

Comparative Analysis of the Efficiency of Molybdenum Trioxide Extraction from a Spent Hydraulic Catalyst

Elena Yu. Nevskaya^{1*}, Olga A. Egorova¹, Sergey P. Perekhoda²

¹⁾ *Peoples' Friendship University of Russia (RUDN University), Moscow, Russia*

²⁾ *Baikov Institute of Metallurgy and Materials Science, RAS, Moscow, Russia*

Abstract: The technological process uses catalysts containing oxide compounds of molybdenum, cobalt or nickel deposited on an alumina substrate. After a certain time, the activity of the components decreases and the unrecoverable spent catalysts usually become toxic waste. Technogenic residues are prohibited for disposal, and it is advisable to use the exhausted catalyst components for subsequent recycling. Recycling of industrial waste is a solution to an environmental problem. Processing should be organized with the extraction of valuable components, in particular expensive molybdenum oxide (VI). This work is devoted to finding ways to optimize the process of extracting molybdenum from spent hydrotreating catalysts.

Keywords: hydrotreating catalysts, molybdenum-containing catalysts, kinetic regularities

1. INTRODUCTION

Despite the periodic regeneration, the life of the hydrotreating catalysts is short. In the technological process, catalysts are used that represent a system of oxide compounds of molybdenum, cobalt or nickel deposited on an alumina support. After a certain time, the activity of the components decreases and spent catalysts that cannot be restored usually become toxic waste.

Technogenic residues are prohibited for burial, and it is advisable to use catalyst components that have exhausted their resource for subsequent recycling. Disposal or recycling of industrial waste is the solution to an environmental problem. Processing should be organized with the extraction of valuable components expensive molybdenum (VI) oxide [10,20].

At present, pyrometallurgical [1,13,25] and hydrometallurgical [2,11,17] methods have been developed, which make it possible to extract molybdenum and associated metals from spent catalysts.

Hydrometallurgical processes, in comparison with pyrometallurgical ones, pollute the environment less with harmful emissions and, most importantly, allow selective extraction of valuable metals.

According to various researchers, the highest degree of extraction of molybdenum by the hydrometallurgical method reaches from 80 to 95% [9,14,18,19]. For "wet" leaching, inorganic strong acids, aqueous solutions of ammonia or soda ash are used. However, the literature provides conflicting information on the carbonate extraction of molybdenum.

This work is a continuation of the search for optimal conditions for the selective extraction of molybdenum from spent molybdenum-containing hydrotreating catalysts.

The aim of this study is to comparatively study the kinetic regularities of the interaction of solutions of nitric acid (HNO₃) and sodium carbonate (Na₂CO₃) with a molybdenum-containing catalyst, as well as to determine the optimal conditions for extracting molybdenum from molybdenum (VI) oxide MoO₃.

* Corresponding author: nevskaya-eyu@rudn.ru

2. EXPERIMENTAL PART

The object of the study was the most common industrial catalyst for hydrotreating diesel fuel, GKD-205.

The spent aluminum-nickel-molybdenum (ANM) catalyst is cylindrical granules (2.0 × 4.0-7.0 mm) of blue, gray-brown and black color.

The active components of the GKD-205 catalyst are oxide compounds of d-metals of variable valence, resistant to poisoning with various poisons: molybdenum, nickel and other elements deposited on a substrate (matrix) of the low-temperature unstable modification γ -Al₂O₃. Durable high-purity alumina Al₂O₃ with optimal acid-base properties forms a specific porous structure of the catalyst and thus ensures the maximum content of molybdenum (VI) oxide MoO₃. Chemical analysis of the GKD-205 brand sample, carried out by atomic emission spectral analysis (AES) with inductively coupled plasma on an Ultima-2 optical emission spectrometer, showed a content of 6-12.2 wt% molybdenum (VI) oxide MoO₃; up to 3.14% of the mass promoter (nickel oxide NiO) and up to 88.02% of the mass aluminum oxide Al₂O₃. By means of X-ray diffraction analysis (X-ray powder diffractometer DRON-3M, CuK α - and CoK α -radiation) it was found that the spent catalyst matrix consists mainly of two modifications of aluminum oxide - α -Al₂O₃ and γ -Al₂O₃. Alumina Al₂O₃ is identified on diffraction patterns in the composition of nickel aluminates NiAl₂O₄, NiAl₂₆O₄₀ and sodium Na₂Al_{2x}O_{3x}, which have the closest cubic packing of the spinel type. Molybdenum and nickel are found in the oxide forms of molybdenum (VI) trioxide MoO₃ and nickel (II) oxide NiO, including in the spinel structures Al₂(MoO₄)₃, NiMoO₄, Na₂MoO₄. IR spectroscopic data in the range of 400-4000 cm⁻¹ were recorded on a SPECORD M-80 spectrometer and an AVATAR360 ESP Fourier spectrometer. Chemical analysis for the content of molybdenum in the spent hydrotreating catalysts was carried out in accordance with the procedure described in Standard 11930.11-79 [15].

The study of the leaching kinetics of the Mo-containing catalyst was carried out with solutions of nitric acid and sodium carbonate under isothermal conditions by sampling. A portion of 30 g of the spent ANM catalyst, crushed to a particle size of 0.5-1 mm, was loaded into a thermostatically controlled reactor with a volume of 200 cm³. The concentrations of nitric acid HNO₃ were (mol / l): 1.67, 3.54 and 5.62. The ratio of solid and liquid phases was 1: 5. The concentration of soda ash Na₂CO₃ was (mol / l): 0.498, 1.064 and 1.658. The ratio of solid and liquid phases was 1:10. The thermostatic reactor was kept at temperatures of 338 and 368 K. The dissolution time of the catalyst weighed portion was recorded from the moment of loading. The study was carried out in the free-floating mode of particles with continuous stirring of the reaction solution with an electric mixer. The mixer rotations were constant (650 rpm), and this allows us to assume that there are no external diffusion braking in the system.

At a certain time, interval, 1.0 ml samples were taken from the reaction mixture using a suction device with a filter attachment. The content of dissolved components in the samples was determined by inductively coupled plasma atomic emission spectral analysis on an Ultima-2 optical emission spectrometer with an accuracy of $\pm 2.0\%$.

3. RESULTS AND DISCUSSION

Based on the results of the experimental data, the fraction of dissolved molybdenum trioxide MoO₃ (α) was calculated according to the equation:

$$\alpha = \frac{G_1 \cdot V}{m \cdot C} \quad (1)$$

In this mathematical dependence:

C_l – concentration of molybdenum (VI) in solution, which was determined according to known methods [15-17];

V – volume of solution in the reactor, cm^3 ;

m – weight of the spent catalyst, g;

C – metal content in the spent catalyst, wt. fraction.

To describe the results from the standpoint of formal heterogeneous kinetics [4,7,21], the kinetic parameters were processed using the MathCAD 11 software using the nonlinear regression method. For this, the experimental data were presented in the form of the dependence of the degree of conversion of the solute (α) on time (τ) $\alpha = f(\tau)$ and described by the equation of the chain mechanism. This equation takes into account the formation of active centers (crystal lattice defects) on the surface of particles during dissolution (Fig. 1 (a; b)):

$$\alpha = 1 - \exp(- A \cdot \text{sh}(W_i \cdot \tau)) \tag{2}$$

Here:

α – the proportion of dissolved molybdenum (VI) oxide;

A – a constant proportional to the average number of active centers (the number of crystal lattice defects) on the surface of one particle of the spent catalyst;

W_i – dissolution rate constant, min^{-1} ;

τ – time, min.

To calculate the values of the constants A and W_i , the kinetic curves were rearranged in the coordinates $\alpha - \tau / \tau_{0.5}$: the degree of conversion of the solute (α) versus the reduced time ($\tau / \tau_{0.5}$) (Fig. 1).

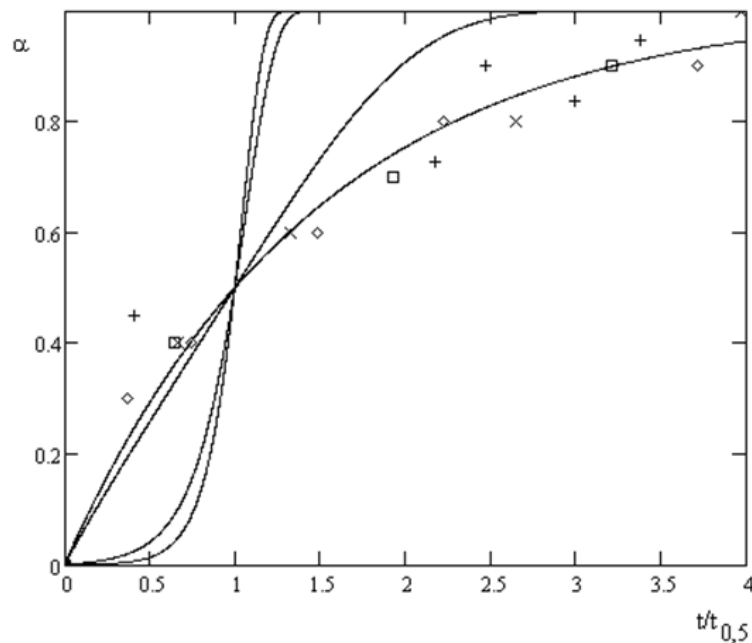


Fig. 1. Kinetic curves in the coordinates $\alpha - \tau / \tau_{0.5}$ for nitric acid HNO_3

From Fig. 1 it follows that, considering the error, all the experimental data fall on one curve, which indicates the invariance of the dissolution mechanism at different parameters of the solution. The plotted curve in the coordinates $\alpha - \tau / \tau_{0.5}$ was superimposed on the grid of theoretical curves of equation (2), which made it possible to determine the constant A of equation (2), equal to 5.

The results of processing the experimental data according to equation (2) are presented in table 1, which shows the values of the constant dissolution rate W_i .

Table 1. The rate constant of dissolution (W_i) in solutions of nitric acid and sodium carbonate, calculated according to equation (2), $A = 5$

T, K	$C (HNO_3),$ mol / l	W_i, min^{-1}	$C (Na_2CO_3),$ mol / l	W_i, min^{-1}
338	1,67	0,005	0,498	0,007
	3,54	0,008	1,064	0,007
	5,62	0,01	1,658	0,0075
368	1,67	0,01	0,498	0,013
	3,54	0,01	1,064	0,038
	5,62	0,019	1,658	0,088

To determine the order of the dissolution rate of molybdate (MoO_3) included in the spent catalyst, based on the concentration of nitric acid [HNO_3] and the concentration of soda ash [Na_2CO_3], the experimental data were expressed in coordinates $\log (W_i) - \log (C)$.

The order of the rate of dissolution of molybdate in a nitric acid solution in terms of HNO_3 concentration is 0.60 ± 0.03 . The order of the dissolution rate of molybdenum (IV) oxide in sodium carbonate solution in terms of Na_2CO_3 concentration is lower and equal to 0. The obtained values of the reaction orders with respect to the reagent lie in the range from 0 to 2, which allows us to conclude that the processes are proceeding in the kinetic region.

The calculation of the activation energy (E_{ACT}) was carried out according to the Arrhenius equation (3):

$$k = A \cdot \exp\left(-\frac{E_{ACT}}{R \cdot T}\right) \quad (3)$$

where

k – reaction rate constant, min^{-1} ;

E_{ACT} – activation energy, J / mol.

The activation energy (E_{ACT}) of the transition to a solution of nitric acid HNO_3 of molybdenum trioxide in the spent catalyst was 20.00 ± 0.1 kJ / mol, which indicates the progress of the process in the intermediate region. For sodium carbonate Na_2CO_3 solutions, the activation energy is in the range of $80.00 \div 120.00$ kJ / mol, which confirms the course of the dissolution process in the kinetic region.

With an increase in the concentration of mineral acid, the rate of transition of the oxide compound of molybdenum (VI) into the HNO_3 solution increases. The empirical equations describing the rate of release of the oxide compound of molybdenum (VI) from the aluminum-nickel-molybdenum catalyst into the solution of nitric acid HNO_3 (4) and into the solution of sodium carbonate Na_2CO_3 (5) have the form:

$$W_i (MoO_3) = W_0^1 [HNO_3]^{0,60 \pm 0,03} \cdot \exp\left(-\frac{20000}{RT}\right) \quad (4)$$

$$W_i (MoO_3) = W_0^1 [Na_2CO_3] \cdot \exp\left(-\frac{80000}{RT}\right) \quad (5)$$

where

W_0^1 – the constant of the specific dissolution rate: in nitric acid 0.090 ± 0.005 min^{-1} , and

in a solution of soda ash 0.20 ± 0.02 min^{-1} .

Thus, under these conditions, the rate of extraction of molybdenum by nitric acid solution is minimal. It depends only on the pH value of the solution and does not depend on the concentration of the nitrate anion.

Based on the data [8,22,23,24] describing the behavior of molybdenum (VI) in electrolyte solutions and the experimental data of this work, we have optimized the scheme [12,23]

showing the distribution of molybdenum-containing ions in electrolyte solutions at different pH values. This makes it possible to derive the dependence of the rate of dissolution of molybdate (MoO_3) on the concentration of nitric acid $[\text{HA}]$ and on temperature, which can be described by a Langmuir-type function. In general:

$$W_i = W_0^1 \cdot \left[\frac{[\text{HA}]}{[\text{HA}] + K_A} \right] \quad (6)$$

Surface concentration is expressed through the concentration of monobasic mineral acid, which coincides with the empirical relationship (4):

$$W_i = W^0 \cdot \left(\frac{C(\text{HNO}_3)}{C(\text{HNO}_3) + 0.090 \pm 0.005} \right) \cdot \exp(-38000/RT) = W^0[\text{HNO}_3]^{0.60 \pm 0.03} \quad (7)$$

where

W^0 – constant of the specific rate of dissolution, min^{-1} .

Influence of the pH of the medium on the number of acid-base centers on the surface of molybdate was established by the method of IR spectroscopy. Thus, the spectroscopic data show the presence in the selected aliquots of a compound of empirical composition MoO_2OHA , the transition of which into the solution limits the rate of dissolution. It is shown that the dissolution of MoO_3 and the transition of Mo^{6+} ions from the spent catalyst into the solution proceeds in a stepwise dependence on the pH of the solution. It was found that with an increase in the acidity of the solution, the number of active Lewis and Bronsted weakly basic and weakly acidic centers decreases symbatically with a decrease in the activity of the catalysts. The dissolution of molybdenum (IV) trioxide with an increase in the concentration of mineral acid (HNO_3) is associated with the formation of poorly soluble compounds of various compositions on the catalyst surface.

The rate of dissolution of MoO_3 , considering the influence of the concentration of sodium carbonate solution, was calculated based on the fact that the value of adsorption of Na^+ and carbonate ions on the surface is determined by the equation:

$$W = W^0 \cdot \left(\frac{C(\text{Na}_2\text{CO}_3)}{C(\text{Na}_2\text{CO}_3) + 0.2 \pm 0.02} \right) \cdot \exp(-80000/RT) = W^0[\text{Na}_2\text{CO}_3]^0 \quad (8)$$

Studies of the kinetics of soda decomposition of an aluminum-nickel-molybdenum catalyst for hydrotreating with solutions of different concentrations have confirmed that as the leaching duration and reagent concentration increase, the degree of molybdenum extraction naturally increases.

Based on the experimental results obtained on the solubility of molybdenum (VI) oxide in solutions with different pH values and kinetic data, the conclusion was clarified that in alkaline media, in comparison with acidic media, the dissolution of molybdenum (VI) oxide occurs deeper at lower concentrations of reagents.

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