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STUDY OF COMPOSITE CATALYSTS CONTAINING SLUDGE OF FERROALLOY PRODUCTION IN THE PROCESS OF CYCLOHEXANE OXIDATION

Abstract. Wastes from metallurgical production contain a significant amount of valuable elements such as iron, chromium, manganese, titanium, aluminum. The introduction of small and dispersed fractions in the smelting furnace leads to disturbances in the technological regime. Therefore, these wastes are accumulated in various types of storages. To increase the efficiency of the use of resources, it is necessary to utilize these wastes. The main ways of utilization are agglomeration, as well as the addition in building materials as additives. It is proposed to combine these ways with a new approach to utilization – the production of catalysts for processing hydrocarbon raw materials. We have obtained catalysts using sludge from the system of wet gas cleaning (WGCS) as an active phase and inorganic oxides Al_2O_3, SiO_2, ZnO as carriers. Elemental analysis has shown significant presence of chromium – 6-12% and iron 1.5-3.2% (5.7% in initial WGCS). Mn was found in trace amounts in clear WGCS. Surface analysis has shown significant increasing in value of specific surface approximately in two times in case of using SiO_2 as a carrier. So, it was shown that using of carriers of various nature can lead to change some surface properties in given direction. In the studied process of cyclohexane oxidation over the obtained catalysts in the given conditions (temperature - 40 °C, the reaction duration - 240 min) the conversion of cyclohexane achieved 6-9%. Finally, it was found that there is a notable dependence between the value of specific surface and catalytic activity of studied samples.
Keywords: cyclohexane, oxidation, ferroalloys, waste, catalyst.

Introduction

It is known, that approximately 700 million tons of industrial waste are produced in Kazakhstan every year. According to the Ministry of environmental protection, «in our country more than 22 billion tons of waste are accumulated. More than 16 billion tons from them are technogenic mineral concretion and about 6 billion tons are dangerous waste» [1].

The problem of industrial waste utilization is actual not only for Kazakhstan, but for the wide range of other countries, which has developed industry [2]. The waste of metallurgical industry have great importance because of content. It is known, that a number of valuable elements, especially transitional metals, such as chromium, iron, manganese, vanadium, titanium are in the content of ashes and slimes of metallurgical industry. The content of some of these elements in metallurgical waste achieves such level, that waste storages can be considered as a secondary mine for mining of these valuable metals.

Utilization of metallurgy industry waste is necessary for creation of a closed-loop production with maximal economic and ecological efficiency [3]. A closed-loop production in metallurgy is mainly based on using of the waste in building materials production [4]. However, the valuable elements presented in the waste are used without enough effectiveness at production of building materials. It is much more effective to obtain catalysts from that kind of waste.

At ferroalloy plants, ferromanganese, ferrosilicon, ferrochromium are produced. Industrial products determine the composition of waste. Thus, in sludge of ferroalloys production, significant amounts of manganese and chromium are contained in addition to iron [5]. These elements are catalytically active and are included in the active phases of many catalysts [6-10]. Waste of aluminum production besides iron compounds also contains valuable components - aluminum and titanium. These metals are also actively involved in catalytic processes [11-14].

The preceding discussion points that utilization of industrial waste of ferroalloy plant by obtaining of catalysts for various chemical processes is a prospective and actual way. We have researched the wastes of ferroalloy plants of Kazakhstan (Aksu ferroalloy plant, Aktobe ferroalloy plant). In our work, we offer another way of utilization of ash and sludge wastes of ferroalloy production – obtaining of catalysts for various processes of hydrocarbon-containing raw materials refining. The way is characterized by high economic efficiency because it is offered not just to utilize the waste, but obtain on their basis of new profitable product.

Experimental

Preparation of catalysts. Samples of wet gas cleaning sludge (WGCS) were dried in drying oven at the temperature of 100 °C within 1 hour and grinded in a mortar. Composite catalysts were prepared based on WGCS and oxides: Al_2O_3, SiO_2, ZnO. To obtain a catalyst of the type WGCS/X, where X is the carrier we took sample of WGCS – 1,0 g, sample of carrier – 1,0 g, then placed it in a weighing bottle with a ground cover, poured 10 ml. of distilled water and stirred for 3 hours. After mixing, excess water was poured off, the remaining suspension was air dried for 24 hours.

Elemental analysis. Analysis was performed using energy dispersive x-ray fluorescence spectroscopy with energy dispersive system for microanalysis INCA Energy 450, set on scanning electron microscope JSM-6610LV ("JOEL", Japan). Spectra were obtained three times with calculation of average value.

The surface investigation. The surface investigation was performed by low-temperature nitrogen adsorption using method BET on "AccuSorb" unit ("Micromeritics", USA). A charge of sample (0.1 g) was placed in a special vial, then vacuumed at 200 °C within 3 – 4 hour. The definition of the surface of a catalyst was performed with measurement of nitrogen adsorption at the temperature of –196 °C. Calculation of porosity by isotherms of nitrogen adsorption and desorption in the pores of the sample was performed with kit software.

Cyclohexane oxidation

The oxidation of cyclohexane was carried out on the installation, composed from magnetic stir, thermostatic three-neck glass reactor and volumetric burette. Acetonitrile as a solvent (1.2 ml), sample of catalyst (0.03 g), cyclohexane (0.3 ml), and hydrogen peroxide (0.9 ml of 30% aqueous solution) as an oxidant were consistently placed into the reactor. Stirring of reaction mixture was conducted using magnetic stir. Temperature - 40 °C. The pressure - atmospheric. Duration of the reaction – 240 minutes.

Chromatographic analysis

Reaction products were analyzed using GLC. Analysis was carried out on chromatograph Chromos GC-1000 (Russia).

Results and discussion

Elemental analysis of catalysts showed redistribution of elemental composition with characteristic increase of containing of elements dominating in supporter in comparison with initial sample of WGCS

(Tables 1-4). Catalyst WGCS/Al_2O_3 shows increased containing of aluminium, WGCS/SiO_2 – silicon, WGCS/ZnO – zinc. The results are quite natural. As well in the case of supported catalysts in comparison with the initial WGCS some elements, presented in small amounts (Zn, Mn, S, K), are disappeared. This can be explained by the sensitivity of the device to the elements present in negligible concentrations.

Table 1 – Results of elemental analysis of WGCS

	Containing of element (wt.%)												
	C	O	Mg	Al	Si	S	K	Ca	Cr	Mn	Fe	Zn	Total
Spectrum 1	15.55	31.84	29.35	1.32	7.15	1.22	0.08	0.29	6.95	0.30	5.73	0.22	100.00
Spectrum 2	15.42	32.68	29.58	1.21	7.25	1.25	0.11	0.34	6.23	0.21	5.52	0.21	100.00
Spectrum 3	14.62	31.94	29.90	1.09	7.35	1.21	0.08	0.34	7.05	0.28	5.85	0.27	100.00
Average	15.20	32.15	29.61	1.21	7.25	1.23	0.09	0.32	6.74	0.26	5.70	0.23	100.00

Table 2 – Results of elemental analysis of catalyst WGCS/Al_2O_3

	Containing of element (wt.%)							
	O	Mg	Al	Si	Ca	Cr	Fe	Total
Spectrum 1	40,67	5,59	36,70	3,26	0,15	10,84	2,80	100,00
Spectrum 2	38,06	7,97	27,46	3,32	0,35	18,27	4,57	100,00
Spectrum 3	41,53	7,97	33,40	5,59	0,25	8,92	2,35	100,00
Average	40,08	7,17	32,52	4,06	0,25	12,68	3,24	100,00

Table 3 – Results of elemental analysis of catalyst WGCS/SiO_2

	Containing of element (wt.%)							
	O	Mg	Al	Si	Ca	Cr	Fe	Total
Spectrum 1	44,77	5,98	1,00	35,54	0,30	9,68	2,72	100,00
Spectrum 2	47,15	5,00	0,68	38,03	0,20	6,88	2,06	100,00
Spectrum 3	45,86	6,42	0,99	34,65	0,15	9,42	2,51	100,00
Average	45,92	5,80	0,89	36,07	0,22	8,66	2,43	100,00

Table 4 – Results of elemental analysis of catalyst WGCS/ZnO

	Containing of element (wt.%)								
	O	Mg	Al	Si	Ca	Cr	Fe	Zn	Total
Spectrum 1	22,86	6,10	1,01	2,25	0,12	7,51	1,82	58,33	100,00
Spectrum 2	22,01	5,44	0,82	2,13	0,14	5,12	1,57	62,78	100,00
Spectrum 3	22,53	6,75	0,95	2,77	0,24	5,44	1,52	59,79	100,00
Average	22,47	6,10	0,93	2,39	0,16	6,02	1,64	60,30	100,00

The surface investigation

Results of analysis are shown in figures 1-4. Calculated values of pore volume and specific surface are given in table 5.

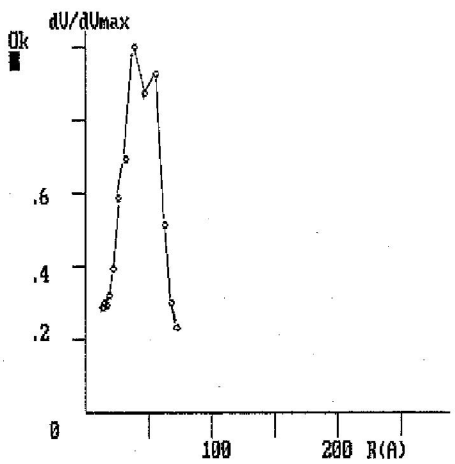

Figure 1 – BET analysis of WGCS

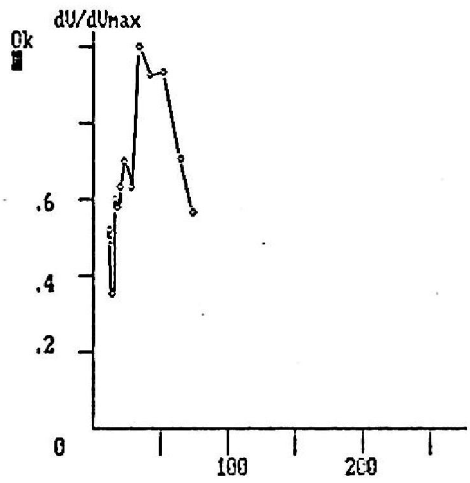

Figure 2 – BET analysis of catalyst WGCS/SiO_2

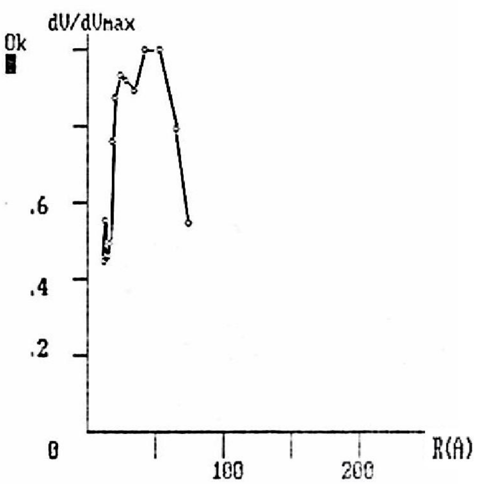

Figure 3 – BET analysis of catalyst WGCS/Al_2O_3

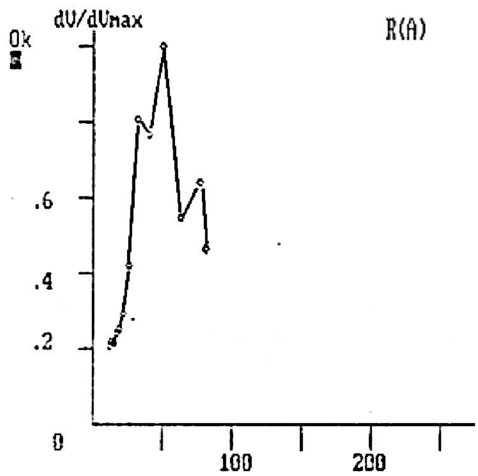

Figure 4 – BET analysis of catalyst WGCS/ZnO

Table 7 – Results of BET method analyses of composite catalysts based on FPW

Sample	Total pore volume $V_{ads\ max}$, ml/g	Specific surface S_W, m^2/g
WGCS	149,19	23,81
WGCS/ZnO	89,45	17,55
WGCS/Al_2O_3	155,88	43,58
WGCS/SiO_2	166,04	56,08

Thus, as a result of comparing analysis of composite catalysts with activy phase – WGCS it was found significant increase in surface properties when using as a supporter aluminium and silicon oxides. Using WGCS as an active phase of composite catalyst it is possible to improve structural properties of developed catalyst.

Cyclohexane oxidation

Powder catalysts WGCS/ZnO, WGCS/Al_2O_3, WGCS/SiO_2 were tested in the reaction of liquid phase oxidation of cyclohexane with hydrogen peroxide. In the process cyclohexanone (C-one) and cyclohexanol (C-ol) are produced.

When using powdered composite catalysts based on WGCS and inorganic oxide carriers as catalysts in the given conditions, the conversion of cyclohexane as well as selectivity of the process was sufficiently low. However, it has been observed that catalysts using silica and aluminum oxides as a carrier showed higher activity in this process than the catalyst containing zinc oxide. This result agrees with the results of the investigation of surface properties obtained by the BET method. The BET method has shown that when using SiO_2 and Al_2O_3 as carriers, the total pore volume and the specific surface area are significantly higher than when using ZnO. Thus, in this example, the dependence of the activity of the catalyst on its surface properties is clearly traced. Low yields of products may be due to the fact that during the preparation of this type of catalysts, high-temperature catalyst treatment has not been carried out, which, as previously shown [15], leads to an increase in the porosity and specific surface area of the catalyst. Therefore, this process appears to have a significant activating effect on the catalyst. The results of the experiments are given in Table 8.

Table 8 – The results of the oxidation of cyclohexane with hydrogen peroxide on powdered catalysts, based on the wet gas cleaning sludge of ferroalloy production

№	Catalyst	Products		Conversion, %	Selectivity, %
		C-one, %	C-ol, %		
1	WGCS /SiO_2	4,9	4,4	9,3	S_{C-one}–52,7 S_{C-ol} –47,3
2	WGCS /Al_2O_3	3,8	4,8	8,6	S_{C-one}–44,2 S_{C-ol} –55,8
3	WGCS /ZnO	3,7	2,3	6,0	S_{C-one}–61,7 S_{C-ol} –38,3

Conclusion

Thus, we have obtained catalysts using waste of ferroalloy production – sludge from the system of wet gas cleaning – as an active phase and inorganic oxides Al_2O_3, SiO_2, ZnO as supporters. Elemental analysis has shown significant presence of chromium – 6-12% and iron 1.5-3.2% (5.7% in initial WGCS). Mn was found in trace amounts in clear WGCS. Surface analysis has shown significant increasing in value of specific surface approximately in two times in case of using SiO_2 as a carrier. So, it was shown that using of carriers of various nature can lead to change some surface properties in given direction. In the studied process of cyclohexane oxidation over the obtained catalysts in the given conditions (temperature - 40 °C, the reaction duration - 240 min) the conversion of cyclohexane achieved 6-9%. Finally, it was found that there is a notable dependence between the value of specific surface and catalytic activity of studied samples.

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ФЕРРОҚОРЫТПА ӨНДІРІСІНІҢ ҚАЛДЫҚТАРДАН ҚҰРАСТЫРЫЛҒАН КОМПОЗИТТІК КАТАЛИЗАТОРЛАРДЫ ЦИКЛОГЕКСАН ТОТЫҒУЫ ПРОЦЕСІ НЕГІЗІНДЕ ЗЕРТТЕУ

Аннотация. Металлургия өндірісінің қалдықтары темір, хром, марганец, титан, алюминий сияқты пайдалы элементтерден бірқатар мөлшерінде құрастырылған. Ұсақ және дисперстік фракцияларды қорыту пештерге енгізуі технологиялық тәртібін бұзуына келтіреді. Сондықтан, осы қалдықтары әртірлі қоймаларда жиналып қалады. Ресурстар қолдану тиімділігін көтеру үшін осы қалдықтарды кәдеге жарату керек. Агломерация және құрылыс материалдырға қосымшалар ретінде қолдануы кәдеге жаратудын басты жолдары боп есептеледі. Кәдеге жарату үшін осы жолдарды жаңа көмірсутекті шикізат ұқсату үшін катализаторларды дайындау тәсілімен қиыстыруға ұсыныс жасалып тұр. Біз сулы газдан тазалау (СГТ) жүйесінен алыңған қалдықтарды қолдану арқылы активтік фаза ретінде катализатор дайындадық және Al_2O_3, SiO_2, ZnO органикалық емес оксидтерді тасушы ретінде дайындадық. Элементтік талдыуы хромдін 6-12 % маңызды мазмұнын, темірдің 1,5-3,2% (алғашқы СГТ-да 5,7%) мазмұнын көрсетті. Алғашқы СГТ-да Mn іздік құрамында табылған. Сыртқы талдауы меншікті беттін маңызды көбеуінің көрсетті, мысалы, екі есе көбеуі SiO_2 тасушы ретінде пайдалынған кезде көрсетілінген. Сонымен, әрлүрлі табиғатты тасушыларды қолдануы кейбір сырттын қасиеттерінің берілген бағытта өзгеруіне әкелу мүмкін. Зерттелген циклогексан тотығуы процесінін дайындалынған катализаторлар бойынша берілген шарттарымен (температурасы - 40 ° С, реакцияның ұзақтылығы - 240 мин) циклогексаннын конвериясы 6-9% жетті. Ақыр аяғында, меншікті беттін көлемінін және зерттелген үлгілердің каталикалық белсенділігінін арасында маңызды тәуелділік бар боп табылған.

Кілт сөздер: циклогексан, тотығуы, ферроқорытпа, қалдықтар, катализатор.

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ИЗУЧЕНИЕ КОМПОЗИТНЫХ КАТАЛИЗАТОРОВ СОДЕРЖАЩИХ ШЛАМ ФЕРРОСПЛАВНОГО ПРОИЗВОДСТВА В ПРОЦЕССЕ ОКИСЛЕНИЯ ЦИКЛОГЕКСАНА

Аннотация. Отходы металлургического производства содержат значительное количество ценных элементов, таких как железо, хром, марганец, титан, алюминий. Введение мелких и дисперсных фракций в печи выплавки приводит к нарушениям технологического режима. Поэтому эти отходы накапливаются в хранилищах различного типа. Для повышения эффективности использования ресурсов необходимо утилизировать эти отходы. Основные пути утилизации это агломерация, а также введение в строительные материалы в качестве добавок. Предлагается комбинировать эти пути с новым подходом к утилизации - получением катализаторов для переработки углеводородного сырья. Мы получили катализаторы с использованием шлама из системы мокрой газоочистки (ШМГ) в качестве активной фазы и неорганических оксидов Al_2O_3, SiO_2, ZnO в качестве носителей. Элементный анализ показал значительное присутствие хрома - 6-12% и железа 1,5-3,2% (5,7% в исходном ШМГ). Mn был обнаружен в следовых количествах в исходном ШМГ. Поверхностный анализ показал значительное увеличение удельной поверхности, примерно в два раза, в случае использования SiO_2 в качестве носителя. Таким образом, было показано, что использование носителей различной природы может привести к изменению некоторых свойств поверхности в заданном направлении. В изученном процессе окисления циклогексана по полученным катализаторам в данных условиях (температура - 40 ° С, продолжительность реакции - 240 мин) конверсия циклогексана достигала 6-9%. В конечном счете, было обнаружено, что существует заметная зависимость между величиной удельной поверхности и каталитической активностью исследованных образцов.

Ключевые слова: циклогексан, окисление, ферросплавы, отходы, катализатор.

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