

EFFECT OF CATALYST COMPOSITION ON
QUINOLINE AND ACRIDINE HYDRODENITROGENATION

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INTRODUCTION

Recently there has been increased interest in the hydrodenitrogenation of nitrogen-containing aromatic compounds typical of those found in petroleum, coal-derived liquids and shale oil. Because of the high nitrogen contents of coal-derived liquids and shale oil, hydrodenitrogenation will become increasingly important in the future. Mars and Coworkers (1-4) have clarified the reaction network and kinetics associated with the hydrodenitrogenation of pyridine. Their work was done on unsulfided Co-Mo/Al₂O₃ catalyst. Although several authors (5-9) have studied hydrodenitrogenation, neither the reaction network, nor the reaction kinetics have been adequately defined for anything but pyridine. We have recently established the reaction networks and reaction kinetics of the hydrodenitrogenation of quinoline (10, 11) and of acridine (12) over sulfided hydroprocessing catalysts under high-pressure liquid-phase conditions.

Both the prior literature and our work shows that hydrodenitrogenation of nitrogen-containing compounds occurs via a complex reaction network involving hydrogenation of the aromatic rings followed by carbon-nitrogen bond breaking. This is in contrast to hydrodesulfurization, in which sulfur removal occurs directly without hydrogenation of the associated aromatic rings (13). It is therefore important to understand how catalyst composition affects the relative rates of hydrogenation and of bond breaking in the complex nitrogen-removal reaction network. This bifunctional nature of the reaction network requires an appropriate balance between the catalyst hydrogenation and catalyst bond-breaking functions to provide the most active catalyst. A quantitative definition of the relative kinetic role of the two catalyst functions in hydrodenitrogenation is not available.

Generally Ni-Mo/Al₂O₃ or Ni-W/Al₂O₃ have been reported to be more active for hydrodenitrogenation than Co-Mo/Al₂O₃, the catalyst of choice for hydrodesulfurization, and the enhanced behavior is often assumed to be due to higher hydrogenation activity (9, 14, 15). This is not confirmed by

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quantitative experimental data, particularly under typical hydroprocessing conditions with multi-ring nitrogen-containing compounds. In this work we have evaluated the relative behavior of commercial hydroprocessing catalysts of differing metal composition and support under high-pressure liquid-phase conditions. The catalysts were examined in the oxidic form, the sulfided form and the sulfided form with H₂S in the system. First-order rate constants for all hydrogenation and bond breaking steps in the reaction networks were determined as a function of catalyst type and catalyst pretreatment. Our objectives were to determine how the catalyst type and pretreatment affected the rate of each individual step in the hydrodenitrogenation reaction network and thus to elucidate the fundamental differences in the catalysts.

EXPERIMENTAL

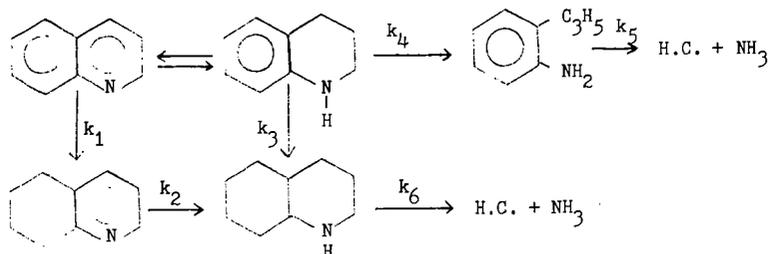
The experiments were carried out in a one-liter stirred autoclave (Autoclave Engineer) with glass liner; the autoclave was operated in batch mode. A special reactant-oil-catalyst injection system was attached to the autoclave to inject catalyst and reactant (nitrogen-containing compound) in carrier oil into the autoclave after it had been stabilized at the operating temperature and pressure. Consequently, the problems of reaction and catalyst deactivation during the long heat-up time frequently encountered in autoclave studies were eliminated, and zero time was precisely defined. The system has been described elsewhere (10, 11); operating conditions were:

Temperature: quinoline, 342 ±1°C; acridine, 367 ±1°C
Total pressure: quinoline, 34 atm; acridine, 136 atm
Reactant concentration: quinoline, 1.0 wt%; acridine 0.5 wt %
Catalyst: 0.5 wt % in carrier oil; 150-200 mesh;
 sulfided (quinoline, 2 hr at 325°C; acridine 2 hr at
 425°C) in 160 cc/min of 10% H₂S in H₂
Carrier Oil: 500 cc highly paraffinic White Oil;
 0.05 wt % CS₂ added to give 1.4 vol % H₂S in the
 gas phase
One-liter autoclave, stirred at 1700rpm

Analysis of reaction products was by G. C. using a 10' X 1/8' Chromosorb 103 glass column for quinoline, a 50m OV101 SCOT glass column for acridine and a nitrogen-specific detector so that individual nitrogen-containing compounds could be identified.

RESULTS

The reaction network for quinoline hydrodenitrogenation with specific rate constants identified, as established by Shih et al. (10, 11), is:



The behavior of different catalysts in quinoline hydrodenitrogenation is given in Table I. Ni-Mo/Al₂O₃ is a slightly better catalyst for the removal of nitrogen from quinoline than Co-Mo/Al₂O₃ or Ni-W/Al₂O₃ as shown by the pseudo first-order rate constants for total nitrogen removal. The Ni-containing catalysts appear to be more active for hydrogenating the benzenoid ring (k_1 and k_3); whereas the Mo-containing catalysts appear to be more active in hydrogenating the heteroaromatic ring (k_2). The pseudo first-order rate constants for the cracking steps (k_4 and k_6) are more dependent on the source of the alumina (catalyst) than on the metals present as demonstrated better by other studies not reported here.

TABLE I
HYDRODENITROGENATION OF QUINOLINE OVER DIFFERENT CATALYSTS

Rate constant, min ⁻¹	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)	Co-Mo/Al ₂ O ₃ (Cyanamid HDS-16A)	Ni-W/Al ₂ O ₃ (Nalco NT-550)
k_1	3.10	1.49	2.17
k_2	1.11	1.51	0.52
k_3	0.63	0.26	0.33
k_4	0.077	0.067	0.073
k_5	0.61	1.51	0.36
k_6	2.54	3.56	1.11
$k_{\text{Total N-removal}}$	0.30	0.20	0.19

Operating conditions: Catalysts were presulfided, no CS₂ added to the system, T = 342°C, P = 34 atm.

Presulfiding has a marked effect on the total nitrogen removal rate (Table II); the rate constant for total nitrogen removal almost doubles. However there seems to be little or no gain in going from the oxidic form to the sulfided form of the catalyst in steps that involve carbon-nitrogen bond breaking. The rates for these steps remain basically the same, as can be seen upon comparing k_5 and k_6 for the oxidic and sulfided catalyst in Table II. Presulfiding has a marked influence on the rate of hydrogenation of the benzenoid and heteroaromatic ring (k_1 , k_2 and k_3). However, there seems to be a preference for hydrogenation of the benzenoid ring over the heteroaromatic ring in quinoline; there is a 4-fold increase in the value of k_1 and k_3 as compared to only a 1.5-fold increase in k_2 . The reaction path involving *o*-propylaniline is of negligible importance for the oxidic form.

TABLE II
EFFECT OF PRESULFIDING ON THE HYDRODENITROGENATION OF QUINOLINE

Rate constant, min ⁻¹	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)	
	oxidic	presulfided
k_1	0.72	3.10 (4.3X)
k_2	0.75	1.11 (1.5X)
k_3	0.18	0.63 (3.5X)
k_4	0.0023 ^a	0.077
k_5	0.75	0.61
k_6	2.2	2.54
$k_{\text{Total N-removal}}$	0.17	0.3

Operating conditions: catalyst presulfided at 325°C for 2 hr in 10% H₂S/H₂, no CS₂ added, T = 342°C, P = 34 atm.

^aThis value was so small for the oxidic form that its value is uncertain.

The effect of CS₂ (H₂S) on the reaction system is shown in Table III. H₂S increases the rate of total nitrogen removal. The presence of H₂S enhances the carbon nitrogen bond breaking rates (i.e., k_6 and particularly k_4). However, k_5 is negatively affected since the transformation of *o*-propylaniline to a hydrocarbon and ammonia involves first a hydrogenation

step (10, 11); k_5 is a compound pseudo first-order rate constant. Little advantage of having H_2S present is seen in the hydrogenation rates (k_1 , k_2 and k_3). For the Co-Mo/ Al_2O_3 catalyst there is no enhancement of the hydrogenation of the heteroaromatic ring, but the benzenoid ring hydrogenation capacity is slightly enhanced. For the Ni-Mo/ Al_2O_3 and Ni-W/ Al_2O_3 catalysts the converse is true; they experience a decrease in their benzenoid ring hydrogenation activity and an increase in their heteroaromatic ring hydrogenation activity with gas-phase H_2S .

TABLE III

EFFECT OF H_2S ON THE HYDRODENITROGENATION OF QUINOLINE

Rate constant, min ⁻¹	Ni-Mo/ Al_2O_3 (Cyanamid HDS-9A)		Co-Mo/ Al_2O_3 (Cyanamid HDS-16A)		Ni-W/ Al_2O_3 (Nalco NT-550)	
	A	B	A	B	A	B
	k_1	3.10	3.09	1.49	1.51	2.17
k_2	1.11	1.57	1.51	1.51	0.52	1.24
k_3	0.63	0.32	0.26	0.24	0.33	0.21
k_4	0.077	0.13	0.067	0.18	0.073	0.15
k_5	0.61	0.13	1.51	0.78	0.36	0.38
k_6	2.54	3.89	3.56	3.64	1.11	2.94
$k_{total N_2 removal}$	0.30	0.57	0.20	0.41	0.19	0.60

Operating conditions: All catalysts were presulfided at 325°C in 10% H_2S/H_2 for 2 hrs, T = 342°C, P = 34 atm.

A: without CS_2 ; B: with 0.05 wt % of CS_2 in white oil to give gas phase H_2S .

The differences between Co-Mo/ Al_2O_3 and Ni-Mo/ Al_2O_3 increase with severity of operating conditions as shown in Table IV. Under the more severe operating conditions Ni-Mo/ Al_2O_3 is superior by a factor of about 2 for total nitrogen removal rate. The hydrogenation rates (k_1 , k_2 , k_3 and k_5) are all significantly higher over the Ni-Mo/ Al_2O_3 than over Co-Mo/ Al_2O_3 . The behavior for nitrogen-carbon bond rupture is consistent with the relative behavior observed for the less severe conditions.

TABLE IV

CATALYTIC HYDRODENITROGENATION OF QUINOLINE AT MORE SEVERE CONDITIONS

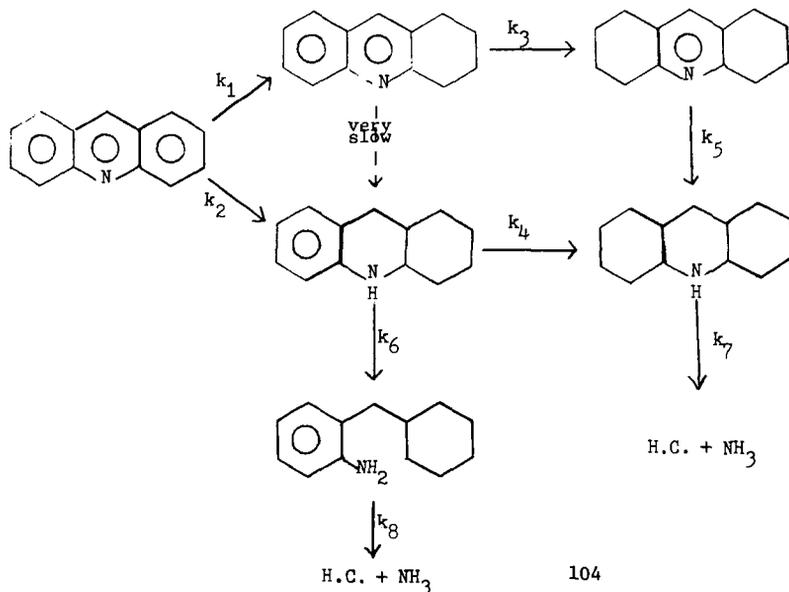
Rate constant, min^{-1}	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)		Co-Mo/Al ₂ O ₃ (Cyanamid HDS-16A)	
	mild*	severe**	mild*	severe**
k_1	3.09	4.95	1.51	0.69
k_2	1.57	10.55	1.51	2.95
k_3	0.32	4.67	0.24	2.28
k_4	0.13	0.50	0.18	0.51
k_5	0.13	3.40	0.78	1.91
k_6	3.89	10.58	3.64	3.45
$k_{\text{total N-removal}}$	0.57	2.42	0.41	1.22

All catalysts presulfided at 325°C in 10% H₂S/H₂ for 2 hrs, 0.05 wt % CS₂ was added to all runs.

*mild operating conditions: temp., 342°C; total pressure, 34 atm.

**severe operating conditions: temp, 367°C; total pressure, 136 atm.

For acridine the hydrodenitrogenation reaction involves the following reaction network (12):



The effect of different catalysts on the hydrodenitrogenation of acridine is shown in Table V. Hydrogenation rates (k_1 , k_2 , k_3 , k_4 and k_5) are typically more rapid over the Ni-Mo/Al₂O₃ and Ni-W/Al₂O₃ catalysts than over the Co-Mo/Al₂O₃; the Ni-Mo/Al₂O₃ catalysts has a slight advantage over Ni-W/Al₂O₃. The Ni-Mo/Al₂O₃ catalyst shows distinctly higher activity for the carbon-nitrogen bond rupture steps and thus is overall the superior of the catalysts used in these studies.

TABLE V
EFFECT OF CATALYST TYPE ON THE HYDRODENITROGENATION OF ACRIDINE

Rate constant, min ⁻¹	Ni-Mo/Al ₂ O ₃ (Cyanamid HDS-9A)	Co-Mo/Al ₂ O ₃ (Cyanamid HDS-16A)	Ni-W/Al ₂ O ₃ (Nalco NT-550)
k_1	5.0	3.1	7.7
k_2	36.2	19.0	43.0
k_3	7.2	3.67	4.0
k_5	0.38	0.015	0.15
k_4	8.8	2.91	3.77
k_6	1.14	0.43	0.41
k_8	2.20	0.79	0.77
k_7	2.19	0.73	0.76
$k_{\text{total N-removal}}$	1.25	0.48	0.54

Operating conditions: T = 367°C; P = 136 atm; All catalysts presulfided at 425°C for 2 hr in 10% H₂S in H₂; 0.05 wt % of CS₂ in white oil was used in all runs.

Because of the complexity of the hydrodenitrogenation reaction network, involving hydrogenation and carbon-nitrogen bond rupture as distinct reaction steps, the evaluation and further development of hydrodenitrogenation catalysts can be greatly aided by knowledge of the rate of the various intermediate reaction steps in the reaction network. This work shows that Ni-Mo/Al₂O₃ is typically better for hydrodenitrogenation because it has higher hydrogenation activity than Co-Mo/Al₂O₃; Ni-W/Al₂O₃ appears to be slightly less active than Ni-Mo/Al₂O₃. The cracking activities appear to be more dependent on the source of the support and are also very important in determining the relative ranking of overall catalyst behavior. This aspect of catalyst behavior was not sufficiently investigated in this work to allow for firm conclusions.

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