Hetero-Polyaromatic Ring Opening Reactions in scCO$_2$

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ABSTRACT

This paper describes work directed towards hydrogenolysis of hetero-polyaromatic hydrocarbons (HPH) using an environmentally benign solvent; viz. supercritical carbon dioxide (scCO$_2$). Reactions were carried out on model substrates using a variety of commercially available or synthesized heterogeneous catalysts. Substrates investigated include quinoline, indole, benzothiophene and 2-(2-pyridyl) benzothiophene. Optimization of H$_2$:CO$_2$ ratios resulted in high levels of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), and to fully or partially hydrogenated products.

INTRODUCTION

A challenging area in the petrochemical and energy industries involves the hydrogenation and hydrogenolysis of HPH, particularly those with N- and S- functionalities which can be utilised in a variety of chemical processes.[1-3] The largest deposit of oil sand in the world is located predominantly along the Athabasca river in Alberta, Canada; this deposit contains an estimated 1.7 trillion barrels of oil. Around 25% of the world's coal reserves are located in the United States, coal will continue to be the workhorse of the nation's electric power industry, supplying more than half of the electricity consumed by the US.[4] The hydrotreatment of HPHs is not trivial, and generally requires forcing reaction temperatures (300+ °C) and high H$_2$ pressures (>10 MPa) to obtain low levels of conversion to fully hydrogenated materials.[5] Conventional HDS/HDN reactions are performed at higher temperatures (350+ °C), and utilize the toxic sulfiding agent H$_2$S.[6] HDS and HDN reactions of these types of molecules are of great importance to the petroleum industry, and have been the subject of many studies over the last two decades.[7] The beneficial combination of Canadian oil sands and American coal deposits provides an essential component to North American energy self sufficiency and security. Successful upgrading of bitumen into synthetic crude oil and the clean conversion of coal to liquid fuel sources (methanol, ammonia and diesel), will offer North America capabilities to be self–sufficient in energy without unacceptably polluting the environment. To achieve energy sustainability that satisfies current and impending environmental regulations of sulfur and nitrogen levels in transportation fuel, a clean conversion technology and methodology is fundamental. The main objective of this project is to explore the utility of scCO$_2$ for upgrading and hydrotreatment of oil sand and coal. Sc CO$_2$ has the potential to play several roles in bitumen upgrading and the advancement of clean coal technologies; these include bitumen extraction and the drying of coal using

$scCO_2$, as well as its use as a reaction medium for catalytic hydrogenolysis and hydrogenation.[8] Here we report preliminary studies of the hydrogenation and ring-opening of quinoline, indole, benzothiophene and 2-(2-pyridyl)benzothiophene in conventional solvents and in $scCO_2$ under remarkably mild conditions.

MATERIALS AND METHODS

Typical experimental procedure: A 20 mL high-pressure vessel was charged with substrate (0.84 mmol) and catalyst (50 mg), and equipped with a magnetic stirrer bar. The vessel was attached to a high-pressure manifold and heated to the desired temperature. Hydrogen (7.2-18.9 MPa) was added to the vessel, followed by CO_2 (8.6 MPa -10.3 MPa) *via* syringe pump. the vessel was sealed and the reaction was stirred for the desired period, after which the vessel was allowed to cool to room temperature. The gases were vented through a conc. NaOH trap and the catalyst was separated *via* simple filtration. The contents of the vessel were washed with hexane and the resulting solution was filtered to separate the catalyst from the products. The reaction products were identified quantitatively using GC-MS analysis (Agilent 7890A and 5975MSD).

$CoMoS_4/TiO_2$-Al_2O_3 was synthesised *via* a urea matrix combustion method:[9] A mixture of $Co(NO_3)_2.6H_2O$ (0.34 mmol), $(NH_4)_2MoS_4$ (1.65 mmol), urea (19.94 mmol), and distilled water (7.5 mL) was stirred at room temperature to form a homogeneous slurry. Once homogeneity was achieved, a ball-milled mixture of 95wt% TiO_2 (47.63 mmol) and 5wt% γ-Al_2O_3 (1.48 mmol) was added and the mixture was heated to 50 ^{o}C for 3 h. This paste was ignited at 500 ^{o}C (Lindberg Hevi-Duty furnace temperature) in static air for 10 min, to produce blue-tinted black powder.

The synthesis of $NiMoW/Al_2O_3$ was carried out by a wetness co-impregnation method:[6] A mixture of $NiNO_3.6H_2O$ (0.89 mmol), γ-Al_2O_3 (50.15 mmol), and distilled water (7.5 mL) was stirred for 16 h at room temperature in a round-bottom flask. Another mixture that contained $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (1.00 mmol), $(NH_4)_{10}H_2(W_2O_7)_6$ (0.25 mmol), and methanol (7.5 ml) was stirred for 16 h at room temperature. The two mixtures were combined and calcined at 500 ^{o}C (Lindberg Hevi-Duty furnace temperature) in static air for 8 h, yielding a fine black powder.

RESULTS

Vaccari *et al.* demonstrated that quinoline could be partially hydrogenated to 1,2,3,4-tetrahydroquinoline (py-THQ) in *iso*-propanol in the presence of Rh/Al_2O_3 and H_2 (2.0 MPa).[10] In order to obtain full conversion to DHQ, another aliquot of catalyst was added once the reaction had terminated, as the authors believed that the intermediate was poisoning the catalyst. We repeated this reaction, but without addition of the second aliquot of catalyst. Higher H_2 pressures were also investigated (Scheme 1). Quinoline (1.16 mmol) was hydrogenated in *iso*-propanol (15 mL) with Rh/Al_2O_3 or Rh/C (50 mg). The reactions were carried out at 100 °C, and the results are shown in Table 1.

Scheme 1

| Quinoline | X = C or Al$_2$O$_3$ | py-THQ | DHQ |
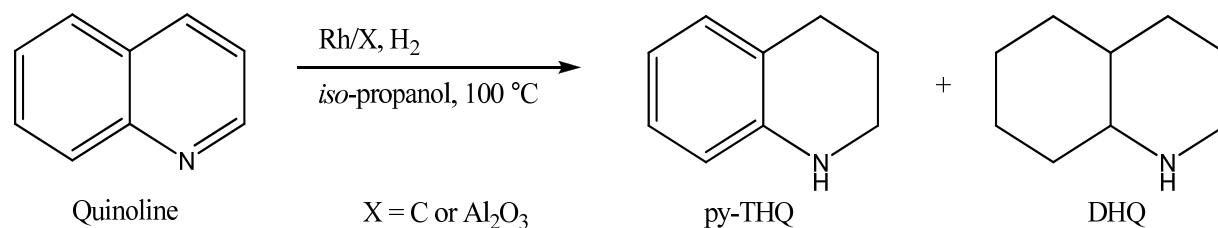
The results demonstrated that DHQ can be obtained with high conversions within only two hours using higher H$_2$ pressures (10.8 MPa); this is a significant improvement in comparison to the current literature precedent. Reactions carried out in scCO$_2$ resulted in only the partially hydrogenated product being formed (Table 2). High conversions were obtained in scCO$_2$, however only very small amounts of DHQ were observed.

Table 1

Entry	Catalyst	Reaction Time (hours)	H$_2$ Pressure (MPa)	Conversion[a] (%)	Py-THQ[a] (%)	DHQ[a] (%)
1	Rh/Al$_2$O$_3$	2	10.8	100	25.2	74.8
2	Rh/Al$_2$O$_3$	16	7.5	100	5.4	94.6
3	Rh/C	4	9.0	100	17.7	81.3
4	Rh/C	16	9.0	100	4.8	95.2
5	Rh/C	18	8.0	100	4.8	95.2

a = determined by GC-MS

Table 2 (All in CO$_2$ at 8.6 MPa)

Entry	Catalyst	Reaction Temp (°C)	Reaction Time (hours)	H$_2$ Pressure (MPa)	Conversion[a] (%)	Py-THQ[a] (%)	Propyl-cyclo-hexane[a] (%)	DHQ[a] (%)
1	Pd/C	200	16	8.8	97.9	97.9	0	0
2	Rh/Al$_2$O$_3$	100	36	7.6	96.9	96.3	0	3.6
3	Ru/C	100	16	8.6	87.9	84.2	0	3.7
4	Ru/C	100	24	8.3	67.0	55.1	5.9	6.0
5	Rh/C	100	20	8.0	98.0	96.2	0	1.8

a = determined by GC-MS

Model Compounds for HDS and HDN in scCO$_2$

Benzothiophene HDS and indole HDN reactions were performed in scCO$_2$ using various heterogeneous catalysts (Scheme 2). The results in scCO$_2$ are shown in Table 3; reactions were also carried out in hexane for comparison (Table 4). For benzothiophene, HDS products were predominant using Pd/Al$_2$O$_3$, whereas the hydrogenation pathway was observed when using Rh/Al$_2$O$_3$. The major product was the partially hydrogenated HPH. Indole HDN proved to be more difficult to achieve using commercial and in-house-synthesized catalysts, but encouraging results were obtained at lower hydrogen pressures. Reactions were performed over the temperature range of 100-225 $^{\circ}$C, with the optimal HDN temperature being 200 $^{\circ}$C. The fully hydrogenated product (**4**) was observed in scCO$_2$ only with the commercial catalysts; however no such product was observed when using hexane as the reaction medium.
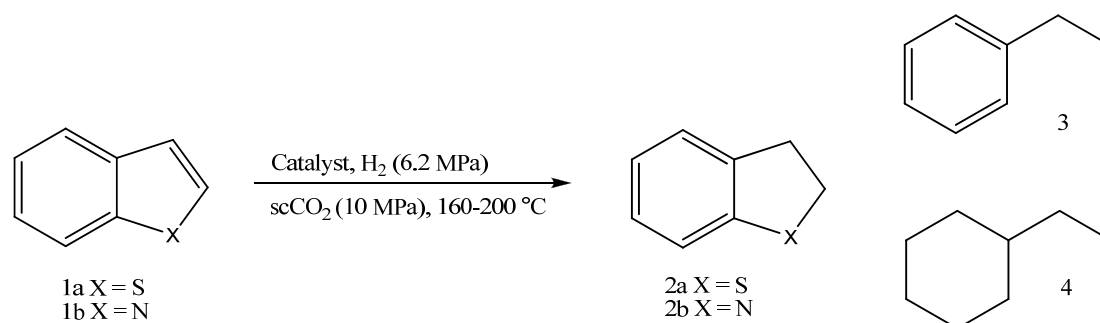
Scheme 2

1a X = S
1b X = N

2a X = S
2b X = N

3

4

Table 3 (All in CO$_2$ 8.6 MPa)

Entry	Reaction temperature ($^{\circ}$C)	Reaction time (hours)	Substrate	H$_2$ Pressure (MPa)	Conversion[a] (%)	Partial hydrogenation[a] **2** (%)	Ethyl benzene[a] **3** (%)	Ethyl cyclohexane[a] **4** (%)
1	160	16	Benzothiophene[b]	10.3	49.7	49.7	0	0
2	180	18	Benzothiophene[b]	10.3	85.8	85.8	0	0
3	180	18	Benzothiophene[b]	18.9	74.1	66.8	7.3	0
4	180	20	Benzothiophene[c]	15.5	94.5	14.8	79.8	0
5	200	20	Indole[d]	7.2	39.8	0	25.6	14.1
6	200	20	Indole[e]	7.2	35.2	10.0	15.2	8.9
7	200	20	Indole[f]	16.5	38.3	23.2	15.1	0

a = determined by GC-MS, b Rh/Al$_2$O$_3$, c Pd/Al$_2$O$_3$, d Rh/C (dry), e Pd/C, f NiMoW/Al$_2$O$_3$

Table 4 (All in 15ml of hexane)

Entry	Reaction temperature (°C)	Reaction time (hours)	Substrate	H_2 Pressure (MPa)	Conversion[a] (%)	Partial hydrogenation[a] **2** (%)	Ethyl benzene[a] **3** (%)	Ethyl cyclohexane[a] **4** (%)
1	180	24	Benzothiophene[b]	15.5	21.7	19.1	2.6	0
2	180	20	Benzothiophene[b]	15.2	43.2	37.8	5.4	0
3	180	20	Benzothiophene[c]	16.9	54.2	49.6	4.6	0
4	200	18	Indole[d]	7.6	32.2	31.7	0.5	0
5	200	18	Indole[e]	7.6	34.8	34.6	0.2	0

b Pd/Al2O3, c Rh/Al2O3, d Rh/C (wet), e Rh/C (dry)

Combined HDS/HDN in scCO$_2$

Due to the success achieved with other HPHs in scCO$_2$, 2-(2-pyridyl)benzothiophene was chosen as an example of a substrate containing both N and S functionalities (Scheme 3). Combined HDS/HDN experiments using far lower temperatures and $(NH_4)_2S_2O_3$ as the sulfiding agent were performed. These reactions showed high levels of hydro-cracking products, with the major one being ethylcyclohexane (Table 5). Up to 76% ethylcyclohexane was observed; an unprecedentedly high yield. In this case, the synthesised catalyst performed equally as well as the commercial catalyst; $CoMoS_4/TiO_2-Al_2O_3$ (15mg) was presulfurised with $(NH_4)_2S_2O_3$ (50mg/0.34 mmol) by mixing in distilled water (5.0mL) at 90 °C for 2 h. To date we have not attempted photochemically activated HDS/HDN reactions; however we are commencing a study to explore whether mixed TiO$_2$ supported catalysts can act as photo-catalysts.
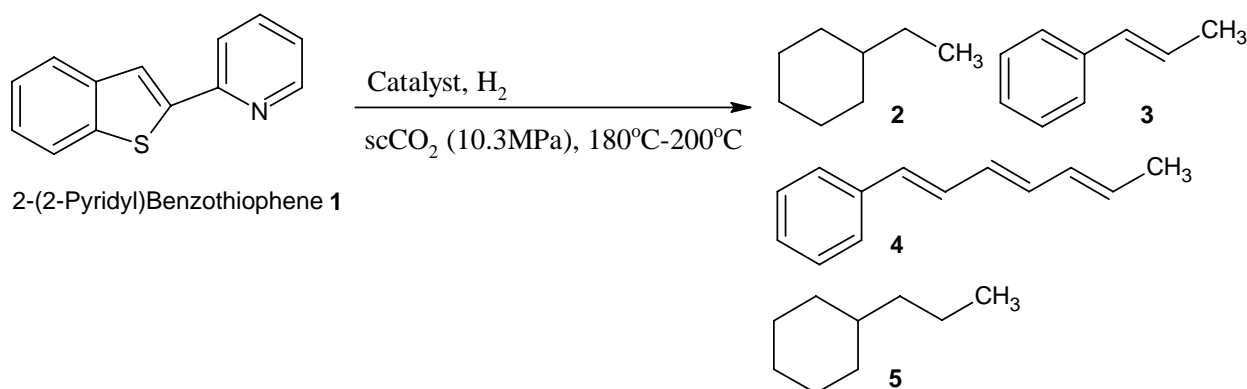
Scheme 3

2-(2-Pyridyl)Benzothiophene **1**

Catalyst, H$_2$

scCO$_2$ (10.3MPa), 180°C-200°C

Table 5

Entry	Reaction temperature (°C)	H_2 Pressure (MPa)	Conversion (%)	Reaction time (hours)	Ethyl cyclohexane[a] 2 (%)	Propenyl benzene[a] 3 (%)	Hept-2,4,6-enyl benzene[a] 4 (%)	Propyl cyclohexane[a] 5 (%)
1[b]	180	13.8	13.7	4	1.5	1.0	7.9	3.3
2[c]	180	9.5	87.8	24	48.5	38.1	1.2	0
3[d]	200	9.5	84.2	20	43.1	27.4	5.5	8.2
4[e]	200	10.5	93.1	16	76.1	16.2	0.8	0

a = determined by GC-MS, b Pd/Al$_2$O$_3$, c CoMoS$_4$/TiO$_2$-Al$_2$O$_3$, d Rh/C, e NiMoW/Al$_2$O$_3$

CONCLUSIONS

1. Superior HDS and HDN conversions were obtained in scCO$_2$ in comparison to conventional solvents (hexane).
2. The ring-opening results of the model systems are remarkable; up to 79.8% observed for HDS and 39.8% for HDN.
3. Combined HDS/HDN reactions are encouraging and have set the foundation for future hydro-treating experiments on real substrates, such as bitumen derived from Athabasca oil sands and lignite from Northwest Louisiana.
4. Future work will focus on more complex compounds for HDS and HDN as well as model compounds for hydrodeoxygenation (HDO) to emulate coals, and hydrodemetallization (HDM)/ hydrodeasphaltenization (HDAs) to simulate bitumen.

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