

Kontsevoy A. L.

Igor Sikorsky Kyiv Polytechnic Institute

Kontsevoi S. A.

Igor Sikorsky Kyiv Polytechnic Institute

THE INFLUENCE OF DEPOSITION CONDITIONS ON THE ACTIVITY OF THE IRON-CHROME CATALYST

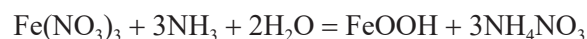
The article is devoted to optimization of technological parameters of the process of manufacturing a precipitated medium-temperature catalyst for steam conversion of carbon (II) oxide. A feature of the manufacture of an iron-chromium catalyst within the framework of this article is the use of a solution of iron and chromium salts obtained by leaching the spent catalyst with a solution of nitric acid. By draining the solution of nitrates and ammonia water, a precipitate is obtained – a mixture of iron and chromium hydroxides. To characterize the properties of the precipitate, the value of the specific resistance during filtration (SRF) was used, on which the filtration speed and the choice of filtration equipment depend. The aim of the work was determined: to study the dependence of the SRF of the precipitate, the specific surface area and the activity of the catalyst obtained from the precipitate on the precipitation parameters: the concentration of the salt solution, which is determined by the concentration of nitric acid Z_1 (from 20 to 40 %) during leaching of the spent catalyst, the concentration of ammonia water Z_2 (from 5 to 20 %) and the aging time of the precipitate Z_3 (from 3 to 90 minutes). Using the Excel LINEST function, a second-order equation was obtained, for example, to estimate the catalyst activity (rate constant): $K_{calc} = 0.91576 + 0.133555 \cdot Z_1 - 0.01079 \cdot Z_2 - 0.01529 \cdot Z_3 - 0.00253 \cdot Z_1^2 - 0.00063 \cdot Z_2^2 + 0.00012 \cdot Z_3^2$. Using the Excel Solver add-in, the optimal (maximum rate constant) conditions for precipitation were found: $Z_1 = 26.4$ %, $Z_2 = 5$ %, $Z_3 = 3$ min. A similar processing of experimental data was carried out for the specific surface area of the catalyst and the SRF of the precipitate. The calculation determined the conditions for the maximum specific surface area: $Z_1 = 21.9$ %, $Z_2 = 5$ %, $Z_3 = 3$ min. and the minimum specific resistance of the precipitate: $Z_1 = 20$ %, $Z_2 = 5$ %, $Z_3 = 27$ min. The obtained data indicate the need to use 20–26 % nitric acid when leaching the spent catalyst, 5 % ammonia water and the minimum aging time of the precipitate after precipitation. The closeness of the values of the optimal parameters Z_i for the three objective functions is confirmed by the close relationship between them: the pair correlation coefficients are in the range of 0.83–0.98. Taking into account the fact that the best dissolution of the spent catalyst occurs in 40 % acid, the resulting nitrate solution must be diluted twice before precipitation.

Key words: catalyst, activity, deposition, specific resistivity, specific surface area, mathematical model, optimal conditions.

Formulation of the problem. Modern ammonia production technologies involve a number of sequential processes, one of which is the steam conversion of carbon (II) oxide in two stages on medium- and low-temperature catalysts: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 + \text{Q}$.

Medium-temperature catalysts (MTC: up to 90 % Fe_2O_3 and up to 8 % Cr_2O_3) are prepared, as a rule, by the method of precipitation of iron carbonate or hydroxide from a solution of iron (II) sulfate with ammonium carbonate or ammonium hydroxide. Then the precipitate is filtered, a chromium compound is added, dried, calcined and formed. The service life of iron-chromium catalysts for CO steam reforming is up to 4 years. A feature of the manufacture of an iron-chromium catalyst within the framework of

this article is the use of a salt solution obtained by leaching spent MTC with a solution of nitric acid. By draining a solution of metal nitrates and ammonia water, a precipitate is obtained – a mixture of iron and chromium hydroxides:



Analysis of recent research and publications. Iron-chromium catalysts for steam conversion of CO are widely used in the production of process gas for ammonia synthesis. Physicochemical properties and technology of their production are given, for example, in manuals [1, p. 183; 2, p. 108]. The search for new methods of manufacturing MTC continues. Thus, method [3] involves the use of chlorides of starting

metals as raw materials. The deposition process largely determines the properties of the resulting catalyst. The main parameters that determine the properties of deposited catalysts are the temperature and pH of deposition, the concentrations of starting reagents, the aging time of the precipitate, the order and rate of reagent discharge. The authors of the article [4] investigated the influence of the pH of precipitation on the properties of the catalyst. It was found that at pH = 5 the specific surface area of chromium phosphate is 81 m²/g, at pH = 7 the specific surface area of chromium phosphate is 79 m²/g. An increase in pH to 9 leads to an increase in the specific surface area of chromium phosphate to 170 m²/g. In the work [5] the concentration parameters of the starting salts and the precipitant were determined: catalyst samples were prepared by co-precipitation from concentrated nitrate salts of zinc, chromium and copper with ammonium carbonate at pH = 7.1–7.4. The concentration of aqueous solutions was: zinc nitrate: 240–250 g/l; nitric acid chromium: 220–230 g/l; copper nitrate: 210–220 g/l; ammonium carbonate: 200–250 g/l. The properties of the obtained precipitate determine the quality of the catalyst. The influence on the filtration rate of the suspension is also important – the stage that determines the period of sediment dehydration and the type of equipment (vacuum filter or press filter). The properties of the precipitate are characterized by the specific resistance during filtration. The authors of [6] determined the value of the electrolyte dose to obtain a precipitate with a minimum specific resistance during filtration. The influence of the reagent concentration was studied in [7]. It was found that the specific resistance during filtration decreases with increasing CaCl₂ concentration. The authors [8] note that the accurate determination of the filtration rate of suspensions and the specific resistance of the filter cake layer as a function of pressure is a key factor for analyzing the efficiency of filtration operations. The study [9] of the filtration of calcium carbonate and talc minerals under different conditions of filtrate flow rate and suspension concentration presented a complete and understandable methodology for investigating the significance of the average resistance in subsequent filtration stages. The aim of the paper [10] was to study the filterability of sediments as a function of particle shape and particle size distribution. Different shapes of calcium carbonate and uranium oxalate particles (sphere, cube, needle and plate) were obtained by precipitation. The authors of [11] used well-known equations to calculate the specific volume resistance of the sediment as a function of the pressure drop during filtration.

Task statement. The purpose of the work was to study the dependence of the properties of the precipitate and the activity of the catalyst on the precipitation parameters: the concentration of the salt solution (determined by the concentration of nitric acid during leaching of the spent catalyst), the concentration of ammonia water, and the aging time of the precipitate.

Presentation of the main material. The starting solutions for the preparation of the catalyst were obtained by leaching the spent MTC catalyst with nitric acid. The kinetics of this process were considered by us in the article [12]. Previous experiments determined the rational conditions of precipitation: pH at the level of 7.2–7.6; temperature 353 K (80 °C); solution drain rate 200 cm³/min. In order to determine the influence of precipitation parameters on the properties of the precipitate and the catalyst obtained from it, the following precipitation parameters were adopted: nitric acid with a concentration of 20 % to 40 % (factor Z₁, table 1) was used to prepare the starting solutions of iron and chromium nitrate, the concentration of ammonia water was from 5 % to 20 % (factor Z₂, table 1), the aging time of the precipitate was from 3 to 90 minutes (factor Z₃, table 1). The kinetics of filtration of co-precipitated iron and chromium hydroxides was studied at a pressure drop of 0.043 MPa (330 mm Hg), the filter material was belting fabric. During the filtration process, the filtrate volume Q was recorded over time and the final sediment height h . After calculating the specific amount of filtrate (with a filter surface F , m²) $q = Q/F$ (m³/m²), a graph was constructed in the coordinates $\tau/q = f(q)$, where τ is the filtration time, seconds. A similar approach is described in the monograph [13, p. 45–46]. By processing the obtained straight line according to the well-known method of V.O. Zhuzhikov, the sediment resistance during filtration R and the average specific resistance of the sediment $r = R/h$ (sec/m²) were calculated. The catalyst was prepared from the sediment: washing, drying, calcination and molding. The specific surface area of the obtained catalyst S (m²/g) was determined by the BET method by adsorption of benzene vapor. The catalytic activity (rate constant K of the first-order equation, sec⁻¹) was determined on a flow-through installation at 623 K (350 °C) in the CO steam conversion reaction. The obtained experimental results are given in Table 1.

In order to describe the dependence of, for example, the rate constant on the deposition parameters by a second-order equation, the data in Table 1 are expanded in the form of Table 2. Using

Table 1

Conditions and results of experiments

№	Conditions			Results		
	Z_1	Z_2	Z_3	$r \cdot 10^{-6}$	S	K
1	40	20	90	27,56	23	1,4
2	40	10	90	8,91	28	1,63
3	30	15	45	5,04	36	1,9
4	20	10	90	3,56	36,5	1,95
5	40	20	3	8,97	27,5	1,65
6	20	20	3	3,37	37,5	2,05
7	40	10	3	4,91	37	2
8	35	5	3	1,11	42	2,4
9	30	10	3	1,02	42,5	2,42
10	20	13	3	0,89	42,5	2,35

the Excel LINEST function, the following equation was obtained:

$$K_{\text{exp}} = 0,91576 + 0,133555 \cdot Z_1 - 0,01079 \cdot Z_2 - 0,01529 \cdot Z_3 - 0,00253 \cdot Z_1^2 - 0,00063 \cdot Z_2^2 + 0,00012 \cdot Z_3^2. \quad (1)$$

The quality of the description is assessed by the deviation of the calculated values of the rate constant K_{calc} from the experimental K – the last column. The average deviation is 1.53 %.

According to equation (1), the optimal parameters (maximum rate constants) were determined using the Excel add-in “Solution Search”: $Z_1 = 26.4$ %, $Z_2 = 5$ %, $Z_3 = 3$ min., $K_{\text{opt}} = 2,57 \text{ s}^{-1}$.

To identify the dependence of the specific surface area of the catalyst on the deposition conditions, table 3 was created.

A dependence was obtained that describes the experimental data with an average deviation of 1.85 %:

$$S = 35,784 + 1,09788 \cdot Z_1 - 0,15623 \cdot Z_2 - 0,08468 \cdot Z_3 - 0,02511 \cdot Z_1^2 - 0,01785 \cdot Z_2^2 + 0,0000236 \cdot Z_3^2. \quad (2)$$

According to equation (2), the optimal parameters (maximum specific surface area) were determined using the Excel add-in “Solver Add-in”: $Z_1 = 21.9$ %, $Z_2 = 5$ %, $Z_3 = 3$ min, $S_{\text{opt}} = 46.3 \text{ m}^2/\text{g}$.

Similarly to the above, the filtration data for the specific resistance of the sediment were processed. Despite the low quality of the description of the obtained dependence, the optimal parameters (minimum specific resistance) were determined: $Z_1 = 20$ %, $Z_2 = 5$ %, $Z_3 = 27$ min.

Thus, the obtained data indicate the need to use 20–26 % nitric acid when leaching the spent catalyst,

Table 2

Matrix for calculating the coefficients of the second-order equation (objective function: rate constant)

№	Z_1	Z_2	Z_3	Z_1^2	Z_2^2	Z_3^2	K	K_{calc}	% dev.
1	40	20	90	1600	400	8100	1,4	1,34	4,13
2	40	10	90	1600	100	8100	1,63	1,64	0,56
3	30	15	45	900	225	2025	1,9	1,90	0,00
4	20	10	90	400	100	8100	1,95	2,00	2,50
5	40	20	3	1600	400	9	1,65	1,70	3,29
6	20	20	3	400	400	9	2,05	2,06	0,68
7	40	10	3	1600	100	9	2	2,00	0,06
8	35	5	3	1225	25	9	2,4	2,38	0,76
9	30	10	3	900	100	9	2,42	2,43	0,56
10	20	13	3	400	169	9	2,35	2,29	2,76

Table 3

Matrix for calculating the coefficients of the second-order equation (objective function: specific surface area)

№	Z_1	Z_2	Z_3	Z_1^2	Z_2^2	Z_3^2	S	S_{calc}	% dev.
1	40	20	90	1600	400	8100	23	21.83	5.08
2	40	10	90	1600	100	8100	28	28.75	2.67
3	30	15	45	900	225	2025	36	36.0	0.0
4	20	10	90	400	100	8100	36.5	36.92	1.15
5	40	20	3	1600	400	9	27.5	29.01	5.48
6	20	20	3	400	400	9	37.5	37.18	0.86
7	40	10	3	1600	100	9	37	35.92	2.91
8	35	5	3	1225	25	9	42	41.97	0.07
9	30	10	3	900	100	9	42.5	42.52	0.05
10	20	13	3	400	169	9	42.5	42.4	0.24

5 % ammonia water and a minimum aging time of the precipitate after precipitation. The closeness of the values of the optimal parameters for the three objective functions is confirmed by the close relationship between them: the pair correlation coefficients are in the range of 0.83–0.98. The results of the study [12] indicate better dissolution of the spent catalyst in 40 % acid. Therefore, the resulting nitrate solution must be diluted twice before precipitation.

Conclusions. The relationship between the specific resistance of the precipitate during

filtration, the specific surface area and the activity of the catalyst obtained from the precipitate with the precipitation conditions, namely the concentration of the starting solutions and the aging time, has been established and described by a second-order equation. The search method in Excel has found the optimal conditions for the precipitation process of a mixture of iron and chromium hydroxides, which ensure maximum catalyst activity and minimum specific resistance of the precipitate during filtration.

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Концевой А. Л., Концевой С. А. ВПЛИВ УМОВ ОСАДЖЕННЯ НА АКТИВНІСТЬ ЗАЛІЗО-ХРОМОВОГО КАТАЛІЗАТОРУ

Стаття присвячена оптимізації технологічних параметрів процесу виготовлення осажденного середньо температурного каталізатора парової конверсії карбону (II) оксиду. Особливістю виготовлення залізо-хромового каталізатора в рамках даної статті є використання розчину солей заліза і хрому, отриманого витруванням відпрацьованого каталізатора розчином нітратної кислоти. Зливом розчину нітратів і аміачної води отримують осад – суміш гідроксидів заліза і хрому. Для характеристики властивості осаду використано величину питомого опору при фільтруванні (ПОФ), від якої залежать швидкість фільтрування і вибір фільтрувального обладнання. Визначено

мету роботи: вивчення залежності ПОФ осаду, питомої поверхні і активності отриманого з осаду каталізатору від параметрів осадження: концентрації розчину солей, що визначається концентрацією нітратної кислоти Z_1 (від 20 до 40 %) при вилугуванні відпрацьованого каталізатору, концентрації аміачної води Z_2 (від 5 до 20 %) і часу старіння осаду Z_3 (від 3 до 90 хвилин). З використанням функції ЛІНЕЙН середовища Excel отримано рівняння другого порядку, наприклад, для оцінки активності каталізатору (константи швидкості): $K_{розр} = 0,91576 + 0,133555 \cdot Z_1 - 0,01079 \cdot Z_2 - 0,01529 \cdot Z_3 - 0,00253 \cdot Z_1^2 - 0,00063 \cdot Z_2^2 + 0,00012 \cdot Z_3^2$. За допомогою надбудови «Пошук рішення» середовища Excel знайдено оптимальні (максимум константи швидкості) умови проведення осадження: $Z_1 = 26,4 \%$, $Z_2 = 5 \%$, $Z_3 = 3$ хв. Аналогічна обробка експериментальних даних проведена і для питомої поверхні каталізатору та ПОФ осаду. Розрахунком визначено умови для максимальної питомої поверхні: $Z_1 = 21,9 \%$, $Z_2 = 5 \%$, $Z_3 = 3$ хв. та мінімального питомого опору осаду: $Z_1 = 20 \%$, $Z_2 = 5 \%$, $Z_3 = 27$ хв. Отримані дані свідчать про необхідність використання 20–26 % нітратної кислоти при вилугуванні відпрацьованого каталізатору, 5 % аміачної води і мінімального часу старіння осаду після осадження. Близькість значень оптимальних параметрів Z_i для трьох цільових функцій підтверджується тісним зв'язком між ними: коефіцієнти парної кореляції знаходяться в інтервалі 0,83–0,98. Враховуючи той факт, що краще розчинення відпрацьованого каталізатору відбувається у 40 % кислоті, отриманий розчин нітратів необхідно розбавляти вдвічі перед осадженням.

Ключові слова: каталізатор, активність, осадження, питомий опір, питома поверхня, математична модель, оптимальні умови.