CHEMISTRY LETTERS, pp. 909-912, 1985.

EFFICIENCY OF TWO-STAGE HYDRODENITROGENATION OF AROMATIC NITROGEN COMPOUNDS

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A high hydrodenitrogenation (86%) of acridine on a Ni-Mo/Al_2O_3 catalyst was achieved by successive reactions at 370 °C for 2 h and 420 °C for 3 h, respectively, while the single stage reaction at 420 °C for 5 h removed only 67% nitrogen. The effective hydrodenitrogenation is postulated due to the extensive hydrogenation in the first stage and C-N bond fission in the second stage.

Selective denitrogenation of coal liquid to refined oil is an urgent task in the practice of coal liquefaction since nitrogen in coal liquid is a potential source of NOx.1)

The catalytic hydrodenitrogenation reaction has been extensively investigated in the petroleum refinery using nickel-molybdenum catalyst.2) Nevertheless, the denitrogenation of coal liquid is never practical, because of low reactivity, severe catalyst deactivation3) by the coking, large consumption of hydrogen for deep denitrogenation, and excess hydrocracking at higher temperatures among other problems.

In the present letter, the authors report an enhanced efficiency of a two stage hydrodenitrogenation at different reaction temperatures using acridine and carbazole as moldel compounds and a commercial nickel-molybdenum catalyst. Extensive hydrogenation of the rings occurs at the lower reaction temperature4) of the first stage and selective fission of the C-N bond at the higher temperature of the second stage. Optimum conditions for these consecutive reactions are best achieved by use of two stages independently controlled.

Acridine(1), carbazole(2), and 1-methylnaphthalene using in the present study are commercially available reagents (GR grade). They were used without further purification. A commercial catalyst HDN-30 which has obtaind reputation for high catalytic activity for the hydrodenitrogenation was supplied by courtesy of American Cyanamid Co. The catalyst was presulfided in a 5 vol% H_2S/H_2 atmosphere for 6 h at 360 °C before the catalytic reaction.

A mixture of nitrogen compound(2 g), 1-methylnaphthalene (8 g) (N: 1.6 - 1.7 wt%), and the catalyst (0.5 g) was charged to an autoclave of 200 ml capacity. After complete replacement of air with hydrogen flow, the hydrogen pressure was raised to a level, which could give the maximum pressure (ca. 250 atm) allowed at the reaction temperature. The reaction was carried out under stirring at 350 °C or 370 °C in the first stage. After cooling and displacing the atmosphere in the autoclave with fresh hydrogen, the second stage reaction was performed at 420 °C, 210 atm. The heating rates were ca. 5 °C/min both in the first and second stages.

Denitrogenation of acridine(1) is summarized in Table 1. Only 51% of nitrogen in acridine was removed by the reaction at 420 °C for 3 h (Run 1). The longer time of 5 h at 420 °C allowed 67% denitrogenation (Run 2). The reaction at 350 °C removed only 25% of its nitrogen after 8 h. The successive hydrodenitrogenation removed 69% of its nitrogen to achieve as high as 94% removal altogether (Run 3). A higher temperature of first stage of 370 °C removed only 12% by the reaction of 2 h, however 61% of overall removal was provided by the second stage of 1 h (Run 4). Further increase of reaction time of the second stage (3 h) allowed 86% of overall denitrogenation which is much higher than that achieved in the single reaction at 420 °C for 5 h (Run 5). Thus, the two stage hydrodenitrogenation is very effective to remove nitrogen from acridine.

Table 1. Two-stage Hydrodenitrogenation Reaction of Acridine (1)

Run No.	Temp °C	H_2ini. press. kg cm^{-2}	Time h	N-removal %
1	420	100	3	51
2	420	100	5	67
3	350	140	8	25
	420	100	3	94$^{a)}$
4	370	140	2	12
	420	100	1	61$^{a)}$
5	370	140	2	12
	420	100	3	86$^{a)}$

a) Total nitrogen removal.

Table 2. Two-stage Hydrodenitrogenation Reaction of Carbazole (2)

Run No.	Temp °C	H_2ini.press. kg cm^{-2}	Time h	N-removal %
1	420	100	3	90
2	350	140	8	49
	420	100	3	100$^{a)}$
3	350	140	4	28
	420	100	1	95$^{a)}$
4	370	140	2	34
	420	100	1	97$^{a)}$

a) Total nitrogen removal.

Denitrogenation of carbazole(2) is summarized in Table 2. Carbazole was readily hydrodenitrogenated by the two stage, the successive reactions at 350 °C for 8 h and 420 °C for 3 h allowed 100% (overall) of denitrogenation, while a single stage reaction at 420 °C allowed 90% removal for 3 h. Much shorter reaction times(for the first stage of 4 h and for the second stage of 1 h) still allowed 95% of overall denitrogenation. Carbazole was more reactive for hydrodenitrogenation than acridine under the same conditions, a higher denitrogenation level being achieved by the shorter reaction time.

The analyses of reaction products from acridine are summarized in Table 3.

Table 3. Analyses of Single- and Two-stage Hydrodenitrogenation Products of Acridine (1)

	Products yield/%$^{a)}$			
Conditions	3	4	5	others
Single-stage HDN (420 °C, 3 h)	49	23	25	3$^{b)}$
Two-stage HDN				
1st-stage (350 °C, 8 h)	23	70	5	2$^{c)}$
2nd-stage (420 °C, 3 h)	93	0	0	7$^{b)}$

a) Quantitative analysis by GC-FID
GC conditions; Column: SE-30 (2m),
Column Temp: 100 → 270 °C (10 °C/min).

b) Non-indentified cracked products.

c) Incompletely hydrogenated products other than 5.
(Ex.:cis, trans-1,2,3,4,4a,9,9a,10-octahydroacridine)

Dicyclohexylmethane(3), perhydroacridine(4), and 1,2,3,4,5,6,7,8,-octahydroacridine(5) were formed at the ratio of 2:1:1 in the single-stage hydrodenitrogenation at 420 °C for 3 h. In a marked contrast, the product of first-stage reaction at 350 °C for 8 h was almost exclusively perhydroacridine(4) with very minor amount of the incompletely hydrogenated acridine(5). All products of the first stage were completely denitrogenated in the successive reaction at 420 °C for 3 h.

Hydrodenitrogenation mechanism of acridine has been reported by Shih et al.[5)] to proceed through its hydrogenated forms as shown in Fig.1 (single-stage).

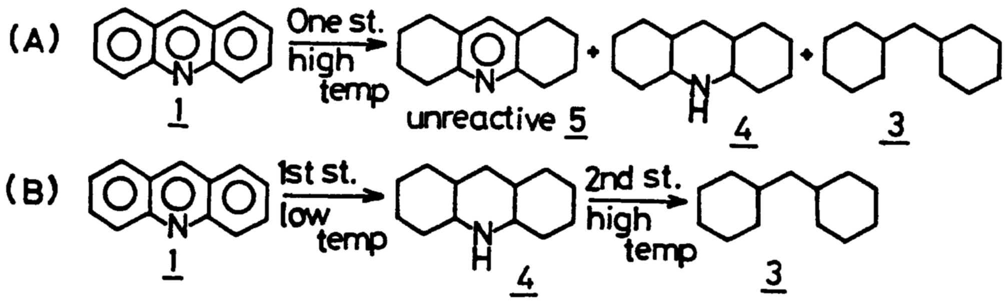

Fig.1. Single-(A) and Two-stage(B) Hydrodenitrogenation Schemes of Acridine.

According to this scheme, perhydroacridine (4) is easily denitrogenated, whereas an incompletely hydrogenated product(5) is very unreactive. The single stage denitrogenation under the present conditions left a considerable amount of the incompletely hydrogenated one(5). The reason for the insufficient hydrogenation is that the higher temperature is not favorable for the complete hydrogenation. The remaining product (5) may retard the denitrogenation of 4 because of its strong adsorption on the catalyst. Hence, the extensive hydrogenation at the first stage at a low reaction temperature and the selective fission of hydrogenated C-N bond at the second stage at a high temperature can be designed to achieve the effective denitrogenation of condensed aromatic nitrogen compounds. Such a scheme can be illustrated in Fig.1 (first and second stages). In fact, perhydroacridine(4) was the major product at the first stage of a lower temperature. The second stage reaction at a higher temperature effectively denitrogenates perhydroacridine(4) to achieve a better removal as expected.

The structural analyses of polycondensed aromatic hydrocarbons in a hydrotreated heavy coal liquid suggested that insufficient hydrogenation of the aromatic rings including the heterocyclic part under single-stage reaction conditions was a major reason for its low denitrogenation.6) Thus, the present two-stage denitrogenation is applicable to the heavy distillate of a coal liquid. Preliminary investigation revealed that the two stage process (380 °C, 3 h and 420 °C, 3 h) allowed 80% removal of nitrogen from the heavy distillate (b p : 350 - 500 °C Wandoan Coal liquid) using fluoranthene as a component of solvent, while the single stage process (420 °C,3 h) gave only 34%. Further details as for the coal liquid including application of much lower pressure will be reported.

The authors are grateful to Ministries of Education and International Trade and Industry for their financial supports. They are also grateful to NEDO and Sumitomo Metal Industries, Ltd. for their providing a coal liquid.

References

1) C.C. Kang, Prep.Div.Petrol.Chem., Am.Chem.Soc., 23, 277 (1978).
2) A.H. Steven and F.T. Lila, Fuel, 62, 709 (1983).
3) M.M. Ahmed and B.L. Crynes, Prep.Div.Petrol.Chem., Am.Chem.Soc., 22, 971 (1977).
4) M. Nagai, K. Sawahiraki, and T. Kabe, Nippon Kagaku Kaishi, 1979, 1350.
5) S. Shih, E. Reiff, R. Zawadzki, and J.R. Katzer, Prep. Div.Fuel Chem., Am.Chem. Soc., 23(1), 99 (1978).
6) I. Mochida, K. Sakanishi, Y. Korai, and H. Fujitsu, Nenryo Kyokai Shi, 64, 184 (1985).

(Received March 27, 1985)