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The Manufacturing and Use of Catalysts for Petrochemistry: The State of the Art and Problems[1]

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Abstract—The present state of the art in the manufacturing of catalysts for petrochemistry is discussed. The problems of provision with feedstock and equipment are considered. Examples are given for the relationship between the nature and purity of starting materials and the performance characteristics and service life of catalysts for hydrocarbon dehydrogenation.

INTRODUCTION

Catalytic processes play an important role in the manufacturing of many petrochemical products, including monomers for synthetic rubber and plastics. For this purpose, many Russian plants produce various dehydrogenation catalysts.

The OAO Research Institute Yarsintez (Yaroslavl) produces the following catalysts:

– The ferrite catalyst K-28 for styrene synthesis;

– The iron-containing catalyst K-28MKh for α-methylstyrene synthesis;

– The iron–nickel catalyst K-32 for divinylbenzene synthesis; and

– The aluminum–chromium SPS new-generation catalyst for the dehydrogenation of C_2–C_{20} alkanes to alkenes in a fluidized bed.

In addition to this list, Yarsintez produces the chromium-containing catalyst IM-616 for the complete oxidation of organic detrimental impurities.

The OAO Kauchuk (Sterlitamak) produces the following catalysts:

– The iron–chromium K-24I and phosphate IM-2204 catalysts for the synthesis of diene hydrocarbons by olefin dehydrogenation and

– The aluminum–chromium IM-2201 catalyst for alkane dehydrogenation.

The OAO Nizhnekamskneftekhim (Nizhnekamsk) produces the iron-containing catalyst KIM for isoprene synthesis. The OAO Novokuibyshevskii Petrochemical Plant produces the aluminum–chromium catalyst IM-2201 for the dehydrogenation of alkanes.

[1] Proceedings of the IV Russian Conference on Scientific Bases for Catalyst Preparation and Technology (Sterlitamak, August 29–September 1, 2000).

CATALYSTS FOR THE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS

The most efficient catalysts for the dehydrogenation of alkylaromatic hydrocarbons are based on iron oxides promoted with alkali metals (K-28, K-28MKh, K-24PM, K-32, and others).

Figure 1 shows data on the production of catalysts (all trademarks account) for the dehydrogenation of alkylaromatic hydrocarbons in 1994–1999. The low production in 1996–1997 is explained by a general

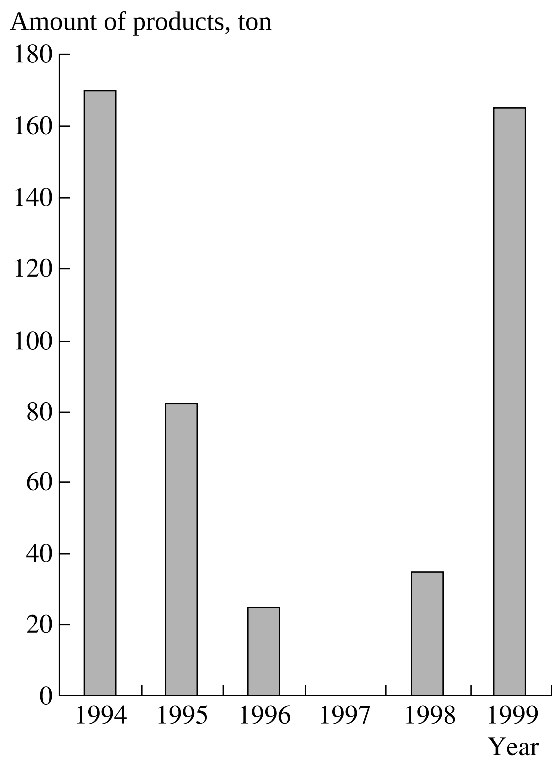

Fig. 1. Productions of catalysts for the dehydrogenation of alkylaromatic hydrocarbons in 1994–1999.

downswing in industrial production in Russia. Since 1998, some revival was seen in the manufacturing of vinylaromatic monomers and this created demand for dehydrogenation catalysts. A positive trend in the catalyst and monomer manufacturing has been anticipated for the year 2000.

The highly efficient ferrite catalyst K-28 for ethylbenzene dehydrogenation (and its modification K-28Ts) is actively used in the synthesis of styrene. The K-28 and K-28Ts catalysts are used at several plants in Russia. K-28 is competitive with the best foreign analog in all performance characteristics [1]. Table 1 shows data on the performance of commercial catalysts in Russia and Kazakhstan.

Recently, the OAO Yarsintez developed a new catalyst for the dehydrogenation of alkylaromatic hydrocarbons that is capable of working at a lower concentration of steam compared to K-28 (half the weight concentration) and providing the same catalytic activity as K-28 at dehydrogenation temperatures of 586–640°C, which are 5–10°C lower than the operating temperature of K-28 (Fig. 2).

Before the 1990s, the iron oxide K-22 and KNS catalysts were used for the process of isopropylbenzene dehydrogenation. Currently, the K-28MKh catalyst is used instead of them. Table 2 shows the performance characteristics of different catalysts in α-methylstyrene synthesis. It can be seen that the K-28MKh catalyst is the best one.

For the process of divinylbenzene synthesis by ethylbenzene dehydrogenation, the OAO Yarsintez developed a highly efficient iron–nickel catalyst K-32. It was

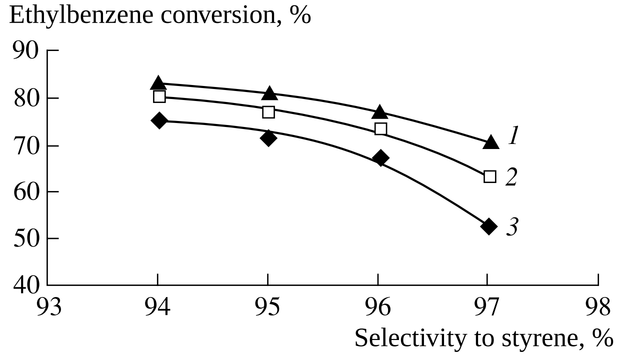

Fig. 2. Tests of the new domestic catalyst in ethylbenzene dehydrogenation to styrene at (*1*) 0.5; (*2*) 0.7; and (*3*) 1.0 atm at T = 580–640°C.

tested at the AOOT Omis (Omsk) and has been used since 1998 at the OAO Azot (Cherkassy). Table 3 compiles data on the yield of diethylbenzene dehydrogenation products on the K-32 catalyst compared to analogous data for other domestic and foreign catalysts.

In the late 1980s, the OAO Yarsintez developed and tested the K-24PM catalyst for methylethylpyridine dehydrogenation to methylvinylpyridine. Unfortunately, the manufacturing of methylvinylpyridine in Omsk was shut down during the general downswing in industrial production, and the catalyst is not produced now.

CATALYSTS FOR OLEFIN DEHYDROGENATION

For the process of butene dehydrogenation to butadiene at the OAO Kauchuk (Sterlitamak), the iron–

Table 1. Characteristics of catalysts for ethylbenzene dehydrogenation in industrial reactors at different plants

Characteristic	Plastic Plant in Shevchenko (Kazakhstan)		OAO Neftekhimik in Perm		OAO Angarskaya Neftekhimicheskaya Komapaniya						
	Catalyst										
	G-64C		K-28Ts		K-28Ts		K-28				
Operation time, h	200	4000	200	4000	200	4000	200	4000	8000	12000	16000
Temperature over the catalyst bed, °C											
1st stage	615	620	610	621	603	612	603	602	603	607	614
2nd stage	625	647	621	626	600	604	596	597	602	605	615
Ethylbenzene conversion, %	52.4	50.3	55.4	55.0	55.1	54.7	57.1	56.3	55.6	54.1	54.7
Selectivity to styrene, %	88.7	89.0	91.0	91.3	91.5	91.6	92.6	92.4	92.8	93.0	92.7

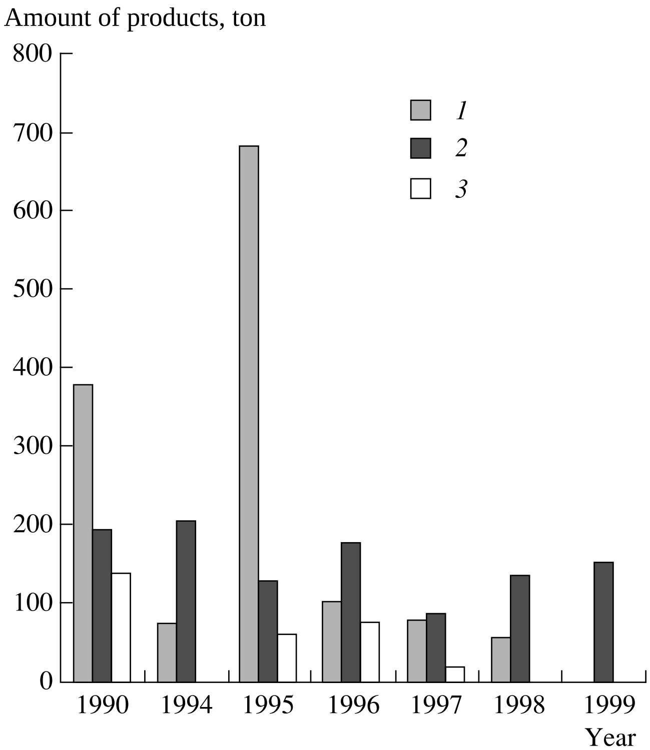

Fig. 3. Production of (*1*) IM-2204, (*2*) K-24I, and (*3*) K-16U4 catalysts in 1993–1999.

chromium–zinc catalyst K-16U was produced before 1998. It worked in short dehydrogenation–regeneration cycles. Currently, this catalyst is not produced because of the generally unfavorable situation in economy, and the plants for butene dehydrogenation are shut down.

The OAO Kauchuk uses the chromium–nickel–phosphate catalysts developed at the OAO Yarsintez for isoamylene dehydrogenation to isoprene: IM-2204 and IM-2204M, which work in short dehydrogenation–regeneration cycles. The iron–chromium K-24I catalyst is also used, which works for long periods without recovery. It requires periodical treatment with steam at 650°C after each 200–500 h of uninterrupted operation. OAO Nizhnekamskneftekhim uses the iron oxide catalyst KIM for the dehydrogenation of isoamylenes. This company produces this catalyst.

Comparison of the catalysts K-24IU and K-28 with catalysts from Shell and Girdler under the same conditions at the laboratory-scale setup at the OAO Yarsintez suggests that domestic catalysts are competitive with the best foreign analogs [2].

Figure 3 shows data on the production of catalysts at the AO Kauchuk (Sterlitamak) for the last few years.

CATALYSTS FOR OLEFIN DEHYDROGENATION BY HYDROCARBONS IN FLUIDIZED BED

Currently, there are four commercial processes of olefin manufacturing worldwide: Oleflex (UOP), Catofin (ABB Lummus Crest), Star (Phillips Petroleum), and FBD (OAO Yarsintez–Snamprodgetti Spa). Table 4 shows the characteristics of these processes. Data on the performance of the Star unit is unavailable.

The process of olefin manufacturing by alkane dehydrogenation in the fluidized bed of the aluminum–chromium catalyst was developed at the NIIMSK (now known as the OAO Yarsintez) and it has been working in the industry since the 1960s. Over 37 industrial units were constructed for the dehydrogenation of isobutane, *n*-butane, and isopentane to produce ~2 million ton of olefins annually. Only 12 dehydrogenation blocks work now for isobutene and isoamylene production.

This process has several advantages over known commercial methods for olefin manufacturing:

– Lower capital costs;

– Permissibility of substantial (up to 50%) variations in the product flows;

– Dehydrogenation and catalyst regeneration separated in different apparatus that enhances process safety;

– The catalyst also plays the role of a heat-transfer agent, which makes the process more economical; etc.

The main catalyst used in Russia is the aluminum–chromium IM-2201 catalyst. Its production volumes are shown in Fig. 4. The main drawback of this catalyst is its high specific expenditure.

Table 2. Performance characteristics of the catalysts K-28MKh, K-22 and KMS in industrial reactors for isopropylbenzene dehydrogenation to α-methylstyrene

Catalyst	Space velocity, h^{-1}	Temperature in the catalyst bed, °C (top/bottom)	Product concentration, wt %	
			α-methylstyrene	styrene
K-28MKh	0.50–0.60	590/540	55–60	1.1–1.5
K-22	0.35–0.45	600/560	45–50	1.5–2.0
KMS	0.35–0.45	600/560	45–52	1.6–2.2

Collaborative research of the OAO Yarsintez and Snamporgetti Spa (Italy) led us to design a new-generation catalysts that have high mechanical strength, chemical and thermal stability and provide high catalytic performance characteristics in C_3–C_4 alkane dehydrogenation. Catalyst expenditure decreased by a factor of ~30 compared to the analogous IM-2201 catalyst. Comparison of the results of tests of the IM-2201 and SPS at the demonstration setup at the OAO Yarsintez and the industrial-scale setup at the ZAO Ekooil (Omsk) pointed to an advantage of the new catalyst over old ones (Table 5).

The process for isobutane dehydrogenation over aluminum–chromium SPS catalyst was improved by the OAO Yarsintez and Snamprodgetti [3] and carried out at

– A demonstration setup in Yaroslavl for 1 year (~2000 ton of isobutylene per year);

– An industrial-scale setup in Omsk (~80000 ton of isobutylene per year);

– An industrial-scale setup in Al Jubail (Saudi Arabia, ~450000 ton of isobutylene per year); the characteristics of its operation are listed in Table 5.

Taking into account a growing interest in propylene, a new SPP catalyst was prepared by modifying the SPS catalyst for propane dehydrogenation. The SPP catalyst showed a high mechanical strength and stability of the chemical composition. These properties made this process competitive in the world market. At the demonstration setup in Yaroslavl, the following characteristics were obtained for propane dehydrogenation using this catalyst:

– Conversion, 35–37%;

– Selectivity to propylene, 85–87%;

– Catalyst expenditure, 0.6–0.9 kg/ton propylene.

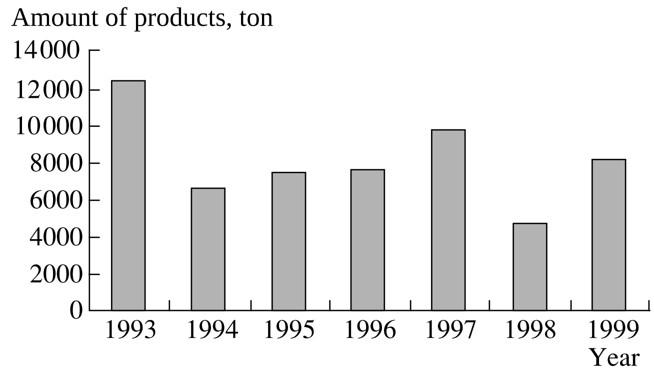

Fig. 4. Production of the IM-2201 catalyst in 1993–1999.

Table 3. Dehydrogenation of diethylbenzene (DEB) and divinylbenzene (DVB) on domestic and foreign catalysts (space velocity, 1.0 h^{-1}; steam dilution ratio based on weight, 1 : 5; 600°C)

Catalyst	Product yield, wt %				DEB conversion, %
	DVB*	EVB*	DVB**	DVB + EVB**	
KMS	24.1	31.6	37.6	87.0	64.1
KS-4***	25.7	30.8	36.9	88.5	69.7
K-22	23.8	30.3	36.0	81.9	66.1
K-24***	31.9	29.8	42.0	81.3	76.0
K-24PM	29.7	31.3	41.8	85.1	71.5
K-28Ts	26.4	30.9	39.4	85.6	67.0
K-32	32.5	30.7	44.6	87.8	74.4
Shell-105	30.3	32.0	40.7	83.7	74.4
Shell-205	14.2	29.5	29.6	90.7	48.0
Shell-305	18.5	29.6	35.7	93.3	51.8
G-64C	29.0	33.3	41.8	89.8	69.4
G-84BX	31.7	33.4	42.7	87.6	74.2

Notes: * The yields of DVB and ethylvinylbenzene (EVB) based on DEB.
** The yields of DVB and DVB + EVB based on decomposed DEB.
*** Out-of-production catalysts produced at the Sterlitamak Synthetic Rubber Plant before 1991.

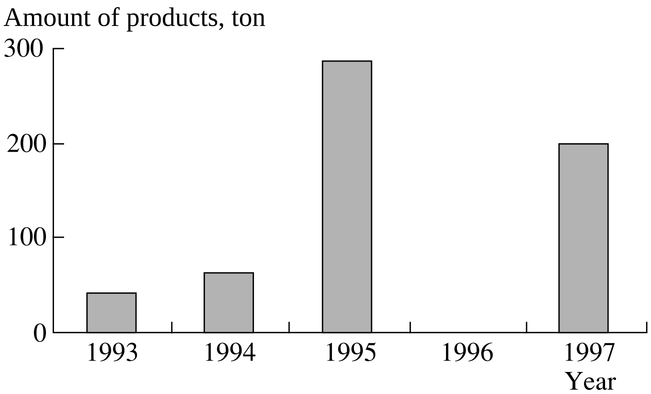

Fig. 5. Production of the SPS catalyst in 1993–1999.

In Russia, the relatively high cost of catalysts, which is only important for the initial filling of the dehydrogenation system, prevents new domestic catalysts from being put into exploitation. At the same time, foreign companies often practice dumping when selling their catalysts to Russian plants in order to knock Russian products out from the domestic catalyst market. Some time ago, Montecatini (Italy) sold a styrene catalyst MST to the AO Nizhnekamskneftekhim. Currently, the AO Nizhnekamskneftekhim purchases isobutane dehydrogenation catalyst from Engelhard although this catalyst is worse than the SPS catalyst.

SPS is produced in Russia in small amounts (Fig. 5). For the unit in Saudi Arabia, the SPS catalyst is produced by Topsoe in Houston (USA) as agreed by the OAO Yarsintez and Snamprogetti. About ~2500 ton of this catalyst was produced for the last three years.

The OAO Yarsintez constructed a unit for the catalyst manufacturing capable of supplying the catalysts to all units operating in Russia.

Table 4. Comparison of different isobutylene synthesis processes

Characteristic	Process		
	Catofin	Oleflex	FBD-4
Productivity based on isobutylene, ton/h	30.6	31.9	31.9
Capital investment, $ million	52.0	44.1	34.3
Specific cost of production, $/ton	365.4	350.9	346.0
Isobutane consumption, ton/ton isobutylene	1.16	1.14	1.14

CATALYST FOR THE COMPLETE OXIDATION OF ORGANIC ADMIXTURES IN EXHAUST GAS

The OAO Yarsintez developed a highly efficient chromium-containing catalyst IM-616 for the complete oxidation of detrimental impurities. The catalyst does not contain noble metals. Table 6 shows the degree of exhaust gas purification from some organic admixtures on this catalyst depending on temperature. Currently, the catalyst is successfully used at several plants for synthetic rubber and paintwork materials at the units of catalytic exhaust combustion. The catalyst service life is 5 years.

CATALYST FOR PETROCHEMICAL HYDROTREATMENT

By now, the units for diesel fuel production with a sulfur concentration of 0.2 wt % were designed for work with domestic catalysts.

The OAO Yarsintez and the OAO Slavneft'–Yaroslavnefteorgsintez developed a highly efficient competitive catalyst for deep hydrodesulfuring of diesel fuel.

Table 7 shows the results of the comparative tests of the new IM-22201 catalyst, the domestic Al–Co–Mo KGM-70 catalyst, and the best foreign catalyst C-448 from Criterion. Our new catalyst shows a much higher efficiency in diesel fuel treatment than commercial Russian samples and is not worse than foreign analogs. This catalyst can be synthesized at the available units of the OAO Yarsintez.

CATALYST FOR *n*-BUTANE ISOMERIZATION

UOP showed the greatest success in developing the process of *n*-butane isomerization. The conversion of *n*-butane on the catalysts of this company can be as high as 55% and the selectivity may achieve 95%.

Unfortunately, the development of a catalyst and a process for *n*-butane isomerization are restricted to laboratory scale, although putting this process into operation is very needed.

A study of this process with a new catalyst at the OAO Yarsintez made it possible to achieve acceptable performance characteristics in *n*-butane isomerization (Fig. 6). Pilot scale tests are needed for this process.

PROBLEMS OF CATALYST TECHNOLOGY AND PROVISION WITH FEEDSTOCK

Earlier, we discussed the problems of catalyst synthesis and use [1]. We also considered the problems of process technology, including catalyst technologies, and we paid attention to the necessity of using pure starting materials because purity determines the formation of active phases and various characteristics of catalysts [4].

The authors of [5, 6] conjectured on the basis of their studies that the activity of iron oxide catalysts and the stability of their operation depend on the ratio of alkali metal monoferrite and polyferrites and magnetite [4].

We studied the behavior of various iron oxides in the processes of catalyst preparation for styrene and isoprene manufacturing [4, 7].

It is notable that α-Fe_2O_3 obtained from alcoholate, magnetite Fe_3O_4, and Fe_2O_3 obtained by the thermal decomposition of pure sulfate almost without admixtures provide the highest selectivity. The higher concentration of the active ferrite phase is probably achieved in this case rather than in the presence of admixtures.

The catalyst for ethylbenzene dehydrogenation, K-28, prepared with an account of the results of tests with pure iron oxide worked at the OAO Angarskaya NKhK for more than 16000 h without changes of high performance for worse. During the operation period, the catalyst was permanently exposed to the action of unfavorable factors: frequent process shut-downs and re-starts, as well as “hot” idle periods. Nevertheless, high performance characteristics were preserved: a conversion of 54–57%, a selectivity to styrene of 92–93%. The temperature at the catalyst bed entrance was as low as 615°C (Table 1).

A study of the effect of purity and the nature of initial iron oxide allowed us to propose a more efficient catalyst for isoamylene dehydrogenation [8]. Currently, this catalyst passes through pilot-to-industrial scale tests. It works stably for more than a year and shows high performance characteristics.

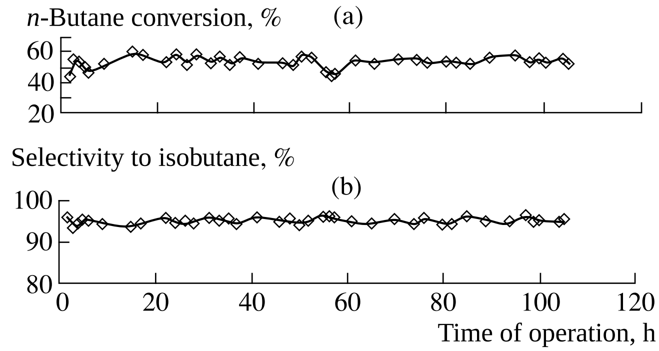

Fig. 6. (a) Conversion and (b) selectivity of the low-temperature isomerization of *n*-butane on the new catalyst developed at the OAO Yarsintez (200°C; 31 atm; space velocity, 2 h^{-1}; $H_2 : C_4H_{10}$ = 0.3 mol/mol).

In the manufacturing of supported microspherical catalyst of alkane dehydrogenation, an important requirement to the support (Al_2O_3) is purity.

Note that several foreign companies also give special attention to the purity of alumina. Thus, Condea (Germany) developed the technology for obtaining alu-

Table 5. Characteristics of the catalysts for isobutane dehydrogenation

Characteristic	Demonstration unit in Yroslavl, 2000 t/year		Industrial unit in Omsk, 80000 ton/year		Industrial unit in Al Jubail, 450000 ton/year
	catalyst				
	IM-2201	SPS	IM-2201	SPS	SPS
Isobutane conversion, %	49	52	39	46	48
Selectivity to isobutylene, %	84	88	85	89	87–89
Catalyst consumption, kg/t *iso*-C_4H_8	32	0.4	28	1.8	0.7

Table 6. Degree of purification (%) from some organic impurities on the chromium-containing catalyst IM-616 depending on temperature

T, °C	Butane	Gasoline	Methyl acrylate	Ethyl chloride	Vinyl chloride	Methyl chloride	Toluene
300	–	–	99.7	74.5	77.2	–	89.7
345	86.3	98.7	100	98.4	100	82.8	95.8
400	100	100	–	100	–	91.8	100
430	–	–	–	–	–	100	–

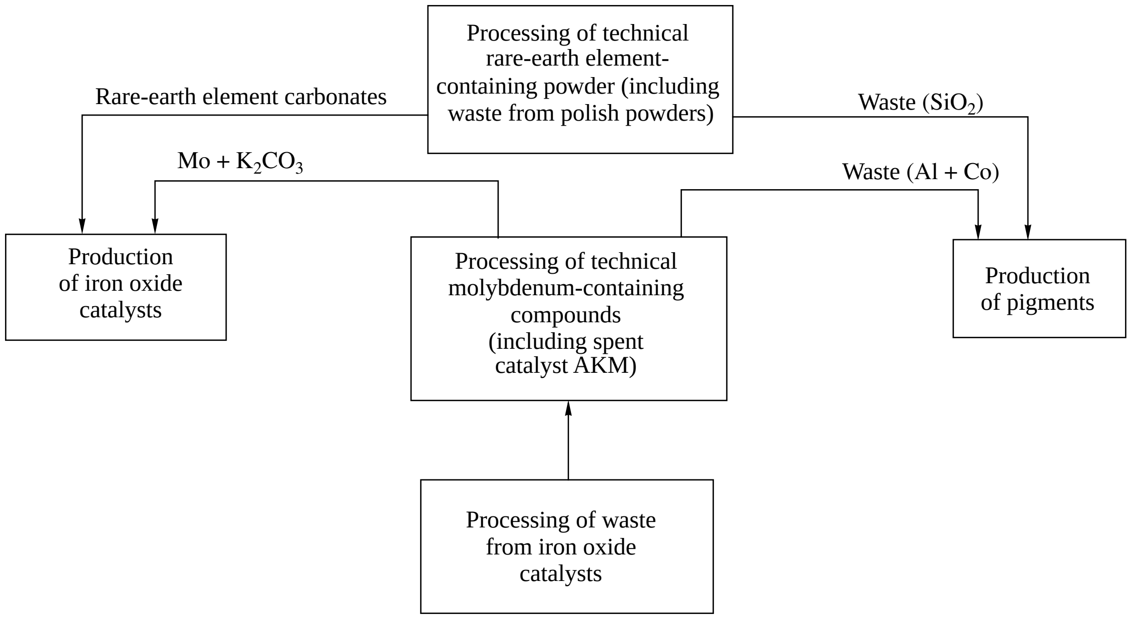

Fig. 7. Schematic of manufacturing the iron oxide catalysts using rare-earth element compounds and molybdenum extracted from industrial waste.

mina by the hydrolysis of aluminum alcoholates. These are obtained from pure metal and further refined by distillation.

We studied the effect of the nature of initial alumina on the specific surface area and the catalytic properties of the aluminum–chromium catalyst for isobutane dehydrogenation (Table 8). These catalysts operate at high temperatures (680°C) and the support is artificially aged by calcination at 1000°C. Table 8 shows that a catalyst prepared from highly pure alumina does not change its properties after thermal treatment. This points to the high thermal stability of a catalyst and its ability to work for a long time without the deterioration of performance characteristics.

A specific feature of catalyst manufacturing is the use of rare-earth metals, refractory noble metals, and alkali and alkali-earth metals as promoters, the stabilizers of an active phase, and as other components. The annual demand for these compounds is usually as low as several tons. Taking into account that the requirements to purity are rather high, catalyst manufacturing does not attract companies that produce similar products. Note that after the collapse of the Soviet Union, Russia lacks the capacities to produce rare-earth elements. All plants are now outside of Russia.

One of the possible solutions to this problem is the construction of domestic rare-earth element manufacturing in Yaroslavl. This is oriented toward the needs of catalyst manufacturing and takes into account the high requirement to product purity. Currently, there is a business plan, but the source of financing for construction works is still absent.

The results of our studies of some industrial waste enabled us to develop the technology (Fig. 7) for high-purity rare-earth element extraction to produce materials necessary for the synthesis of iron oxide catalysts.

Another result of our work was the reduction in the use of expensive molybdenum compounds by extracting molybdenum from the spent Al–Co–Mo catalysts. The residual part finds its use as pigments in the manufacturing of dyes (Fig. 7). That is, the method solved multiple problems. The spent aluminum–chromium catalyst is used as a pigment in the lacquer, vanish, and cement manufacturing, as well as in electrometallurgy.

Table 7. Results of tests of the catalysts for diesel fuel purification (pressure, 31 atm; space velocity, 4 h^{-1}; hydrogen supply, 300 nl/l feed; sulfur concentration in the feed, 1.02 wt %)

Catalyst	Concentration of sulfur (wt %) after hydrotreatment at different temperatures, °C		
	340	360	380
KGM-70	0.20	0.07	0.04
Criterion-448	0.10	0.02	0.01
IM-222-01	0.05	0.02	0.01

PROBLEMS OF PROVISION WITH EQUIPMENT

One of the serious problems in the manufacturing of dehydrogenation catalysts is the lack of special equipment for catalyst grinding, formation, and calcination.

Table 8. Effect of the nature of alumina on the specific surface area and the catalytic activity of the microspherical aluminum–chromium catalyst

Alumina	Admixtures		Specific surface area, m^2/g	Isobutane dehydrogenation	
	Na_2O	Fe_2O_3		conversion, %	selectivity, %
From Condea (Germany) before thermal treatment	0.005	0.01	90.7	56.1	89.5
From Condea (Germany) after thermal treatment*	0.005	0.01	89.2	54.5	89.9
From technical $Al(OH)_3$ before thermal treatment	0.200	0.02	101.4	54.4	87.1
From technical $Al(OH)_3$ after thermal treatment*	0.200	0.02	64.7	38.2	78.3

* The thermal treatment of Al_2O_3 was carried out at 1000°C for 24 h.

A bottleneck in the catalyst technology is the stage of extrusive formation. To obtain the catalyst with a desired texture and acceptable physicochemical properties, it is necessary to use molding machines with a die hold-down pressure higher than 160 kg/cm^2, which are capable of working for a long period with corrosive and erosive materials.

A recent trend in the industrialized countries is toward the growth of catalyst production with shaped catalyst grains (stars, tubes, trifoils and quarterfoils, multichannel tubes, etc.). The leading companies—Haldor Topsœe, Engelhard, Unocal, Criterion Catalysts, ICI-CataIko, ICI-Catalysts, BASF, Akzo, United Catalysts, Sud Chemie Group, and others—produce and supply to the market a wide range of shaped catalysts for different processes.

The interest in such catalysts is explained by an increase in the accessible specific surface area (based on the weight or volume) of grains compared to grains with conventional shapes. This results in an increase in the fractional void volume of the catalyst bed and a decrease in the hydraulic resistance. The degree to which catalysts are used and their service life increase. The processes of heat and mass transfer are intensified.

For instance, the use of ribbed extrudates in styrene synthesis results in an increase in the conversion by 2–3% and selectivity by 0.3–0.5% and in a decrease in the pressure drop along the catalyst bed by 15–25% compared to the process with cylindrical smooth extrudate with the same diameter.

The OAO Yarsintez carries out research on obtaining shaped catalysts.

CONCLUSIONS

1. Catalyst production in Russia meets the demands of olefin, diene, and vinylaromatic monomer production in Russia. New-generation catalysts SPS, SPP, K-28 and others were developed that are not worse than foreign analogs. These catalysts are produced at the OAO Yarsintez, which licenses the processes of styrene and olefin manufacturing.

2. The most important problems in catalyst manufacturing are the following:

– The absence of pure starting materials (iron oxides, aluminum, calcium carbonates, rare-earth elements, and molybdenum);

– Russian manufacturers do not produce molding equipment for low-ductile materials; there are substantial difficulties in finding the equipment for calcination, mixing, and automatic dosing.

3. Due to the lack of necessary equipment and feedstock materials with appropriate quality, domestic technologies for catalyst manufacturing are not realized in full strength. In several cases, product manufacturers export catalysts that are no better than domestic catalysts. In many cases, foreign companies decrease first-sale prices for catalysts to knock Russian catalysts out of the market. The variant when “personal” interests of the customer representative dominate the solution of purchasing that or another catalyst is also frequent.

4. Orientation toward imported catalyst that are no better than domestic ones leads to the inadmissible collapse of catalyst production for the largest petrochemical material producers in our country. Such an orientation will make our industry dependent on imports. This situation requires intervention and support at the governmental level.

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