Bioleaching of nickel from equilibrium fluid catalytic cracking catalysts

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Summary

This study investigates the possibility of reusing metal-contaminated equilibrium fluid catalytic cracking (FCC) catalyst after bioleaching. Leaching with *Aspergillus niger* culture was found to be more effective in the mobilization of nickel from the catalyst particles compared to chemical leaching with citric acid. Bioleaching achieved 32% nickel removal whereas chemical leaching achieved only 21% nickel removal from catalyst particles. The enhanced nickel removal from the catalysts in the presence of *A. niger* culture was attributed to the biosorption ability of the fungal mycelium and to the higher local concentration of citric acid on the catalyst surface. It was found that 9% of solubilized nickel in the liquid medium was biosorbed to fungal biomass. After nickel leaching with *A. niger* culture, the hydrogen-to-methane molar ratio and coke yield, which are the measures of dehydrogenation reactions catalysed by nickel during cracking reactions, decreased significantly.

Introduction

The fluid catalytic cracking (FCC) process is used for the conversion of relatively high-temperature boiling hydrocarbons to lower temperature-boiling hydrocarbons in the heating oil and gasoline range. During the cracking process, nickel- and vanadium-containing porphyrins and porphyrin-like complexes from the hydrocarbon feed decompose, leaving metal contaminants on the FCC catalyst surface. These metals increase the production of coke, hydrogen, and light gases formation at the expense of the highly desired gasoline (Cimbalo *et al.* 1972). After reaction in the fluidized catalytic cracking unit (FCCU) spent catalysts are removed from the unit and replaced by fresh catalysts in order to maintain the desired catalytic activity. These spent catalysts are called equilibrium catalysts (ECat). Spent FCC catalysts constitute a significant portion of the solid wastes generated in the petrochemical industry. Furimsky (1996) pointed out that on a world scale about 400,000 tons of spent catalysts from FCCU are produced annually. Spent catalysts can be used as secondary raw materials, or disposed of in land farming or land filling (Hsu *et al.* 1996; Su *et al.* 2001). Since catalysts contain contaminants picked up in the processes for which they were used, there has been an increasing concern about the land disposal of spent catalysts. The ability to restore catalyst activity by using an appropriate demetallization process would greatly reduce toxic waste. Demetallization processes involve the physical removal of the metal contaminants from the catalysts. The process called 'Demet' is claimed to reduce both fresh catalyst addition and spent catalyst disposal when used with any FCC catalyst (Yoo 1998). In this process, first the metals on the catalyst are oxidized, sulphided and chlorinated in the reactor section. Then, the nickel and sodium chlorides are washed from the catalyst. Since chlorination techniques are destructive to zeolite-containing catalyst, they have received less and less consideration in commercial use.

Biotechnological removal of such metal contaminants from used catalysts has not received enough attention. Although the microbial leaching of metals became successful by using chemolithoautotrophic bacteria to solubilize metals from materials containing sulphide and/or ferrous compounds (Sukla *et al.* 1993; Krebs *et al.* 1997), only Myerson & Ernst (1985) mentioned the removal of metal impurities from spent catalysts. The use of fungi was thought to be an interesting alternative (Bosecker 1997) since fungi could solubilize metals from ores by the excretion of organic acids. *Aspergillus niger* and *Penicillium simplicissimum* are the two widely used species for bioleaching of metals from ores. Bioleaching of valuable elements (Al, Co, Cu, Ni) from ores using micro-fungal species like *Penicillia* or *Aspergilli* has been investigated earlier (Sukla *et al.* 1993). In general a pH range between 2 and 8, a temperature range between 20 and 40 °C, and a high resistance to heavy metals are characteristics of leaching processes with fungi (Burgstaller & Schinner 1993). Fungi have been used

in the past for the leaching of carbonaceous low-grade ores and mining wastes (Wenberg *et al,* 1971), industrial filter dusts (Burgstaller *et al.* 1992), electronic scrap (Brandl *et al.* 2001) and coal wastes (Scott *et al.* 1986).

The main objective of this research was the elimination of nickel from equilibrium FCC catalysts so as to recover catalyst activity partially. This study focuses on nickel removal from the metal-contaminated FCC catalysts using *A. niger* culture. Citric acid constituted the major acid produced from *A. niger* strain. For this reason citric acid was used in chemical leaching experiments to mimic the chemical action of *A. niger* culture in order to understand the difference between chemical leaching with citric acid and bioleaching. Besides, the effectiveness of citric acid in solubilizing nickel from ores was reported earlier in the literature (Valix *et al.* 2001). The equilibrium catalysts being subjected to bioleaching and chemical leaching with citric acid were used in the catalytic cracking of gas oil. During the cracking reactions the hydrogen and coke produced by nickel-catalysed dehydrogenation reactions were measured to compare the effects of both bioleaching and chemical leaching on nickel removal from the FCC catalyst.

Materials and methods

Catalyst samples

Commercial equilibrium FCC catalysts supplied by Marathon-Ashland Oil Inc., Ashland (USA) were used in bioleaching and cracking experiments. They are named ECat-LOW, ECat-INT and ECat-HIGH based on their nickel concentration. The concentration of nickel in Ecat-LOW, ECat-INT and ECat-HIGH were 300 nickel 900 and 2600 mg kg^{-1} respectively.

Bioleaching and chemical leaching

A lyophilized culture of *A. niger* from Presque Isle Cultures (Erie, USA) was used, in all bioleaching experiments. First, the lyophilized culture was revived properly and growth of the fungus was observed and monitored by measuring the pH for 21 days. The organism was cultivated on a sucrose medium in baffled 250-ml Erlenmeyer flasks Wid incubated at 30 °C on an orbital shaker at 150 rev min^{-1}. The growth medium contained (in g l^{-1}) sucrose (100), $NaNO_3$ (1.5), KH_2PO_4 (0.5), $MgSO_4 \cdot 7H_2O$ (0.025), KCl (0.025), and yeast extract (1.6). The medium was sterilized by autoclaving at 120 °C to reduce the interference from other microorganisms. The fungal culture was grown in the presence of different amounts of ECat-HIGH catalyst. The pulp densities used in the inhibition experiments were 5 l^{-1} and 10 g l^{-1}. Inoculation was conducted by adding the fungal spores to the mixture of catalyst and growth medium. Fungal growth in the presence of equilibrium catalysts sample was monitored by measuring the pH of the medium for 21 days. In all

cases the initial pH of the growth medium was adjusted to a value of 6.5. All of the bioleaching experiments were conducted at a pulp density of 5 g l^{-1}. The inhibition and control (only culture medium without fungi) experiments were conducted using only the highly nickel-contaminated (ECat-HIGH) catalyst sample. However, both bioleaching and chemical leaching with citric acid experiments were carried out with three catalyst samples named ECat-LOW, ECat-INT and ECat-HIGH based on their nickel concentration.

Controlled chemical leaching experiments with citric acid were also conducted. Citric acid was used because of its ability for solubilizing nickel. This acid also constitutes the major acid produced from the fungus strains. Chemical leaching of the spent FCC catalyst was achieved by adding a solution 39 g citric acid l^{-1} to equilibrium catalyst particles. This concentration value was selected since this was the highest citric acid concentration in the *A. niger* culture at the end of the 21 day incubation period. The slurry mixture was kept at 30 °C on an orbital shaker (150 rev min^{-1}) and leaching was carried out for a period of 21 days. In both chemical and bioleaching experiments, catalyst samples were taken at the end of the incubation period, and were filtered and then washed with distilled water.

The amount of nickel on the catalyst particles was determined using inductively coupled plasma-atomic absorption spectroscopy (ICP-AES) with standard procedures. 0.5 g catalyst sample was weighed into a platinum dish and approximately 20 ml of deionized water was added. After slowly adding 3 ml of concentrated hydrofluoric acid, 5 ml concentrated sulphuric acid and l ml concentrated nitric acid were subsequently added to the platinum dish. Volatile compounds were fumed off until the residue was slightly moist with sulphuric acid. After cooling down, approximately 40 ml of deionized water and l5 ml of hydrochloric acid were added to the platinum dish, wich was warmed until the sample was completely dissolved. The solution was tranferred into a 100 ml volumetric flask and diluted with appropriate amount of deionized water. In a second platinum dish an analogous mixture of deionized water, hydrofluoric acid, sulphuric acid and nitric acid was fumed off and taken up with hydrochloric acid. The solution was transferred into a 100 ml volumetric flask. After appropriate dilution with deionized water it was used as a blank sample. Similarly, acid digestion was used using nitric acid in combination with perchloric acid to determine nickel in the biomass sample.

The amount of citric acid produced by *A. niger* cultures at the end of 21 days was measured by a spectrophotometric method (Marier & Boulet 1958).

Microactivity test (MAT) evaluation

MAT measurements of catalyst activity were performed according to the procedures of ASTM D-3907 using sour imported heavy gas oil (Davison Chemical Co.) feed. The MAT measurements for catalyst samples

named ECat-LOW, ECat-INT and ECat-HIGH based on their nickel concentration were carried out before and after bioleaching experiments. The MAT unit was manufactured by Industrial Automated Systems (Parlin, New Jersey). The microactivity test unit consists of a furnace for maintaining constant cracking temperature (500 °C), a syringe pump whose speed can be varied to inject the cracking feed, a liquid product receiver and a gas collection vessel. Liquid products were condensed at the exit of the reactor by using an ice-water mixture. Product gases were collected by downward displacement of water. To achieve different conversions the reaction severity was varied by changing the catalyst-to-oil ratio (C/O) where C/O ratio is defined as the amount of catalyst divided by the total amount of feed. This ratio was changed by changing the amount of feed while keeping the catalyst amount constant at 5 g. C/O ratios of 3, 5, and 8 were used in the cracking experiments. The distribution of gaseous products was analysed by using a Varian 3600 gas chromatograph. The H_2, C_1, C_2, C_3, C_4, and C_5^+ lumps were determined quantitatively. The liquid products, after weighing, were dissolved in CS_2 solvent and analysed by GC simulated distillation. The D2887 simulated distillation method was used to determine the percentage of the liquid products boiling in the range of gasoline (IBP – 421 F), light cycle oil, LCO (421–640 F), and heavy cycle oil, HCO (640 F and above). A Supelco Petrocol B packed column installed in a Varain 3400 GC was used. Using this method, the conversion as defined by ASTM 3907 was calculated. The yields were calculated as weight percent of reactant. The fractions of gasoline, LCO and HCO were determined by the cut-off points at 421 and 640 F. Conversion was defined as 100 wt% ff (LCO, wt% ff + HCO, wt% ff). The amount of coke on the spent catalyst was determined by temperature-programmed oxidation (Bayraktar & Kugler 2003).

In this study, all experiments were performed at least three times and average values were taken as data points.

Results and discussion

Depostion of metal contaminants (e.g., nickel, vanadium and iron) on the catalyst causes a decrease in catalyst activity. Both coke and hydrogen productions increase at the expense of gasoline. The negative effect of metal contaminants on the yields can be seen from Table 1. Data presented in Table 1 were obtained at a constant MAT conversion of 50%. MAT conversion can be defined as percentage of the feed converted to gas, gasoline and coke during catalytic cracking reactions. The yields of valuable products, gasoline and LCO, decreased whereas coke yield increased when the nickel content on the cracking catalyst increased from 300 mg kg^{-1} (ECat-LOW) to 2600 mg kg^{-1} (ECat-HIGH). With increasing nickel content on the catalyst, gasoline yield decreased from 38.43% (untreated ECat-LOW) to 34.47% (untreated ECat-HIGH). Similarly, LCO yield decreased from 30.87 to 28.74%. On the other hand, coke yield increased significantly from 2.73 to 7.15%. Studies for deposition of these metals on the catalyst showed that nickel was in general homogeneously distributed throughout the catalyst surface (Kugler & Leta 1988). Nickel was found to be primarily responsible for promoting the dehydrogenation activity which produced coke and gaseous products, in particular, hydrogen and methane at the expense of desired liquid products (Venuto & Habib 1979). H_2 yields from MAT experiments have usually been reported by using hydrogen-to-methane (H_2/CH_4) molar ratio. Hydrogen production was found to be very sensitive to catalyst metal contamination (Venuto & Habib 1979). At low catalyst metals level (< 1000 mg kg^{-1}) H_2/CH_4 ratios of less than 1.0 were found to be typical. At metals level of 1000–1500 mg kg^{-1}, which is the normal level for many FCC units, H_2/CH_4 ratios of 1–2 were found to be typical. For the case of severe metals contamination above 5000 mg kg^{-1}, H_2/CH_4 ratios of 10 or higher would be typical (Venuto & Habib 1979). As seen from Figure 1, the H_2/CH_4 molar ratio was very sensitive to

Table 1. Comparison of yields at 50% MAT conversion and nickel recoveries after chemical leaching with citric acid and leaching with *Aspergillus niger* culture.

Catalyst	Pretreatment	Yields wt%						
		Gas	Gasoline	LCO	HCO	Coke	H_2/CH_4	Ni recovery (%)
ECat-LOW	Untreated	8.84	38.43	30.87	19.87	2.73 ± 0.10	1.12 ± 0.15	–
	Leached with citric acid	8.64	38.63	30.67	20.10	2.80 ± 0.07	1.10 ± 0.18	9 ± 0.9
	Leached with fungi	8.80	38.60	30.35	19.70	2.60 ± 0.15	0.96 ± 0.08	16 ± 1.5
ECat-INT	Untreated	8.74	37.10	29.32	21.15	4.05 ± 0.21	3.10 ± 0.12	–
	Leached with citric acid	8.70	37.20	29.52	20.70	3.78 ± 0.10	2.25 ± 0.10	12 ± 1.3
	Leached with fungi	8.62	37.65	30.08	20.45	3.25 ± 0.16	1.95 ± 0.15	26 ± 2.0
ECat-HIGH	Untreated	8.61	34.47	28.74	21.26	7.15 ± 0.18	7.80 ± 0.23	–
	Leached with citric acid	8.55	34.67	27.85	23.33	6.65 ± 0.12	6.50 ± 0.31	21 ± 1.3
	Leached with fungi	9.12	35.10	27.75	22.25	5.35 ± 0.09	4.80 ± 0.20	32 ± 1.0
ECat-HIGH	Treated with culture medium without fungi	8.70	33.95	28.54	20.85	7.35 ± 0.20	7.65 ± 0.33	2.7 ± 0.5

catalyst metal contamination. When the metals on the catalyst increased, this ratio also increased. In this study, the H_2/CH_4 molar ratios were found to be 1.1, 3.1 and 7.8 for ECat-LOW, ECat-INT and ECat-HIGH, respectively, at a constant MAT conversion of 50%. These values were the clear indication of the increase in hydrogen yield with increasing metals concentration on the equilibrium catalysts.

Before performing bioleaching experiments, *A. niger* cultures were grown in the absence and presence of ECat-HIGH catalyst samples. Organic acid production by fungi was monitored by measuring total acidity of the medium. The decrease in medium pH was mainly caused by citric acid produced by fungi. Oxalic acid (0.26 g l^{-1}) production was not significant. Figure 1 shows the profiles of pH during the growth of *A. niger* in the presence of different amounts of ECat-HIGH catalyst samples. It was clear that if the amount of catalyst was increased, the acid production or metabolic activities of *A. niger* cells was inhibited. When there was no catalyst in the growth medium, citric acid concentration was measured as 39 g l^{-1} and the pH of the medium decreased to 2.1 at the end of the 21-day incubation. At 5 g l^{-1} solid concentration acid production was affected less and the pH of the medium decreased to 3. At 10 g l^{-1} solid concentrations, acid production was affected significantly and the pH of medium decreased only up to 4. Most of the pH change occurred within the first 4–5 days of incubation period.

Data presented in Table 1 shows how the H_2/CH_4 molar ratio and coke yield were affected by both bioleaching and chemical leaching with citric acid. In control experiments some ECat-HIGH catalyst samples were not subjected to any treatment and some ECat-HIGH samples were subjected to culture medium in the absence of microorganism prior to catalytic cracking reactions. Some ECat-HIGH samples were subjected to fungal bioleaching and chemical leaching with citric acid. Control experiments with culture medium without microorganism were performed only for Ecat-HIGH catalyst sample. After citric acid leaching and bioleaching treatments, H_2/CH_4 molar ratio and coke yield

decreased compared to the control experiments for all catalyst samples. The decrease in H_2/CH_4 molar ratio and coke yield after bioleaching was more significant compared to chemical leaching with citric acid. Decreases of 7 and 25% in the coke yields were observed after the ECat-HIGH catalysts were subjected to chemical leaching and bioleaching, respectively. Similarly, 17 and 38% decrease in H_2/CH_4 molar ratios were observed for chemical leaching and bioleaching, respectively. The effect of bioleaching and chemical leaching with citric acid was not very significant for ECat-LOW and ECat-INT catalyst. This could be attributed to the relatively lower nickel removal from ECat-LOW and ECat-INT catalysts compared to ECat-HIGH catalysts.

Since the citric acid concentration corresponding to the concentration obtained at the end of 21-day incubation period of *A. niger* culture was used in the chemical leaching experiments the catalyst particles were subjected to higher levels of citric acid for a longer period of time compared to bioleaching experiments. Therefore after chemical leaching higher or closer nickel recoveries were expected compared to bioleaching. However in bioleaching experiments nickel recovery was greater than those obtained from the chemical leaching tests. These results suggested that the bioleaching process could not be explained merely by the leaching effect of citric acid produced by the fungi. Fungi appeared to participate in the leaching process or citric acid appeared to be used more effectively in the presence of the fungus. Similar observations were made by other researchers (Alibhai *et al.* 1993; Kar *et al.* 1995; Castro *et al.* 2000; Valix *et al.* 2001). Kar *et al.* (1995) attributed the enhanced leaching of nickel from lateritic ore to a higher local concentration of the bio-acids formed in the presence of fungus than in fungus-free spent medium. On extended incubation, some researchers found that the fungal mycelium bound some of the solubilized nickel (Alibhai *et al.* 1993, Tzeferlis *et al.* 1994, Kar *et al.* 1995). Removal of heavy metals using the fungus *A. niger* was studied in detail and fungal microorganisms could up take nickel intracellularly (Kapoor & Viraraghavan 1997). Live *A. niger* biomass was found to be more effective in the removal of nickel than dead *A. niger* biomass (Kapoor *et al.* 1999).

Table 1 presents the recovery of nickel from equilibrium catalysts after bioleaching and chemical leaching with citric acid. The nickel recoveries from all catalysts after bioleaching were found to be significantly higher than those after chemical leaching with citric acid (see Table 1). This study showed that bioleaching removed 32% of nickel whereas chemical leaching removed 21% of nickel from the ECat-HIGH catalyst sample. For example, after bioleaching 1765 mg kg^{-1} nickel was determined on the ECat-HIGH catalyst particles by ICP-AES. This means that 32% of nickel (835 mg kg^{-1}) was solubilized and removed from the ECat-HIGH catalyst particles. At the end of 21 day of bioleaching 758 mg kg^{-1} nickel was found to be in the liquid
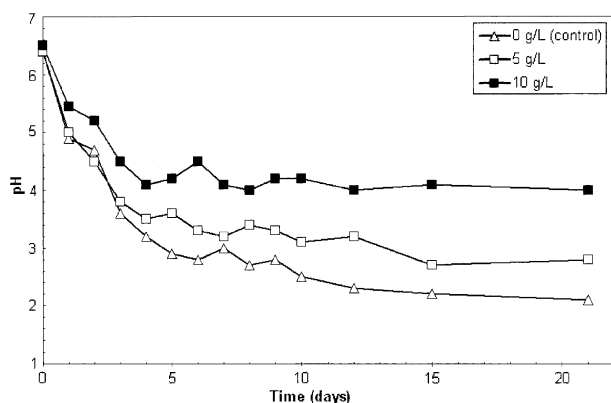

Figure 1. pH profiles of *Aspergillus niger* cultures grown on different concentration of metal-contaminated equilibrium FCC catalysts.

medium. Material balance for nickel revealed that 77 mg kg^{-1} nickel could be bound by the fungal mycelium. Nickel concentration of 77 mg kg^{-1} made up the 9% of the solubilized nickel from the ECat-HIGH catalyst particles. These experiments were repeated three times and 9 $\pm$ 2% of solubilized nickel was found to be biosorbed by the fungal biomass. It was clear that biosorption of nickel by fungus played an important role in the enhancement of nickel leaching from the catalyst particles. Probably the attachment of fungi to the surface of catalyst particles caused the increase in the local acid concentration on the catalyst surface. The higher local acid concentration might enhance the solubilization of nickel deposited on the surface of catalysts. Some of the solubilized nickel can be biosorbed by the fungi, which is in close contact with the catalyst particles. Leaching with fungal microorganisms is based on the complexation of metals by the excreted organic acids and bioaccumulation of metals by the organism's mycelium. Although citric acid is an important leaching agent in the extraction of nickel from equilibrium catalyst particles, biosorption of nickel by fungal mycelium should not be under-estimated. Over longer incubation periods, both biosorption and citric acid leaching act together to give better extraction of nickel from catalyst particles compared to leaching with citric acid alone. Repetition of the bioleaching process would increase the nickel recovery from the catalysts, but this would make the process even slower and more expensive compared to a single-step bioleaching process. In short, bioleaching of contaminant metals from catalysts to increase their activities is far from becoming a commercially competitive large-scale process. The main limitations are slow kinetics of the process, requirement for expensive growth media, and difficulties in maintaining sterile conditions.

Acknowledgements

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