis. After a change of space velocity, the unit was run for 36–48 h to establish a new steady state. Samples for nitrogen analysis at each space velocity were collected each 24-h period for three consecutive days. At the end of each run, the conditions were returned to original space velocity to determine the extent of catalyst deactivation.

Analysis. After collecting the liquid sample for 24 h, dissolved ammonia was stripped from the sample by bubbling nitrogen through the liquid for 10 min. Since quinoline and all of the reaction intermediates are basic nitrogen compounds, total product nitrogen was determined by perchloric acid titration in glacial acetic acid (19–21). Brilliant Green (Baker Chemicals) was used as a visual indicator. Three titrations were made on each 24-h sample. Peri-

odically random samples were submitted to Standard Oil's analytical services for total nitrogen by the Auto Kjeldahl method.

Daily, each product was examined by gas chromatography (10% UCW 982, 1/8 × 20 in.) to determine qualitatively which intermediates were present at each space velocity and temperature.

RESULTS

Two sulfided cobalt/molybdenum catalysts were used for nitrogen removal from quinoline carried in white oil. The product distribution from quinoline hydrodenitrogenation was determined by gas chromatography. Nitrogen-containing compounds and final hydrocarbon products were identified by identical retention times with known samples as well as gas chromatographic mass spectral analysis.

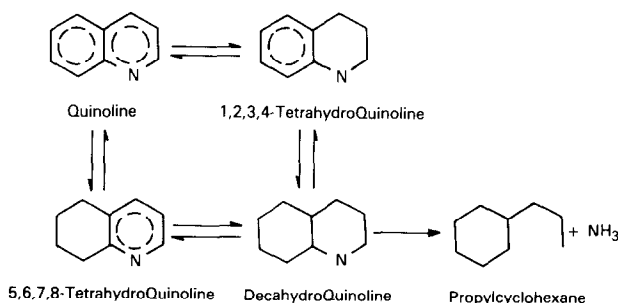
At 330°C under our reaction conditions the following products were observed. At low conversion, the major nitrogen-containing product was 1,2,3,4-tetrahydroquinoline. Decahydroquinoline was present in lower amounts. Unreacted quinoline was present but in very low concentration. The major hydrocarbon product was propylcyclohexane with much lesser amounts of propylbenzene. At high conversion the only nitrogen compound was decahydroquinoline, and nearly all of the hydrocarbon product was propylcyclohexane.

At 375°C different reaction intermediates were observed. At low conversion, 1,2,3,4-tetrahydroquinoline was still the major re-

action product; however, 5,6,7,8-tetrahydroquinoline was also present as a product. Small amounts of decahydroquinoline were present as was observed at lower temperature. At the higher reaction temperature, the quinoline concentration was higher than was observed at lower temperature. Propylcyclohexane was again the major hydrocarbon product. At high temperature and high nitrogen conversion, decahydroquinoline was the final observed nitrogen-containing product.

At equivalent nitrogen conversions, no differences in product distribution were observed for the two catalysts at either 330 and 375°C. The presence of the zeolite did not alter the products of the reaction. Also, neither 2-propylalanine or 2-propylcyclohexylamine were observed under any reaction conditions. The reactive sequence is presented in Scheme 1 (2, 8, 16).

A white oil containing 9560 ppm nitrogen was hydrotreated at 330°C by the two sulfided cobalt-molybdenum catalysts. For the CoMo/Al₂O₃ catalyst, product nitrogen concentrations at each space velocity are presented in Table 1. The space velocities were selected to produce products with a full range of nitrogen conversions. At the highest space velocities, approximately 10–15% denitrogenation was obtained; while, at the lowest space velocities, over 99% of the nitrogen was removed from the feed. Denitrogenation kinetics for CoMo/Al₂O₃ are plotted in Fig. 1. If hydrodenitrogenation were first order in nitrogen concentra-



SCHEME 1. Reaction sequence and products of quinoline denitrogenation.

TABLE 1

Product Nitrogen Concentration, N_p , for Quinoline Denitrogenation^a

Catalyst	LHSV (cm ³ /h oil/cm ³ cat)	N_p (ppm)
CoMo/Al ₂ O ₃	0.19	15
	0.32	1305
	0.57	4340
	1.07	6810
	1.33	7320
	2.29	8300
	3.19	8490

^a Temp = 330°C; 6.89×10^3 kPa, feed nitrogen = 9650 ppm.

tion, a plot of the log of product nitrogen concentration versus space time, or the reciprocal of space velocity, would be linear. At an initial nitrogen concentration of 9560 ppm, denitrogenation kinetics are less than first order.

Similar results are presented for the CoMo/USY-Al₂O₃ catalyst, Table 2 and Fig. 1. At 330°C, under the same conditions CoMo/Al₂O₃ is a better denitrogenation catalyst than CoMo/USY-Al₂O₃. For example, at a given space velocity, the CoMo/Al₂O₃ catalyst yields a product with lower

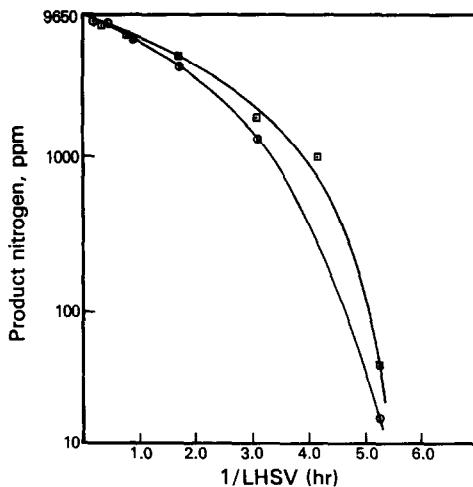


FIG. 1. Denitrogenation kinetics of quinoline at 330°C and 6.89×10^3 kPa. $N_0 = 9650$ ppm; \odot , CoMo/Al₂O₃; \square , CoMo/USY-Al₂O₃.

TABLE 2

Product Nitrogen Concentration, N_p , for Quinoline Denitrogenation^a

Catalyst	LHSV (cm ³ /h oil/cm ³ cat)	N_p (ppm)
CoMo/USY-Al ₂ O ₃	0.19	35
	0.24	981
	0.32	1930
	0.57	4920
	1.33	7260
	2.66	8180

^a Temp = 330°C; 6.89×10^3 kPa, feed nitrogen = 9650 ppm.

nitrogen concentration than does the CoMo/USY-Al₂O₃ catalyst at the same space velocity.

The CoMo/Al₂O₃ catalyst was additionally tested at 330°C with a feed having an initial nitrogen concentration of 1780 ppm. The results are given in Table 3 and Fig. 2.

At the end of each test period, each catalyst was returned to the original space velocity and tested for deactivation. Catalysts tested at 330°C showed no deactivation during the test period. The longest test lasted 18 days. At a constant space velocity, the product nitrogen obtained at the end of the test period was identical to the product nitrogen at the beginning of the test period. At 375°C, however, both catalysts were observed to continuously deactivate. In addi-

TABLE 3

Product Nitrogen Concentration, N_p , for Quinoline Denitrogenation^a

Catalyst	LHSV (cm ³ /h oil/cm ³ cat)	N_p (ppm)
CoMo/Al ₂ O ₃	0.63	113
	0.79	228
	1.06	455
	1.59	801
	2.39	1151

^a Temp = 330°C; 6.89×10^3 kPa, feed nitrogen = 1780 ppm.

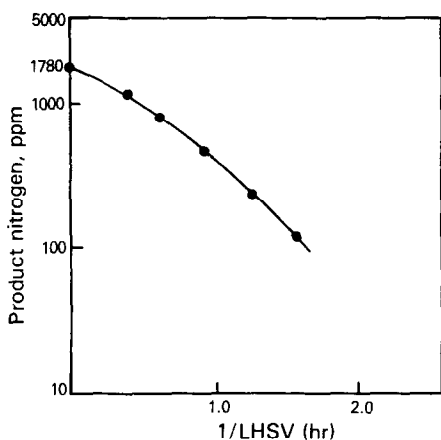


FIG. 2. Denitrogenation kinetics of quinoline at 330°C and 6.89×10^3 kPa. $N_0 = 1780$ ppm; ●, CoMo/ Al_2O_3 .

tion, both catalysts deactivated at approximately the same rate. The effect of catalyst deactivation at constant space velocity can be seen in Table 4. Initially, there was a rapid change in activity for the first 4 days followed by a more gradual activity decline. In order to minimize the effects of deactivation, all products were collected for catalysts tested from days 7 to 13. During days 7 to 13 catalyst activity decline was more gradual and corrections for loss in activity could be made.

TABLE 4

Catalyst Deactivation and Activity at 375°C and 6.89×10^3 kPa^a

Catalyst	Day	LHSV	N_p	Activity ^b
CoMo/ Al_2O_3	2	1.02	2689	1.44
	3	1.02	3319	1.23
	4	1.02	3655	1.15
	5	1.02	4014	1.07
	6	1.02	4225	1.03
	7	1.02	4357	1.00
	8	1.02	4472	0.98
	9	1.02	4570	0.97
	12	1.02	4902	0.89
	13	1.02	4876	0.89

^a Feed nitrogen = 14,030 ppm.

^b First-order deactivation, day 7 assigned as 1.00 activity.

In order to make corrections for catalyst deactivation, the kinetics of deactivation must be known. In this study deactivation kinetics were not studied and first-order kinetics were assumed. In addition, day 7 was assigned as having an activity of 1.00. The initial nitrogen concentration of the feed for catalysts tested at 375°C was 14,030 ppm. The activity for each day, x , is determined from the data in Table 4 using

$$\text{Activity} = \log(N_0/N_p)_x / \log(N_0/N_p)_7 \quad (1)$$

N_0 and N_p represent the nitrogen concentration of the feed and the product, respectively.

The space time was corrected for catalyst deactivation by multiplying the catalyst activity times the actual space time. Results at 375°C corrected for deactivation are presented in Tables 5 and 6 for CoMo/ Al_2O_3 and CoMo/USY- Al_2O_3 catalysts, respectively. Denitrogenation kinetics are presented in Fig. 3. At the higher temperature, denitrogenation kinetics for CoMo/ Al_2O_3 are nearly pseudo-first order, despite the high initial nitrogen concentration. For the CoMo/USY sieve- Al_2O_3 catalysts, however, denitrogenation kinetics are lower than first order.

In addition, at 375°C, the molecular sieve

TABLE 5

Product Nitrogen Concentration, N_p , for Quinoline Denitrogenation^a

Catalyst	LHSV (Day)	N_p	Activity ^b	1/LHSV (corrected)
CoMo/ Al_2O_3	0.34	168	0.92	2.70
	0.45 (7)	348	1.00	2.22
	0.45 (12)	734	0.87	1.93
	0.63	1487	0.97	1.59
	1.02 (7)	4357	1.00	0.98
	1.02 (9)	4516	0.97	0.95
	1.02 (12)	4889	0.87	0.85
	2.04	8388	0.93	0.46

^a Temp = 375°C; 6.89×10^3 kPa; feed nitrogen = 14,030 ppm.

^b First-order deactivation, day 7 assigned as 1.00 activity.

TABLE 6

Product Nitrogen Concentration, N_p , for Quinoline Denitrogenation^a

Catalyst	LHSV (Day)	N_p	Activity ^b	1/LHSV (corrected)
CoMo/USY-	0.46	49	0.94	2.19
Al ₂ O ₃	0.55 (7)	168	1.00	1.82
	0.55 (13)	346	0.90	1.63
	0.55 (18)	389	0.85	1.53
	0.68	1066	0.94	1.37
	0.73	1228	0.88	1.21
	1.02	2714	1.00	0.98
	1.69	6204	0.90	0.53

^a Temp = 375°C; 6.89×10^3 kPa; feed nitrogen = 14,030 ppm.

^b First-order deactivation, day 7 assigned as 1.00 activity.

containing catalyst, CoMo/USY-Al₂O₃, is more effective for nitrogen removal than the CoMo/Al₂O₃ catalyst. The reverse was true at lower temperature. The addition of the zeolite component has not only influenced the apparent reaction order for nitrogen removal, but has also enhanced the rate of nitrogen removal at the higher temperature.

DISCUSSION

The product distribution obtained for denitrogenation of quinoline under our re-

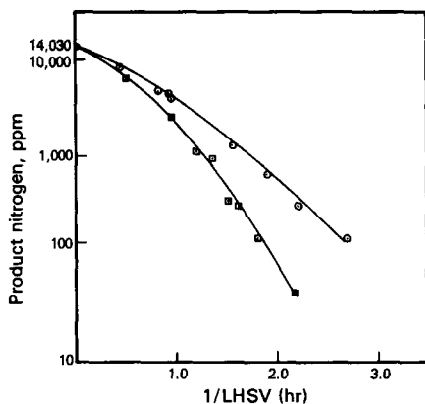


FIG. 3. Denitrogenation kinetics of quinoline at 375°C and 6.89×10^3 kPa. $N_0 = 14,030$ ppm; \circ , CoMo/Al₂O₃; \square , CoMo/USY-Al₂O₃.

action conditions was similar to previous mechanistic quinoline denitrogenation studies (2, 8, 16).

Unlike previous kinetic studies of quinoline denitrogenation, in this study the rate of nitrogen removal was not, in general, pseudo-first order, but less than first order. In addition, when the data was fit to a power law kinetic model, the apparent order of the reaction changed with initial concentration and temperature. For example, with the CoMo/Al₂O₃ catalyst and at a reaction temperature of 330°C, the power law kinetic order was 0.49 when the initial nitrogen concentration was 9560 ppm. At an initial nitrogen concentration of 1780 ppm, however, the kinetic order was 0.95. As a result a Langmuir-Hinshelwood rate expression was adopted to account for these observations. The simplest expression assumes that only nitrogen compounds are strongly adsorbed on the catalyst surface and that the reaction order is first order in both hydrogen and total nitrogen concentration (1). The rate expression is

$$\frac{-dN}{dt} = \frac{k(P_H)[N]}{\left(1 + \sum_i K_{N_i}[N_i] + K_{NH_3}[NH_3]\right)} \quad (2)$$

where k is the rate constant and K_N is equilibrium adsorption constant for the i th nitrogen component of the reacting feed stream. In Eq. (2), since the molar ratio of hydrogen to total nitrogen concentration is large, the total number of moles of hydrogen remains approximately constant. The rate expression can be simplified

$$\frac{-dN}{dt} = \frac{k'[N]}{\left(1 + \sum_i K_{N_i}[N_i] + K_{NH_3}[NH_3]\right)} \quad (3)$$

Analysis of the kinetic data was made using two additional assumptions. First, all adsorption constants for organic nitrogen compounds are approximately equal (7). Although this is not strictly valid, all nitro-

gen intermediates and quinoline are strongly basic and the catalyst supports and active metals are acidic. The second assumption was that the equilibrium adsorption constant for ammonia much smaller than the adsorption constant for organic nitrogen compounds ($K_N \gg K_{NH_3}$). Although this assumption is difficult to justify based on acid-base properties in aqueous systems, adsorption measurements indicate that organic amines are more strongly adsorbed on cobalt-molybdenum catalysts than is ammonia (3). The final kinetic expression is

$$\frac{-dN}{dt} = \frac{k'[N]}{1 + K_N[N]} \quad (4)$$

$$\ln(N_0/N) + K_N(N_0 - N) = k't \quad (5)$$

Using Eq. (5), the integrated form of Eq. (4), the two empirical rate expression constants can be determined from the data in Tables 1-6.

The calculated constants for the two catalysts at 330 and 375°C are given in Table 7. Using the constants in Table 7 and Eq. (5), kinetic curves for any initial nitrogen concentration can be calculated. For example, for the CoMo/Al₂O₃ catalyst and using the two constants determined at 330°C, a family of kinetic curves at different initial concentrations is given in Fig. 4. In Fig. 4, it can be seen that the apparent reaction order, as obtained from a power law expression, changes with initial nitrogen concentration. For an initial concentration of 100

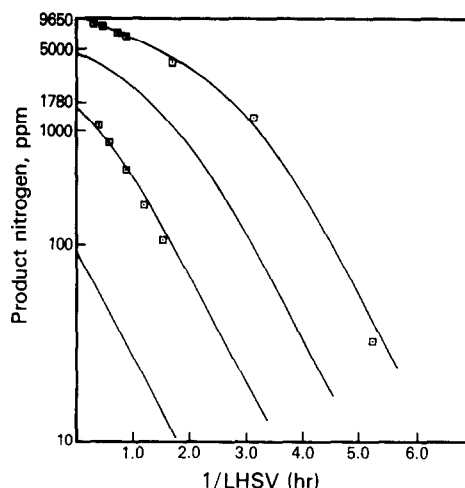


FIG. 4. Denitrogenation kinetics of quinoline at 330°C and 6.89×10^3 kPa for CoMo/Al₂O₃. —, Calculated. □, Experimental.

ppm, the kinetics are first order; while, at an initial concentration of 9650 ppm nitrogen, the kinetics are definitely less than first order.

It should be emphasized that first-order kinetics are predicted for feeds of low initial nitrogen concentration. This results even though the derived kinetic expression was based on the assumption that ammonia is weakly adsorbed on the catalyst surface. In Fig. 4, the experimentally determined quinoline denitrogenation kinetics for the CoMo/Al₂O₃ catalyst at 330°C with an initial nitrogen concentration of 1780 ppm are very nearly identical to the calculated kinetic curve, predicted from the data obtained at an initial concentration of 9650 ppm.

It will be noticed in Fig. 4 that for the non-first-order kinetic curves, the initial denitrogenation performance, for example, up to 50% nitrogen removal, is pseudo-first order. At low nitrogen conversion, little ammonia is produced having little influence on the kinetics, whether the ammonia is strongly adsorbed on the catalyst surface or not. In addition, the pseudo-first-order rate constants determined from the initial kinetics decrease with increasing nitrogen feed

TABLE 7

Catalytic Rate Constants (Eq. (4)) for Quinoline Denitrogenation at 6.89×10^3 kPa

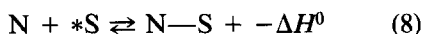
Catalyst	Temp. (°C)	k'^a	K_N (ppm ⁻¹)
CoMo/Al ₂ O ₃	330	2.229	5.913×10^{-4}
CoMo/USY-Al ₂ O ₃	330	2.175	7.199×10^{-4}
CoMo/Al ₂ O ₃	375	2.363	1.250×10^{-4}
CoMo/USY-Al ₂ O ₃	375	3.689	1.679×10^{-4}

^a In (cm³ oil/cm³ cat) h⁻¹.

concentration. The inverse relationship of the first-order rate constant with initial nitrogen concentration has been previously observed for pyridine hydrodenitrogenation (1).

In addition to accounting for apparent, changing reaction order resulting from changing initial nitrogen concentration, Eq. (4) is useful for qualitative understanding of the denitrogenation process and can be used to make some qualitative predictions. The kinetic constants, k' and K_N , of Eq. (4) are not fundamental kinetic constants but are complex functions of fundamental constants, hydrogen partial pressure, nitrogen concentration, temperature, etc. Although not equal to the true kinetic constants, the empirical constants are directly proportional to their respective fundamental constant. As a result, the kinetic response resulting from changes in process conditions or catalyst composition can be predicted by assessing the effects these changes have on the true kinetic rate constants.

In Eq. (4), the extent to which the kinetics deviate from first order is dependent on the magnitude of K_N at a constant initial nitrogen concentration. In the limit of very large K_N , the reaction becomes zero order; however, for $K_N \ll 1$, the reaction becomes first order. The empirical K_N is directly proportional to the equilibrium constant for the adsorption of organic nitrogen compounds on the catalyst,



Since reaction (8) is exothermic, K_N becomes smaller at higher temperature. That is, higher temperature favors desorption. Consequently, at higher temperature K_N is smaller and the observed kinetics are more nearly first order. Experimentally, for both catalysts the reaction kinetics are more nearly first order at 375 than at 330°C. Also K_N is a function of acid strength. Desorption of basic nitrogen compounds from a stronger acid site will be more difficult, and K_N will be larger. Lower order kinetics are predicted for strongly acidic catalysts. In

Fig. 3, lower order kinetics are observed for the more acidic CoMo/USY-Al₂O₃ catalyst at 375°C. Figure 5 shows the effect on the reaction order and the kinetic rate resulting from increased adsorption constant, K_N . Figure 5 represents the performance for a series of hypothetical catalysts with equivalent rate constants, k , and increasing adsorption constants, K_N . Lower order kinetics are observed for the catalyst of higher K_N . In addition, the denitrogenation rate decreases with increasing K_N . Reduction in denitrogenation performance, especially at high nitrogen concentrations, resulting from increasing catalyst acidity has been reported (9, 23).

From Fig. 3, it is observed that at 375°C the addition of zeolites to the CoMo/Al₂O₃ catalyst resulted in a catalyst of improved denitrogenation performance. Since breakage of the secondary carbon-nitrogen bond is rate determining, the reaction rate constant should also reflect changes in catalyst acidity that effect bond breakage. From Table 7, k' for CoMo/USY-Al₂O₃ is larger than k' for CoMo/Al₂O₃ at 375°C. At high temperature, the increased rate constant for the CoMo/USY-Al₂O₃ catalyst indicates that the zeolite is capable of participating in the catalytic sequence, possibly

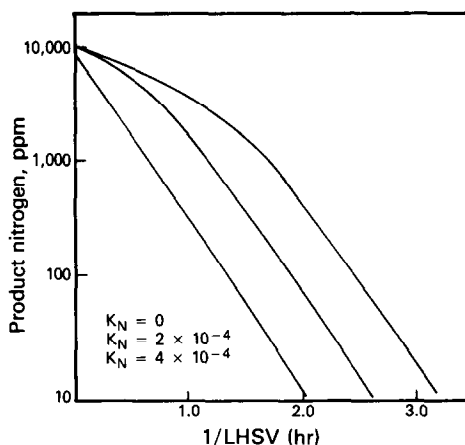


FIG. 5. The effect of increasing adsorption constant K_N on denitrogenation kinetics. Assumed values are $N_0 = 10,000$ ppm and $k' = 3.454$.

assisting in the bond breakage step. At low reaction temperature, however, the acidic zeolite sites did not improve the denitrogenation rate. At lower temperatures, the support acid sites appear to be poisoned by the many basic nitrogen compounds present. Catalyst support acidity is a key element in the denitrogenation process and suggests that support acidic sites can assist in breakage of carbon–nitrogen bonds.

CONCLUSION

The major reaction path for loss of ammonia from quinoline was the same for the CoMo/Al₂O₃ and CoMo/USY–Al₂O₃ catalysts. Many of the reaction intermediates are molecular species. In general, the denitrogenation kinetic reaction order determined for a power law kinetic model is not first order, but less than first order with respect to nitrogen concentration. A Langmuir–Hinshelwood kinetic model in which it was assumed that ammonia was weakly on the catalyst was successful for interpretation of the data. The kinetic expressions not only fit the available data, but could be used to predict, as least qualitatively, results for changes in feed nitrogen concentration, reaction temperature, and catalyst support composition.

Although several examples of non-first-order denitrogenation kinetics were presented, under certain conditions first-order kinetics were obtained. Equation (4) reduces to a first-order expression when either $K_N[N]$ is much less than 1 or when the term $(1 + K_N[N])$ is constant. At low nitrogen concentration, $K_N[N]$ is much less than 1, and the kinetics are first order; therefore, for low nitrogen concentration feeds, the observed kinetics are first order. High reaction temperatures can also lead to observed first-order kinetics by reducing the magnitude of K_N . The adsorption equilibrium constant is a function of the catalyst support acid strength. Weakly acidic catalysts have smaller equilibrium adsorption constants and give more nearly first-order ki-

netics. Kinetic differences due to support acid strength become more pronounced at higher temperature.

For all feed nitrogen concentrations, the initial denitrogenation kinetics will be first order. Over a limited range of nitrogen removal $(1 + K_N[N])$ changes little and is approximately $(1 + K_N[N_0])$. As a result, the pseudo-first-order rate constant determined for the initial denitrogenation kinetics is inversely related to the feed nitrogen concentration. A similar feed concentration dependence for the pseudo-rate constant has previously been reported for pyridine hydrodenitrogenation (1).

The results from this study suggest that the catalyst support directly participates in the reaction sequence for hydrodenitrogenation. The acidic sites of the support assist in the carbon–nitrogen bond breakage reactions. The ability of the zeolite to improve denitrogenation rates is temperature dependent, requiring elevated reaction temperatures. At low reaction temperature, the acid sites are poisoned by the many basic nitrogen compounds present.

Although at high temperature an acidic support may improve the denitrogenation rate by promoting carbon–nitrogen bond breakage, in some cases the acidic function may inhibit the denitrogenation rate. For example, at high nitrogen concentrations, a strongly acidic catalyst will have a large adsorption equilibrium constant. Poor denitrogenation performance may result from surface poisoning by nitrogen compounds.

Non-first-order kinetics effects are complex. Often, catalyst performance resulting from changes in process conditions or catalyst composition are not easy to predict. Deviations from first-order kinetics are more pronounced for high nitrogen content feedstocks, low reaction temperatures and for hydrotreating catalysts of high acidity. Commercially, non-first-order effects will become increasingly important as refineries begin to process high nitrogen feedstocks, e.g., coal liquids, shale oils, and tar sand oils.

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