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EXTRACTION OF COBALT FROM HYDROTREATING CATALYSTS USING SUPERCRITICAL AMMONIA

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ABSTRACT

Experiments were conducted to determine the feasibility of leaching cobalt from a hydrotreating catalyst material using supercritical aqueous ammonia solvents. The effects on cobalt extraction caused by variations in solvent composition, pressure and temperature, including subcritical conditions, were investigated.

Cobalt in the catalyst material was leachable at supercritical and subcritical solvent phase conditions. Cobalt extraction at supercritical phase conditions was generally higher than extraction obtained at any of the other pressure - temperature conditions tested. Leaching enhancement at supercritical conditions was determined not to be solely the result of simple pressure or temperature effects. Rather, leaching enhancement is probably caused by the improved transport properties exhibited by supercritical fluid solvents.

INTRODUCTION

Spent catalysts containing metals of comparatively low value are placed usually in a land fill, without recovering the metals. An example of this is the land filling of spent hydrotreating catalysts used in the petrochemical industry. Other catalysts, containing metals of higher values, are sometimes processed for recovery of these metals. However, these processes often involve undesirable solvents, or are energy intensive. A potential

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alternative method for extracting the residual metals from spent catalysts is the use of supercritical fluid (SCF) solvents. Supercritical fluid extraction processes have been shown to have advantages over conventional extraction processes including lower energy requirements, utilization of less toxic more environmentally acceptable solvents, and the ability to meet process requirements which traditional extraction processes cannot meet (1).

Unique physiochemical properties shown by fluids in the supercritical phase region are what account for the advantages gained by using SCF processes. In the supercritical phase region, fluids have very high, liquid-like densities (1-8), which give rise to correspondingly high capacity for solutes. In addition to the density behavior, SCFs demonstrate gas-like transport properties (1-4, 6-7, 9-11). The viscosity of SCFs is nearly as low as that of gases, and the diffusivity of SCFs is 1-2 orders of magnitude higher than that of liquids. SCFs also have zero surface tension (1). This property makes SCFs an ideal class of solvents for the leaching of solutes from microporous materials. This should allow easy penetration of SCF solvents into a catalyst material. The gas-like transport properties exhibited by SCFs are favorable for solute extraction in terms of mass transfer characterics.

Debenedetti and Reid (10) have studied the transport properties of SCFs. Their results led them to conclude that in systems where the controlling resistance to mass transfer is in the supercritical phase, significant rate enhancement can be expected from using SCFs as solvents.

Until recently, critical phase behavior data on the ammonia-water system (the solvent system used in this study) were very limited. However, in 1985, Rizvi published a thesis (12) which presented a comprehensive phase behavior study of the ammonia - water system. The study included vapor - liquid equilibria over the composition range from pure ammonia to pure water, and over the pressure - temperature range from ambient conditions to the supercritical phase region. Thirty mole percent is the approximate solubility limit of ammonia in water at ambient conditions, making it the practical concentration limit for aqueous ammonia solvents used in the present study. A phase diagram over this concentration range in the supercritical region was reproduced from Rizvi's data, and is shown in Figure 1.

There is no information in the literature on the recovery of cobalt from spent catalyst using ammonia, or any other solvent. The simple cobalt ion is most stable in the bivalent state (13). In most cobalt complexes, including ammines, cobalt is most stable in the bivalent form (13). In an aqueous solution of ammonia, the cobaltic ion readily forms the six-coordinate, octahedral hexamminecobalt (III) ion $(Co[NH_3]_6)^{3+}$ (14).

Laboratory studies on the leaching of cobalt from cobalt metal powder by ammonia solutions have been conducted by Han and Vu (15-19). They reported the overall reaction mechanism at near ambient

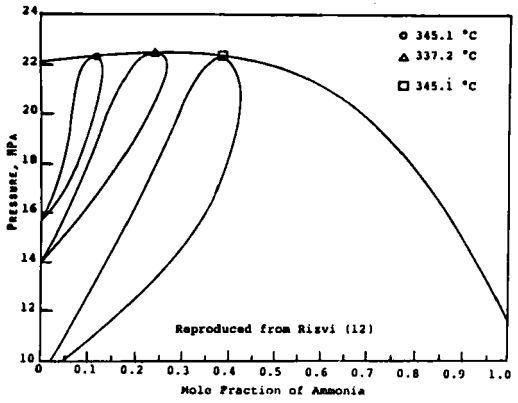

Figure 1. High Pressure Diagram for Ammonia-Water.

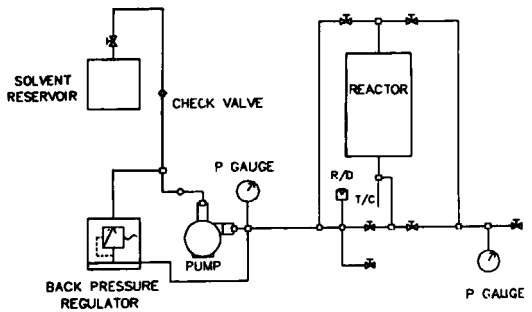

Figure 2. Experimental Apparatus.

conditions as follows:

$$Co + 6\ NH_4^+ + 3/4\ O_2 = Co(NH_3)_6^{3+} + 3/2\ H_2O + 3\ H^+ \quad (1)$$

Han and Vu proposed that in this reaction, the oxygen atoms are first adsorbed to the catalyst surface at a site containing cobalt metal to form an intermediate Co...O.

$$Co + 3/4\ O_2 + H^+ + e^- = Co...O + 1/2\ H_2O \quad (2)$$

The intermediate acts as a cobaltous oxide (CoO) and reacts with ammonium ions to produce a cobaltous ammine complex $Co(NH_3)_6^{2+}$.

$$Co...O + 6\ NH_4^+ = Co(NH_3)_6^{2+} + H_2O + 4\ H^+ \quad (3)$$

This cobaltous ammine complex is then oxidized to form a cobaltic hexamine complex.

$$Co(NH_3)_6^{2+} = Co(NH_3)_6^{3+} + e^- \quad (4)$$

Mass transfer of the oxygen to the solid - liquid interface was determined to be the rate limiting step. The surface reaction is fast and irreversible. An activation energy of 12.54 Kcal/mole was obtained. This indicates a diffusion controlled mechanism.

Cobalt extractions were determined in this study by analyzing leached catalyst material after each experiment for residual cobalt content. The amount of residual cobalt in the catalyst material was then compared to the amount of cobalt present in samples of the catalyst material before leaching to determine the cobalt extraction. The cobalt extraction is defined as:

$$e = 1 - \frac{\text{wt. \% residual Co in leached catalyst}}{\text{wt. \% Co in non-leached catalyst}} \quad (5)$$

Assuming mass transfer of oxygen to the solid fluid interface to be the rate limiting step, the dissolution of cobalt by supercritical aqueous ammonia should be more rapid than dissolution by liquid aqueous ammonia. The much higher diffusivities associated with supercritical fluids should produce a correspondingly small diffusional resistance and therefore, result in a chemical reaction rate limiting step.

In the present study, cobalt extraction from a catalyst material using supercritical aqueous ammonia solvent was compared to cobalt extraction using similar experimental parameters with subcritical aqueous ammonia solvent to determine the extent of leaching enhancement gained by leaching at supercritical conditions. The catalyst material leached was a cobalt hydrotreating catalyst that contained approximately 4 percent cobalt and 17 percent molybdenum. Surface area of the catalyst was approximately 175 m^2/g. Approximate pore volume was 0.50 cc/g.

EXPERIMENTAL

The apparatus used in this study was designed to measure the cobalt extraction obtained in the catalyst material - solvent systems, under conditions ranging from ambient to supercritical. The apparatus consisted of three main components: a solvent delivery unit, an extraction and sampling unit, and a pressure and temperature control unit. A schematic diagram of the experimental apparatus is shown in Figure 2.

SOLVENT DELIVERY UNIT

Solvent to be used in each experiment was stored, at room temperature, in a pressurized autoclave (Autoclave Engineers, Inc., Model #83-07200-00). The autoclave was a bottle closure type vessel and was pressurized with bottled nitrogen fed through an opening in the top of the vessel. The vessel was fitted internally with a glass sleeve, giving it a solvent capacity of approximately 600 ml. Solvent flowed through a check valve and filter via stainless steel tubing to a pump. The pump (Milton Roy, Part #2396-89) was a reciprocating plunger, positive displacement type pump, with two pump bodies mounted on either side of the drive motor. The pump delivered pressurized solvent past a rupture disc assembly to the extraction vessel, via stainless steel tubing.

The rupture disk assembly was a safety feature installed in case of excessive system pressure surges. The assembly (Autoclave Engineers, Inc. Part #SS-4600-1A) features a non-rotating double-cone plug, with an angled rupture disk (Autoclave Engineers, Inc. Part #P-734) constructed of Inconel. The disk has a nominal rupture pressure rating of 10,000 psi.

The extraction vessel (Autoclave Engineers, Inc. Part #CNLX16012) was a vertically mounted, coned and threaded length of tubing connected directly to a collar and gland on both ends. Connected directly to each of the two glands was a reducer coupling, which in turn were connected directly to male/female adapters. Stainless steel screens (60 mesh) were placed inside both the top and bottom couplings to hold the catalyst material inside the extraction vessel during experiments. Extraction vessel assembly had a maximum pressure rating of 20,000 psi.

PRESSURE AND TEMPERATURE CONTROL UNIT

The solvents and catalyst material were heated to the desired reaction conditions inside the extraction vessel, using two ceramic band resistance type heating mantles. The mantles were mounted around the length of tubing that was the body of the extraction vessel. The temperature was controlled by a percentage type temperature controller. The system temperature was measured by a type J thermocouple inserted into the bottom of the extraction vessel.

During experiments solvent was delivered at room temperature and 100 to 200 psi from the autoclave to the pump, where the solvent was pumped to the extraction vessel. As solvent was pumped through the extraction vessel, it was heated to the desired reaction conditions. Catalyst sample weights and initial solvent volumes were virtually the same for all experiments. Supercritical phase experiments were conducted initially, and experimental parameters (extraction time and solvent mass flow rates) for subsequent subcritical phase experiments were matched to those from the corresponding solvent composition supercritical phase experiments. The amount of cobalt leached from the hydrotreating catalyst was determined by analyzing the catalyst material for cobalt after the leaching experiments and comparing these results to the analytical results on the non-leached catalyst. The analysis for cobalt was carried out by a potassium pyrosulfate fusion, followed by a titration with EDTA to a violet end point. Most of the leached residue from the experiments was used during the cobalt analysis. There was insufficient material remaining to be analyzed for residual molybdenum. Experimental conditions are provided in Table 1. Cobalt extraction results are provided in Table 2.

RESULTS AND DISCUSSION

The experimental system as described was capable of attaining supercritical conditions, using the procedures detailed in the Experimental section. There were no optical means available for determining the presence of the supercritical phase in the reactor. However, during the supercritical phase condition experiments, there were very rapid increases of 1,000 to 1,500 psi in the system pressure as critical temperatures were approached isobarically at supercritical pressures. Pressure increases as the liquid-supercritical phase transition was approached were expected due to the much lower density of the supercritical phase.

The cobalt extraction from hydrotreating catalyst material at the various aqueous ammonia solvent compositions tested are given for the four reactions conditions in Table 2. The supercritical phase (supercritical pressure-supercritical temperature) experiments had, in general, the highest cobalt extraction. They were followed in order of decreasing cobalt extraction generally by the supercritical pressure - low temperature experiments, low pressure - low temperature experiments and the supercritical pressure - elevated temperature experiments.

Cobalt leaching was significantly enhanced during the supercritical pressure - supercritical temperature experiments at solvent compositions greater than 5 percent ammonia. The one exception to the supercritical enhancement was at the 15 mole percent ammonia solvent composition. Here, the cobalt extraction was 35.0 percent at supercritical conditions, and 39.1 at supercritical pressure - low temperature conditions. The average increase in e from the supercritical pressure - low temperature experiments to the supercritical pressure - supercritical temperature experiments (with the exception of the 5 mole percent and NH_3 experiments) was 4.0 percent. Results from these series of experiments are shown in Figure 3. Average increase in e from the low pressure low temperature experiments to the supercritical pressure -

Table 1: Experimental Conditions

Solvent Composition, mole % NH_3	Temperature, °C	Pressure KPa x 10^{-3}	Extraction Time,* Minutes
$5^{1)}$	21	1.38	19
$5^{2)}$	21	22.41	20
$5^{3)}$	210	24.13	17
$5^{4)}$	373	22.75	20
$10^{1)}$	21	1.24	15
$10^{2)}$	22	22.41	15
$10^{3)}$	200	24.13	20
$10^{4)}$	361	34.10	17
$15^{1)}$	23	1.03	17
$15^{2)}$	20	22.41	18
$15^{3)}$	192	25.86	23
$15^{4)}$	364	24.59	20
$20^{1)}$	21	1.38	12
$20^{2)}$	21	23.44	13
$20^{3)}$	195	24.82	14
$20^{4)}$	370	22.93	14
$25^{1)}$	23	1.03	11
$25^{2)}$	26	24.13	11
$25^{3)}$	192	24.82	9
$25^{4)}$	360	24.24	9
$30^{1)}$	24	0.69	10
$30^{2)}$	23	25.51	12
$30^{3)}$	188	24.13	10
$30^{4)}$	344	24.18	10

1) Low Pressure Low Temperature
2) S.C. Pressure Low Temperature
3) S.C. Pressure Elevated Temperature
4) S.C. Pressure S.C. Temperature

Table 2. - Cobalt Extraction from Hydroteating Catalyst Materal Cobalt Extration (e), percent

Solvent Composition mole % NH_3	Low Pressure Low Temp.	S.C. Pressure Low Temp.	S.C. Pressure Elvtd. Temp.	S.C. Pressure S.C. Temp
5	0	0	0	0
10	26.7	25.6	5.6	29.3
15	31.6	39.1	24.1	35.0
20	36.1	39.5	35.0	44.3
25	32.3	40.2	35.0	50.0
30	48.9	45.3	39.1	51.1

supercritical temperature experiments (with the exception of the 5 mole percent NH_3 experiments), was 6.8 percent. Results from these series of experiments are shown in Figure 4. Average increase in e from the supercritical pressure - elevated temperature experiments to the supercritical pressure - supercritical temperature experiments with the exception of the 5 mole percent NH_3 experiments, was 14.2 percent. Results from these series of experiments are shown in Figure 5.

The enhancement of cobalt extraction at supercritical conditions appears to be the result of the enhanced transport properties of supercritical solvents. The gas-like diffusion coefficients shown by SCFs lowers diffusional resistance to mass transfer. Enhancement of cobalt extraction gained by pressure or temperature effects not associated with critical phenomena would have been observed in results from experiments conducted at subcritical phase conditions. Although increases in cobalt extraction were observed during supercritical pressure - low temperature experiments, the lowest cobalt extraction (e) values were almost always obtained from the supercritical pressure - elevated temperature experiments, even though temperature and pressure conditions for these two series of experiments were most nearly the same. This indicates that the enhancement is the result of the critical phenomena, most likely mass transfer enhancement.

CONCLUSION

Leaching cobalt from a hydrotreating catalyst material using supercritical aqueous ammonia conditions results in a significant increase in cobalt extraction over that obtained by leaching at any combination of the subcritical conditions tested. Leaching of cobalt at supercritical conditions was enhanced in comparison to leaching at supercritical pressure -elevated temperature, low pressure - low temperature and supercritical pressure - low temperature conditions by an average of 14.2, 6.8 and 4.0 percent respectively. Leaching enhancement at supercritical conditions is made more significant by the low solvent flow rates used in this study. Only 50 to 100 milliliters of solvent at supercritical conditions was introduced into the reactor during the supercritical experiments. The supercritical leaching enhancement is not the result of simple pressure or temperature effects, but is probably caused by the improved mass transfer characteristics of supercritical fluids. These characteristics decrease diffusional resistance to mass transfer and make the process more nearly chemical reaction rate controlled.

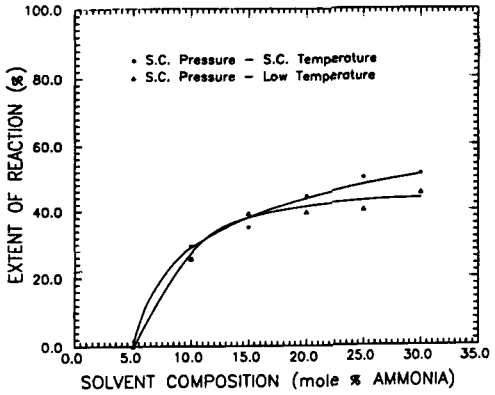

Figure 3. Cobalt Extraction at Supercritical Pressure - Low Temperature Conditions.

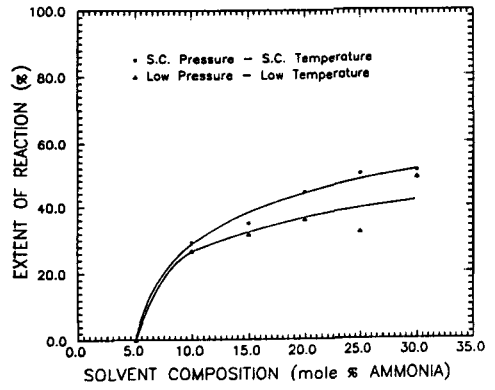

Figure 4. Cobalt Extraction at Low Pressure - Low Temperature Conditions.

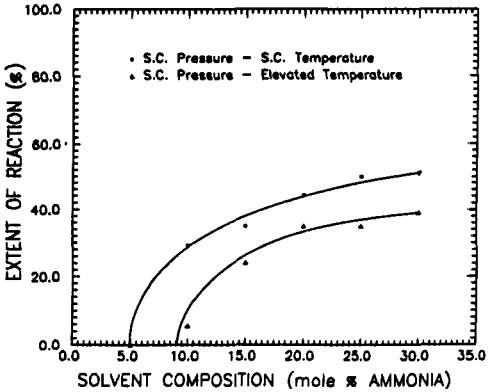

Figure 5. Cobalt Extraction at Supercritical Pressure - Elevated Temperature Conditions.

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