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Hydrodenitrogenation Chemistry, 1: Cleavage of Alkylcarbon-Nitrogen Bonds, Methane and Ammonia Formation in the HDN Reaction of 1,2,3,4-Tetrahydroquinoline with a Nickel Oxide Catalyst Supported on Silica/Alumina

The hydrodenitrogenation reaction (HDN) is one of the most important industrial processes used in the refining of petroleum feedstocks and involves the removal of the nitrogen atom, as ammonia, from polynuclear heteroaromatic nitrogen compounds at high temperatures and high pressures of hydrogen gas (350–500°C and 2000 psi) (*1*a–g). It is interesting to note that most of the reported heterogeneous catalysts require the complete hydrogenation of both the nitrogen heterocyclic ring and the aromatic ring (e.g., quinoline to decahydroquinoline) before carbon–nitrogen bond cleavage can occur (*1*g). This is partly due to the thermodynamics of the aliphatic C—N bond hydrogenolysis reaction, which is more exothermic by 5 kcal/mol than the corresponding aliphatic C—C bond hydrogenolysis reaction. In contrast, the C—N multiple bond cleavage is less favorable thermodynamically than C—C multiple bond cleavage. Obviously, another factor is the thermodynamics of aromatic ring hydrogenation, which is more favorable at the higher hydrogen pressures needed to remove nitrogen from polynuclear heteroaromatic nitrogen compounds at rates necessary for the industrial HDN process.

More importantly, we have recently shown that both homogeneous and polymer-supported transition metal catalysts can regioselectively reduce the nitrogen heterocyclic ring in model coal compounds (2a–e), providing the first step in the overall HDN reaction of polynuclear heteroaromatic nitrogen compounds. Thus, a major breakthrough in the technical and economic aspects of the HDN reaction would take place if, in fact, a catalyst could be found that would selectively cleave the C—N bond in the saturated nitrogen ring and subsequently produce ammonia, without substantial reduction of the aromatic rings, at lower temperatures as well as lower pressures of hydrogen gas.

In this note, we wish to report on a highly loaded nickel oxide catalyst (50% by weight Ni), supported on silica/alumina, that will effectively provide some of the criteria we have stated above for an ideal HDN catalyst. The use of a highly loaded metal catalyst for C—N bond cleavage, with a wide variety of nitrogen compounds, was recently demonstrated by Guttieri and Maier (*3*). In that study, a 40% platinum on silica catalyst was used with polynuclear heteroaromatic nitrogen compounds among others (e.g., quinoline, THQ); however, propylcyclohexane was the major product, i.e., aromatic ring hydrogenation again appears to precede C—N bond cleavage.

RESULTS AND DISCUSSION

Table 1 clearly demonstrates that the nickel oxide catalyst supported on silica/alumina can cleave C—N bonds, form ammonia and methane (GC analysis), while minimizing aromatic ring hydrogenation, using 1,2,3,4-tetrahydroquinoline (THQ) as the substrate, in a flow reactor at 250°C and 1 atm of H_2 gas. Pertinently, no decahydroquinoline, propylcyclohexane or other cyclohexyl derivatives were detected via capillary column gas chromatography–mass spectrometry analysis (GC–MS),

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TABLE 1

HDN Chemistry of 1,2,3,4-Tetrahydroquinoline, 2-Propylaniline, and Propylbenzene with the 50% Nickel Oxide Catalyst[a,b]

Substrate: products (mmol%)	1,2,3,4-Tetrahydroquinoline	2-Propylaniline	Propylbenzene
Benzene	4.9	15.9	Trace
Toluene	0.9	2.1	—
Ethylbenzene	0.4	0.4	—
Propylbenzene	Trace	14.4	—
Aniline	4.6	2.6	—
2-Methylaniline	8.5	5.3	—
2-Ethylaniline	5.8	1.8	—
2-Propylaniline	1.5	30.6	—
Quinoline	21	—	—
5,6,7,8-Tetrahydroquinoline	11	—	—
1,2,3,4-Tetrahydroquinoline	7.3	0.4	—
Indole	1.2	—	—
2-Methylindole	3.6	0.4	—
Unidentified products[c]	7.6	18.0	—
Methane[d]	21.7	8.1	100

[a] Quantitation and identification of the products were accomplished by capillary column gas chromatography with an internal standard and by GC–EIMS. The percentages shown are based on the millimoles of substrate converted to products.

[b] Reaction conditions are 250°C, 30 ml/min hydrogen gas flow at 1 atm. The amount of 1,2,3,4-tetrahydroquinoline used was 3.3 mmol, 2-propylaniline 2.84 mmol, and propylbenzene 2.84 mmol. The reaction time was 3 h using a substrate flow rate of 0.14 ml/h and 0.26 g of catalyst.

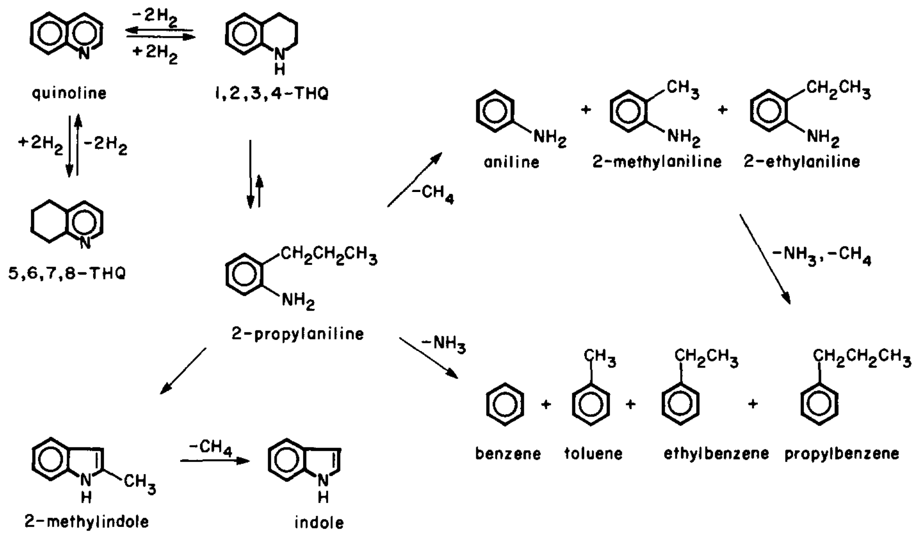
[c] While total identification of these products was not established (GC–EIMS), we did identify several substituted pyridine derivatives such as 2,3-dimethylpyridine.

[d] This is the mmol% of substrate that was not accounted for in the liquid products and is considered to be methane gas (identified via GC analysis). The ammonia gas that was formed was separated (H_2O collection) from methane and was not quantified.

even when we increased the flow rate, i.e., decreased the contact time, in our reactor. The products (Table 1) constitute 78% of the conversion (93%) of THQ, while methane, the only carbon containing gas detected, presumably formed via hydrogenolysis of the products, represented the remaining 22% conversion. A significant amount of a dehydrogenated product, quinoline (21%), was formed along with a smaller amount of the only aromatic ring hydrogenated product detected, 5,6,7,8-tetrahydroquinoline (11%). The small amounts of indole derivatives probably occur via free radical intermediates from the initial C—N bond cleavage of THQ.

We then directed our attention to the reactivity of the first logical C—N bond cleavage product of THQ, 2-propylaniline (OPA), with the nickel oxide catalyst. Table 1 compares the reactivity of THQ to OPA and strongly indicates that after C—N bond cleavage in THQ, loss of ammonia and hydrogenolysis of the propyl side chain predominates, not aromatic ring hydrogenation. It is conceivable that the presence of the nitrogen atom causes an inhibition of catalyzed aromatic ring hydrogenation and to some extent C—C bond hydrogenolysis, and this can be seen comparatively in Table 1 with the reactivity of propylbenzene (PB), in which methane (hydrogenolysis) is the major product with only traces of benzene detected via GC analysis. Additionally, aromatic ring hydrogenation would not be favorable, thermodynamically, under our relatively mild reaction conditions.

In another experiment, we studied the



SCHEME 1. Proposed reaction network for HDN chemistry using the 50% nickel oxide catalyst supported on silica/alumina.

HDN chemistry of quinoline and found decreased amounts of products, (60%), with a higher conversion to methane (40%), as compared to the THQ results. This result clearly demonstrates that prior selective hydrogenation to THQ would enhance the overall HDN reaction to provide a more substantial conversion to substituted benzene and aniline derivatives.

X-Ray photoelectron spectroscopic (XPS) studies, of both the catalyst before use and the pretreated catalyst (H_2, 350°C, 6 h) that had produced the HDN reaction, showed the expected silicon and nickel photoemission lines, along with those of aluminum.[1] The nickel $2p_{3/2}$ binding energies for both the reacted and unreacted catalysts were essentially identical (865.5 and 865.6 eV, respectively, charge referenced to the carbon $1s = 285.0$ eV photoelectron line), but the "shake-up" satellite positions (*4*) with respect to the main line were different (862.7 and 861.7 eV, respectively), thus showing some difference in the surfaces.

The nickel $2p_{3/2}$ binding energies of 865.5 and 865.6 eV were a full 2.5 eV higher than the 854.0-eV binding energy observed for a high-purity NiO (99.99%) standard used in this study and the values reported by other workers (*5–7*). The lineshapes of the nickel $2p_{3/2}$ lines were different from those reported for NiO. Rather, the binding energy data were more consistent with a ternary nickel oxide or a higher valent nickel system. Indeed, the binding energy and satellite data for the catalyst samples are extremely close to those reported for $NiAl_2O_4$ and Ni_2O_3 (*8*). These XPS studies clearly show that nickel (2+) or higher valent nickel oxide surface species are responsible for the HDN chemistry observed and not nickel(0). A transmission electron micrograph (TEM) of this catalyst showed nickel, alumina and silica particle distributions and electron diffraction (ED) patterns revealed three nickel phases, which were tentatively

[1] A Physical Electronics Model 555 X-ray photoelectron spectrometer equipped with a Mg$K\alpha$ (1253.6 eV) anode source was used for obtaining all XPS spectra on the 50% nickel oxide catalyst. All catalysts samples were studied as fine powders mounted on polymer film-based adhesive tape with a metallic backing. The nickel oxide (50% Ni) catalyst supported on silica (26%) with 10% alumina was a commercial product |C46-7-03| of United Catalyst, Inc. Louisville, Ky. The surface area was 250–350 m²/g (40–325 mesh) for the unused catalyst.

identified by X-ray diffraction (XRD) as a nickel oxide and a nickel aluminate on the surface surrounding Ni(0) in the center of the 100-Å particles.

CONCLUSIONS

The conclusions we deem important in these HDN experiments with the 50% nickel oxide catalyst are that alkyl C—N bond cleavage of THQ can occur, to ultimately give, by loss of methane and ammonia, aniline and benzene products. However, the dehydrogenation of THQ to form quinoline appears to compete kinetically with the C—N bond cleavage reaction, while aromatic ring hydrogenation and C—C bond hydrogenolysis appear to be suppressed by the presence of the nitrogen atom (Scheme 1 incorporates all the important pathways mentioned above).

Further studies will be directed toward rates of product formation, optimizing product yields and learning more about the active catalytic sites for C—N bond cleavage with known nickel oxides, silicates, and aluminates as well as determining the effect of sulfur on the hydrogenation–dehydrogenation and hydrogenolysis components of the HDN reaction.

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