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LEACHING OF NICKEL FROM SPENT CATALYSTS IN HYDROCHLORIC ACID SOLUTIONS

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The results of hydrochloric acid leaching of nickel from spent catalysts used for methanation of small quantities of carbon oxide from hydrogen and ammonia synthesis gases (RANG-19), as well as for hydrogenation of benzene to cyclohexane (KUB-3) are reported. The effects of acid concentration, temperature, solid-to-liquid ratio and reaction time on nickel and aluminium leaching were examined. The leaching of nickel is more affected by temperature in the case of KUB-3 catalyst than RANG-19. After one hour leaching at 60^{o}C in 3.0M HCl solution the extraction of nickel from RANG-19 catalyst amounts to 74%, whereas for KUB-3 after 45 min of leaching extraction of nickel is 99%. The highest leaching efficiency of nickel from both the catalysts are found to be: 3.0M HCl solution, temperature 60^{o}C, solid to liquid ratio of 1/10, particle size 3-8 mm. In these conditions 99% of nickel is extracted from KUB-3 catalyst after 3 hours of leaching, and 98% of nickel from RANG-19 after 4 hours of leaching, respectively.

key words: spent catalyst, nickel, leaching, hydrochloric acid

INTRODUCTION

Increasing demand for nickel requires further intensive studies of its extraction methods from low-grade ores and secondary resources. Extraction of nickel can be effectively performed from spent catalysts. Recycling of spent catalysts has become an unavoidable task not only to lower their costs but also to reduce the catalysts waste in order to prevent the environmental pollution. Nickel is widely used as a catalyst in several technological processes: in hydrogenation, hydrodesulphurisation, hydrorefin-

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ing including fat hardening process (Ni, Mo/Al_2O_3, NiO/Al_2O_3, Raney nickel alloy); in refinery hydrocracing (NiS, $WS_3/SiO_2Al_2O_3$); in methanation of carbon oxide from hydrogen and ammonia synthesis gases (NiO/Al_2O_3, $NiSiO_2$) (Thomas, 1970). Typically, nickel spent catalysts contain metallic nickel and nickel oxide, although nickel aluminate, spinel-like compounds and nickel sulphides may occasionally occur, as well as admixtures of coke, hydrocarbons or fat.

Recently, relatively great attention has been paid to the research connected with the recovery of nickel from secondary resources (Mulak et al., 2005).

Invascan and Roman (1975) reported on the recovery of nickel from a spent catalyst used in the ammonia plant by leaching in sulphide acid. The nickel was recovered as $NiSO_4$ with high 99% yield. Al-Mansi and Abdel Monem (2002) studied the sulphuric acid leaching process for the recovery of nickel as a sulphate from a spent catalyst in the steam reforming industry. It was also shown that the high recovery of 99% nickel as nickel sulphate was achieved.

Chaudhary et al.,(1993) reported on hydrochloric acid leaching process for the recovery of nickel as nickel oxide from a spent catalyst containing 17.7% Ni. They found that the maximum of nickel extraction (73%) could be achieved by carrying out the leaching process with 28.8% HCl at 80^oC. In an attempt to further improve the nickel extraction the application of chlorine gas was investigated, however no appreciable change has been observed. Kolosnitsyn et al.,(2006) studied the recovery of nickel from a spent catalyst used for the steam conversion of methane. They found that the leaching of nickel is limited by the bulk of the leaching solution. In turn, Sulek et al.,(2004) and Mulak et al.,(2005) investigated a sulphuric acid leaching of spent catalysts used for methanation as well as for hydrogenation of benzene. The authors reported that nickel extraction from spent methanation catalysts is limited by a surface reaction. In the case of benzene hydrogenation catalyst diffusion through the solid is the slowest step of the process. Several other methods have been also reported for the leaching of nickel from a spent refinery catalyst (Furimsky, 1996).

In this paper the effects of hydrogenation acid concentration, temperature, solid/liquid ratio and the stirring speed on the extraction of nickel and aluminium from two different industrial spent catalysts (KUB-3 and RANG-19) have been investigated.

The main reaction for nickel extraction from both the catalysts is as follows:

$$NiO + 2HCl = NiCl_2 + H_2O, \quad (1)$$

whereas the side reaction is:

$$\alpha\text{-}Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O. \quad (2)$$

The rate of the side reaction is very slow since α-Al_2O_3 is inert towards acids.

EXPERIMENTAL

MATERIALS

Two investigated in the paper spent catalysts (NiO/Al_2O_3) were obtained from Fertilizer Research Institute in Pulawy (Poland). Catalyst KUB-3 was used for hydrogenation of benzene to cyclohexane, whereas RANG-19 was applied for methanation of small quantities of carbon oxide from hydrogen and ammonia synthesis gases. Both spent catalysts were in form of granules with a diameter of 3.0-8.0 mm.

Table1. Chemical analysis of spent catalysts

Element, %	Ni	Al	Ca	Mg	C	H
KUB-3	30.1	18.2	2.55	0.05	2.45	1.17
RANG-19	13.5	40.2	0.33	0.05	1.08	0.31

LEACHING EXPERIMENTS

The leaching experiments were performed in a 500 cm^3 glass reaction vessel immersed in a controlled temperature bath during 60 min. At the start of the process, the spent catalyst sample as granules of size 3.0-8.0 mm (0.25g) was added to 200 cm^3 of hydrochloric acid solution (at desired concentration and temperature). The reaction mixture was agitated at a rate of 600 rev/min. After selected time intervals 1 cm^3 solution samples were taken for determination of nickel by AAS method. The aluminium concentration in the final solution was determined complexometrically.

RESULTS AND DISCUSSION

EFFECT OF STIRRING SPPED

The influence of the stirring speed on the nickel extraction from the spent catalysts (RANG-19 and KUB-3) was investigated in the solution containing 2.0 M HCl at 50^oC. The variation of the stirring speed within the range of 300-1200 rev/min had no effect on the reaction rate. This indicates that the reactant diffusion from the solution toward the surface of particles, as well as the reaction products away from the particles to the solution occurs quickly and hence does not control the leaching rate within the range of the stirring speed tested. All the subsequent experiments were carried out at a stirring speed of 300 min^{-1} to assure invariance of this parameter.

EFFECT OF HYDROCHLORIC ACID

The influence of HCl concentration on the leaching efficiency was determined by varying the initial concentration of the acid from 1.0 to 5.0 M.

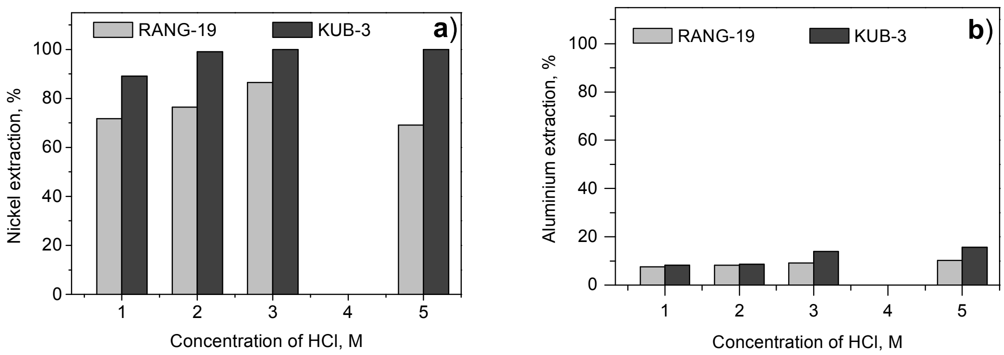

Fig. 1. Effect of hydrochloric acid concentration on nickel and aluminium extraction at 50^{o}C after 1 hour leaching: a) nickel extraction, b) aluminium extraction

The extraction of nickel from KUB-3 catalyst was practically not affected by HCl concentration in the range from 2.0 to 5.0 M. In the case of RANG-19 catalyst, however, increasing the HCl concentration from 1.0 to 3.0 M, the nickel extraction was growing up from 71 to 86%, respectively, whereas for 5.0 M HCl a decrease of leaching efficiency was observed. The latter was probably caused by the fact that all the acid had been already reacted up to this moment. In turn, aluminium is feebly extracted (about 8% for RANG-19, and 15% for KUB-3 catalyst) for the above HCl concentrations.

EFFECT OF TEMPERATURE

The leaching was performed within temperature range 30-70^{o}C with 2.0 M hydrochloric acid solution. The kinetic data for temperature influence on nickel extraction from both the catalysts are presented in Figure 2a and 2b, respectively.

The extraction of nickel is more affected by temperature in the case of KUB-3 catalyst than RANG-19. For instance, after one hour leaching at 50^{o}C the extraction of nickel from RANG-19 catalyst achieved 74%, whereas for KUB-3 after 45 min of leaching the extraction of nickel raised up to 99%. During each one hour leaching the temperature change within the range 30-70^{o}C causes a gradual increase in aluminium extraction from 8 to 14% for RANG-19, and from 2 to 10% for KUB-3. Figure 3 shows the difference in the leaching rate between both the catalysts versus leaching time at 50^{o}C. In order to achieve 98% of nickel from RANG-19 catalyst one needs even up to 5 hours of leaching.

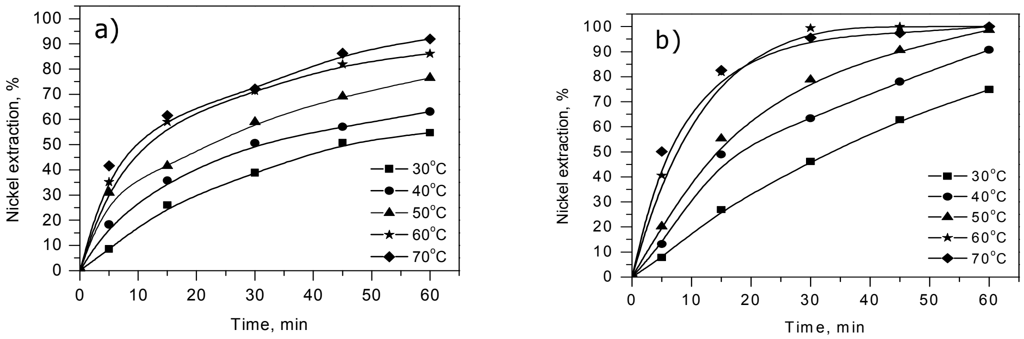

Fig. 2. Effect of temperature on nickel extraction in 2.0 M HCl: a) RANG-19 b) KUB-3.

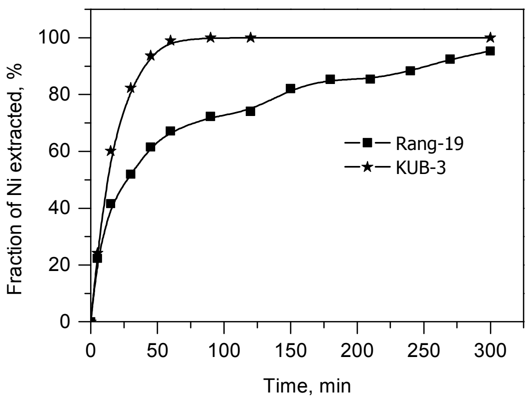

Fig. 3. Influence of leaching time on nickel extraction from the spent catalysts in 2.0 M HCl at 50°C.

EFFECT OF THE SOLID TO LIQUID RATIO

Figure 4 illustrates the influence of the pulp density on nickel extraction at 50°C in 2.0 M HCl after one hour leaching.

The solid to liquid ratio changed in the leaching tests from 1/40 to 1/5 [w/v]. Within this range the pulp density has practically no influence on the extraction of nickel from Rang-19 catalyst. However, for KUB-3 due to the overstoichiometric nickel content (Eq. 1) with respect to the hydrochloric acid in the pulps of high solid to liquid ratio (particularly for w/v =1/5), a decrease in nickel extraction is observed.

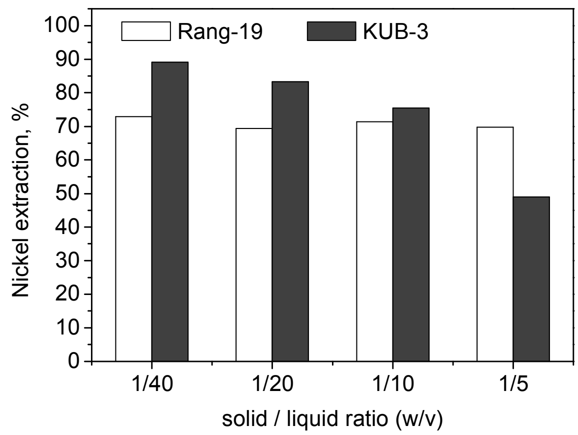

Fig. 4. Influence of the solid to liquid ratio on nickel extraction from the spent catalysts in 2.0 M HCl at 50°C after 1 hour leaching.

CONCLUSIONS

1. The leaching rate of nickel from the investigated spent catalysts is independent of the stirring speed. It indicates that the reaction is not controlled by diffusion in the liqiud phase.
2. The leaching rate of nickel depends more strongly on temperature for KUB-3 catalyst than for RANG-19.
3. For aluminium extraction the effect of temperature variation was also more distinguishable for KUB-3 catalyst than for RANG-19.
4. Based on the leaching experiments on a laboratory scale the highest leaching efficiency of nickel in hydrochloric acid for both the catalysts are found to be: 3.0M HCl solution, temperature 60°C, the solid to liquid ratio of 1/10. The particle size 3-8 mm - such particles were delivered from the technological process. In the above conditions 99% of nickel was extracted from KUB-3 spent catalyst after 3 hour leaching time, and respectively 98% from RANG-19 catalyst after 4 hours of leaching.

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Przedstawiono wyniki ługowania niklu z dwóch zużytych katalizatorów: katalizatora metalizacji (RANG-19) oraz katalizatora uwodornienia benzenu (KUB-3), stosując roztwory kwasu solnego. Określono wpływ stężenia HCl, temperatury, stosunku fazy stałej do ciekłej oraz intensywności mieszania na wydajność ługowania niklu. Wykazano, że temperatura znacznie bardziej wpływa na szybkość ługowania niklu z katalizatora KUB-3 aniżeli z RANG-19. Po 1 godzinie ługowania w temperaturze 60^oC w 3.0M HCl ekstrakcja niklu z katalizatora RANG-19 wynosi 74%, podczas gdy z katalizatora KUB-3 po 45 min wyługowania niklu wynosi 99%. Najwyższą wydajność ługowania niklu z obu katalizatorów bez dodatkowego rozdrobnienia (granulki 3-8 mm) uzyskano w 3.0M roztworze HCl, w temperaturze 60^oC przy stosunku fazy stałej do ciekłej 1/10. W powyższych warunkach ekstrakcja niklu z katalizatora KUB-3 wynosi 99% po 3 godzinach ługowania, natomiast 98% niklu wyługowano z katalizatora RANG-19 po 4 godzinach ługowania.

słowa kluczowe: zużyty katalizator, nikiel, ługowanie, kwas solny