IV RUSSIAN CONFERENCE WITH THE PARTICIPATION OF CIS COUNTRIES ON THE SCIENTIFIC BASES OF CATALYST PREPARATION AND TECHNOLOGY

Pathways to Better Stability of Catalysts for Reforming of Gasoline Fractions

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Abstract—Adsorbents AS-31 and AKD-981 based on zinc oxide and alumina are described. They are used in the purification of hydrogen-containing gas of reforming from hydrogen sulfide at 20–120°C and pressures up to 4 MPa. The second of these adsorbents is capable of forming weak adsorption complexes with hydrogen sulfide and can be recovered 2–3 more times than the first one. To remove sulfur-containing compounds from the gaseous feed of reforming at 350–450°C, the KAS-50 catalyst/adsorbent is proposed, which is prepared by mixing manganese dioxide and aluminum hydroxide. The sulfur capacity of this catalyst is ~20%. New platinum–rhenium reforming catalysts KR-200 and KR-201 are proposed, which have higher stability when they work with purified feedstock. The concentration of the active catalyst is the same or lower, and these catalysts show better activity than their predecessors. All catalysts and adsorbents are tested and work in industry.

Catalytic reforming of gasoline fractions is one of the main processes in manufacture of high-octane gasoline. Catalysts containing 0.25–0.36% Pt and the same or somewhat higher concentration of Re are widely used. These catalysts can work without recovery for two years or longer and make it possible to obtain reformed gasoline with octane numbers of 92–97. The condition for the stable operation of these catalysts is deep purification of feed from sulfur-containing compounds. The most stable catalysts with an increased amount of rhenium are very sensitive to sulfur. A decrease in the concentration of sulfur in the feed of reforming from 1.0 to 0.1 mg/kg can make the service life without recovery 2.5–3 times longer [1].

The Al–Ni–Mo KGU-941 hydrotreatment catalyst developed at the All-Russia Research Institute of Petrochemistry is used at four reforming plants and provides a decrease in the concentration of sulfur in the feed to 0.5 mg/kg. Concentrations lower than 0.1 mg/kg cannot be achieved in usual hydrotreatment because of the reverse reaction between hydrogen sulfide and olefins with the formation of mercaptans. The complete removal of sulfur can only be achieved using adsorption methods.

Circulating hydrogen-containing gas (HCG) introduces 80–90% of sulfur into the reforming zone. Therefore, the purification of HCG from sulfur leads to a decrease in the concentration of sulfur in the product by 4–5 times [2].

The technology for the purification of HCG is rather simple. An adsorber is filled with an adsorbent to consume hydrogen sulfide, and the process is carried out at natural parameters of HCG: 40–50°C before a compressor or 80–120°C after it. Another method for the removal of sulfur from the reforming zone is the simultaneous purification of gaseous feed. Both variants of the process are shown in Fig. 1.

For purification of gaseous feed, hydrogenizate with circulating hydrogen-containing gas of reforming are heated by the gaseous product mixture and pass though the contacts that absorb sulfur at 350–450°C.

Our institute developed a recoverable adsorbent based on zinc oxide and alumina to remove hydrogen sulfide hydrogen sulfide [3] and purify circulating HCG of reforming at natural parameters of circulation.[1]

In the preparation of the adsorbent, the following methods were used:

(1) Mixing aluminum hydroxide with zinc hydroxide,

(2) Coprecipitation of aluminum and zinc hydroxides from the solutions of sodium aluminate and zinc nitrate,

(3) Impregnation of γ-alumina by the aqueous solutions of zinc salts and further thermal treatment

The samples were tested on a laboratory scale to study their adsorption properties toward hydrogen sulfide and their ability to be recovered under in a flow of hydrogen at 320°C. Adsorption properties of samples were estimated by their dynamic capacity; that is, we measured sulfur capacity before hydrogen sulfide started to skip the adsorbent bed.

Figure 2 shows that the mixture containing ZnO and Al_2O_3 in a 1 : 1 molar ratio has a high sulfur capacity, which is lost after the first regeneration. In further cycles sulfur capacity steadily decreases. By contrast to

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[1] B.V. Krasii, I.I. Sorokin, and Yu.I. Emel'yanov took part in the development of the AS-31 hydrogen sulfide adsorbent and the KAS-50 catalyst. N.V. Vasilevsakya carried out X-ray phase analysis of adsorbents.
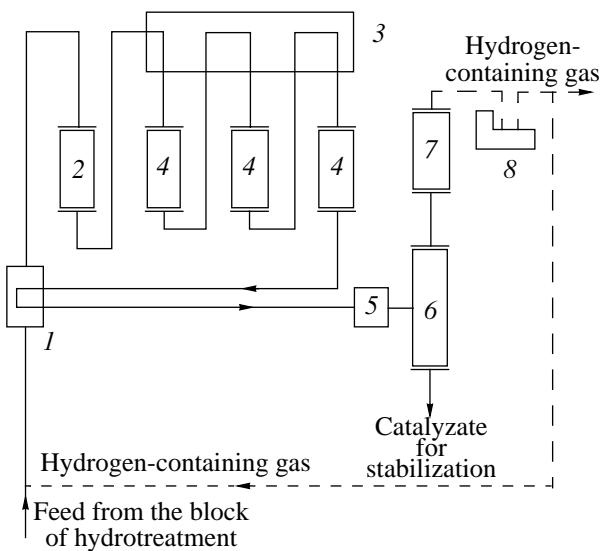
Fig. 1. Technological flowchart of the setup for catalytic reforming of semiregenerative type: (*1*) heat exchanger, (*2*) adsorber for gas-phase purification of feed and gas from sulfur admixtures, (*3*) reforming furnace, (*4*) reforming reactor, (*5*) condenser, (*6*) separator, (*7*) adsorber for purification of circulating hydrogen-containing gas from hydrogen sulfide, and (*8*) compressor.
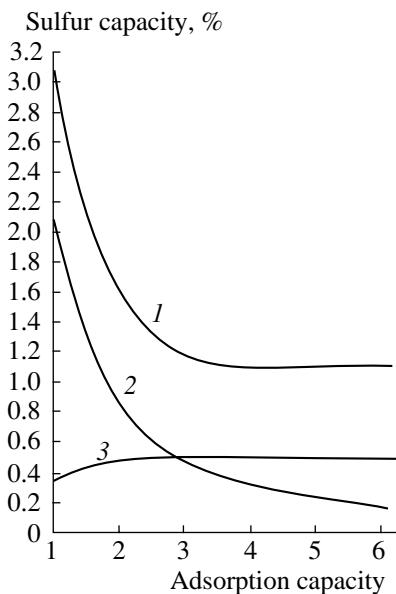
Fig. 2. Sulfur capacity of samples prepared by different methods: (*1*) coprecipitation; (*2*) mixing; and (*3*) impregnation.

that, the sample prepared by impregnation and containing ZnO and Al_2O_3 in a 0.1 : 1 molar ratio is capable of being regenerated many times, but its sulfur capacity is relatively low (~0.5%). The best results were obtained for the sample prepared by coprecipitation, which had a ZnO : Al_2O_3 molar ratio of 1 : 1 (as in the sample

obtained by mixing). It can be regenerated and has a high sulfur capacity.

According to the results of phase analysis, the samples obtained by mixing contained γ-Al_2O_3, the samples obtained by impregnation contained well-crystallized Al–Zn spinel and γ-Al_2O_3, and the samples obtained by coprecipitation contained Al–Zn spinel with various degrees of crystallization where alumina was almost entirely bound with zinc oxide. The degree of crystallization depended on the calcination temperature

For the samples prepared by mixing the true recovery as a result of hydrogen sulfide desorption occurs to a very low degree. Activation dominates over recovery and this is reflected in the appearance of additional adsorption centers after heating in a flow of hydrogen. For the samples prepared by impregnation, true recovery with the desorption of hydrogen sulfide occurs. The samples prepared by coprecipitation are characterized by a combination of regeneration and activation. The optimal combination of sulfur capacity and recoverability was achieved for the samples prepared by coprecipitation. They were taken as a basis in designing the hydrogen sulfide adsorbent AS-331. Our main findings obtained for Al–Zn adsorbents after hydrogen sulfide adsorption are itemized below:

1. The closer the structure of Al–Zn adsorbents to the structure of poorly crystallized Al–Zn spinel, the higher the recoverability of the samples. Samples prepared by the coprecipitation of aluminum and zinc hydroxides that was accompanied by interaction between sodium aluminate and zinc nitrate after thermal treatment at moderate temperatures showed the best results.

2. The degree of sample recoverability increases as the temperature of recovery increases from 200 to 400–500°C.

3. Multiple recovery of an adsorbent by heating in a flow of hydrogen or nitrogen is achieved due to hydrogen sulfide desorption and adsorbent activation.

4. Fresh adsorbent usually has a higher sulfur capacity than a recovered one. Initially adsorbed hydrogen sulfide entirely remains bound to the surface and is not desorbed during the first recovery. In further adsorption/desorption cycles, hydrogen is both adsorbed and desorbed.

Based on the experimental facts and regularities, we propose the following mechanism of hydrogen sulfide adsorption and spinel-type Al–Zn oxide recovery:

Initially, adsorption occurs at a usual temperature:

$$(Z) + nH_2S \longrightarrow [(Z)nH_2S],$$

and, at a high temperature, recovery occurs via the following reactions:

$$[(Z)nH_2S] \begin{cases} \longrightarrow (Z1) + xH_2S \\ \longrightarrow [(Z2)Sy] + yH_2O \\ \longrightarrow [(Z3)zH_2S], \end{cases}$$
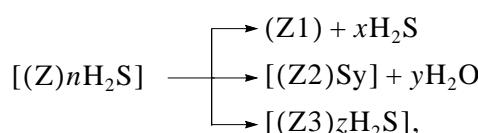
where (Z) is the surface of Al–Zn spinel (involving free zinc oxide if it is present, $[(Z)nH_2S]$ and $[(Z3)zH_2S]$ are the adsorption complexes formed by spinel and hydrogen sulfide; $[(Z2)Sy]$ is the surface, containing zinc sulfide; $(Z) = (Z1) + (Z2) + (Z3)$; $n = x + y + z$.

At ambient temperature (20–30°C), hydrogen sulfide adsorption on the spinel surface is not accompanied by the formation of zinc sulfide.

When the adsorbent saturated by hydrogen sulfide is heated in a flow of hydrogen or nitrogen, the following transformations of the initial adsorption complex may occur:

– H_2S desorption from the regions of the surface with a low adsorption potential and

– chemical interaction of adsorbed H_2S with zinc oxide to form zinc sulfide and water.

The most strongly adsorbed molecules of H_2S remain at the sites, which are characterized by an increased adsorption potential (Z3).

Hydrogen sulfide adsorption on the active site of Al–Zn spinel can be described by the following scheme:

$$
\begin{array}{c}
\text{H} \quad \text{H} \\
\diagdown \diagup \\
\overset{..}{\text{S}} \\
\text{OH} \quad \downarrow \quad \quad \text{O} \\
\mid \quad \quad \quad \mid \\
\text{–Al–O–Zn–O–Al–O–Al–}
\end{array}
$$
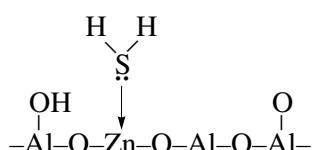
The adsorption/desorption process occurs via the donor/acceptor mechanism. The strength of the zinc–sulfur bond can vary over a broad range and depends on the orbital ($4p$, d, or f) with which an unshared electron pair of sulfur in a hydrogen sulfide molecule interacts.

The AKD-981 adsorbent developed recently forms weak adsorption complexes with H_2S, which is favorable for recovery. The number of efficient recovery cycles for this adsorbent is 2–3 times greater than in the case of AS-31.

A more radical method for the removal of sulfur microadmixtures from the reforming zone is the purification of feed and circulating hydrogen-containing gas from sulfur. The technology for such purification requires an adsorbent capable of absorbing sulfur at 350–450°C. Such an adsorbent/catalyst [4, 5] was developed on the basis of a mixture of manganese and aluminum oxides.

In the reaction medium at 350–450°C, any manganese oxide transforms into MnO. The reduction of initial MnO_2 into MnO is a highly exothermic reaction

$$MnO_2 + H_2 \longrightarrow MnO + H_2O + 105 \text{ kJ/mol}$$
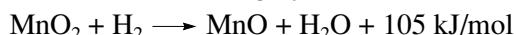
(the plus and minus signs are used throughout the paper in the thermochemical sense). This process leads to substantial overheating and requires special equipment for intensive heat removal; otherwise overheating may lead to a temperature of 1000°C. This complicates the reduction process under the conditions applied on a catalyst preparation factory or a reforming plant.

Using thermochemical calculations, we found a method for the consecutive transformation of MnO_2 into MnO that excludes the occurrence of highly exothermic steps. The method includes

(1) calcination to transform MnO_2 into Mn_2O_3 and aluminum hydroxide into χ-oxide

$$MnO_2 \longrightarrow 1/2Mn_2O_3 + 1/4O_2 - 42.65 \text{ kJ/mol} \text{ and}$$
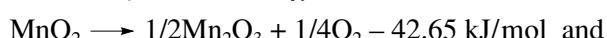
(2) reduction of the sample by hydrogen to transform Mn_2O_3 into Mn_3O_4,

$$1/2Mn_2O_3 + 1/6H_2$$
$$\longrightarrow 1/3Mn_3O_4 + 1/6H_2O + 24 \text{ kJ/mol}.$$
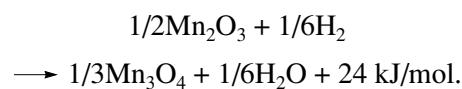
Differential thermal analysis, X-ray phase analysis, and temperature-programmed reduction were used to determine the best conditions for this process: Calcination should be carried out at ~550°C, and reduction should be carried out at 260–300°C.

We found that 380–400°C is enough for the reduction temperature to transform entire manganese into MnO:

$$1/3Mn_3O_4 + 1/3H_2 \longrightarrow MnO + 1/3H_2O + 3 \text{ kJ/mol}.$$

The latter step is carried out right at the reforming plant, since MnO (unlike Mn_3O_4) is a pyrophore and its transportation to the consumer is associated with some difficulties.

The study of used adsorbent by applying a microprobe showed that the distributions of sulfur over a cut of the granule profile are different in the frontal and bottom layers. In the frontal layer, which is completely saturated with sulfur, sulfur is uniformly distributed. In the bottom layer, sulfur is concentrated over the periphery of a granule. Therefore, sulfur initially reacts with an external surface of a manganese oxide granule and then is supplied to the bulk. Probably, the rate of sulfur adsorption is determined by an external diffusion deep into the bulk. Hence, the size of extrudates should be as small as possible (1.8–2.2 mm).

To develop the technology of gaseous feed purification, we tested the catalyst/adsorbent KAS-50. The tests were carried out on a pilot-scale setup at 1.5 MPa. The concentration of sulfur in the feed was 3 mg/kg. Table 1 summarizes data obtained in these tests. At 370–430°C, the concentration of sulfur in the product was 0.1 mg/kg. This was quite a suitable concentration for the use of sulfur-sensitive reforming catalysts. Judging from the overall concentration of aromatic hydrocarbons, this catalyst was inert in other reactions.

Then, in run 1 (Table 2), we studied H_2S adsorption by the sulfur adsorbent. This experiment was carried out in a system consisting of two consecutive reactors. The first reactor was charged with sulfided Al–Co–Mo catalyst for hydrotreatment. The second reactor was charged with sulfur adsorbent. Organic sulfur contained in the feed was converted under the conditions of hydrotreatment 360°C into H_2S. The gaseous flow of

Table 1. Results of KAS-50 catalyst/adsorbent testing

Characteristic	Feed	Catalyzate at purification temperature, °C		
		370	400	430
Average concentration of sulfur, mg/kg	3.000	0.085	0.040	0.095
Overall concentration of aromatic hydrocarbons, %	8.3	8.6	8.6	8.4

Note: The feed is the 85–180°C fraction from the plant in Kirishi. The adsorbent charge is 30 cm^3. The sample was prereduced in a flow of hydrogen at 400°C for 4 h. The conditions of purification: 1.5 MPa, the space velocity of feed is 5 h^{-1} (the flow rate is 150 cm^3/h), hydrogen circulation is 1000 volume units per one volume unit of feed, hydrogen purging is 40 volume units per one volume unit of feed; gas for purging did not contain H$_2$S.

products saturated with hydrogen sulfide entered the second reactor where sulfur was absorbed.

Runs 2–4 were carried out in a setup consisting of a single reactor filled with the manganese adsorbent. Sulfur-free feed was artificially contaminated with octylmercaptan (run 2), polysulfide (run 3), or thiophene (run 4). In these experiments, we determined the reactivity of organosulfur compounds. Mercaptans readily decomposed over manganese oxide. When the feed contained octylmercaptan in an amount of 420 mg/kg, sulfur was adsorbed completely (run 2). Organic polysulfides readily underwent hydrogenolysis. The adsorbent completely extracted sulfur from the feed, when it was present in the form of di-*tert*-butyl polysulfide in an amount of 405 mg/kg (run 3). The sulfur capacity before sulfur started to skip the adsorbent was close to 20%.

Thiophene was poorly adsorbed by the manganese oxide adsorbent as contrasting to hydrogen sulfide, mercaptan, and polysulfide. The degree of thiophene removal was at most 10–15% (run 4) when the concentration of thiophene in the feed was 92 mg/kg based on sulfur. Nevertheless, virtually complete removal of sulfur-containing compounds from feed was possible if

preliminary hydrogenolysis was carried out to form H$_2$S, which was readily adsorbed by manganese oxide. This variant was tested in run 1, in which two reactors were used and the first reactor was charged with the hydrotreatment catalyst. Instead of this catalyst, one might use the aluminoplatinum catalyst for reforming, which accelerates both the hydrogenolysis of organosulfur compounds and naphthene aromatization.

Run 5 was also carried out in the two-reactor setup. The first reactor was charged with by the sulfur-insensitive AP-56 catalyst for reforming (5 cm^3). The second reactor was charged with the KAS-50 catalyst/adsorbent (50 cm^3). Thiophene (35 mg/kg based on sulfur) was added to the feed preliminarily purified from sulfur. Results obtained in this run provide evidence for the possibility of complete sulfur removal when it comes with thiophene. In the check run, we did not apply the aluminoplatinum catalyst, and thiophene sulfur was not removed. The concentration of aromatic hydrocarbons in the products was 16.4 wt % vs. 9.2 wt % in the feed. Thus, the aluminoplatinum catalyst indeed accelerates thiophene hydrogenolysis and aromatization (which is the main reaction of reforming).

Table 3 shows the results obtained for sulfur removal from feed containing reactive organosulfur compounds in a one-reactor pilot setup operating under pressure in the presence of the KAS-50 catalyst/adsorbent. The space velocity of feed, temperature, and a hydrogen : feed ratio were varied. The latter was controlled by changing the supply of fresh hydrogen and/or changing the number of hydrogen/feed cycles. The quality of purification was determined as a degree of sulfur adsorption. The concentration of sulfur in the feed was taken equal to 100%.

When the space velocity of feed was increased, the portion of sulfur that was not absorbed increased. Comparison of the results of runs 1 and 2 with 5 and 6 shows that, under identical conditions at a space velocity of 2 h^{-1}, the extent of sulfur absorption is 98.7%. When the space velocity is 6.7 h^{-1}-the extent of sulfur adsorption is 90.0% in the case of low-sulfur feed and 98.4% in the case of high-sulfur feed.

Table 2. Adsorbent KAS-50 capacity toward different sulfur-containing compounds

No.	Sulfur-containing compounds	Concentration of sulfur in feed, mg/kg	Sulfur absorption, %	Sulfur capacity of adsorbent, %
1	Hydrogen sulfide	410	99.98	20.5
2	Octylmercaptan	420	99.93	15.6
3	Di-*tert*-butyl polysulfide	405	99.90	20.9
4	Thiophene	92	13.00	–
5	Thiophene	35	99.40	–

Note: The feed is the 85–180°C fraction (without purification in run 1 and purified in other runs). The adsorbent charge is 50 cm^3. The sample was prereduced in a flow of hydrogen at 400°C for 4 h. The conditions of purification: 400 ± 1°C 2.0 MPa, the space velocity of feed is 5 h^{-1} (the flow rate is 250 cm^3/h), hydrogen circulation is 1000 volume units per one volume unit of feed, hydrogen purging is 24 volume units per one volume unit of feed. Runs 1 and 5 are carried out in a two-reactor setup; runs 2–4 are carried out in a one-reactor setup.

Table 3. Feed purification from sulfur and purification of hydrogen-containing gas on the KAS-50 adsorbent/catalyst under different conditions

No.	Concentration of sulfur in feed, mg/kg	Adsorption temperature, °C	Feed space velocity, h⁻¹	Circulation of hydrogen-containing gas, vol/vol feed	Supply/purging of H_2, vol/vol feed	Sulfur consumption, %
1	190	400	2	1000	50	98.7
2	38	400	2	1000	50	98.7
3	38	400	2	no	100	98.3
4	38	400	6.7	no	100	97.8
5	38	400	6.7	1000	30	98.4
6	190	400	6.7	1000	30	90.0
7	190	430	6.7	1000	30	94.9
8	190	370	6.7	1000	30	77.7

Note: The volume of sample loading containing 71% MnO is 30 cm³. The pressure is 2 MPa. The feed: the 85–180°C fraction from the plant in Kirishi contained 190 mg/kg sulfur; the 85–180°C fraction from the plant in Surgut contained 38 mg/kg sulfur.

Table 4. Activity of reforming catalysts developed at the All-Russia Research Institute of Petrochemistry

Catalyst	Composition, %		Temperature of run, °C	Yield of stable catalyzate,* %	Concentration of aromatic hydrocarbons in stable catalyzate, wt %	Octane number of stable catalyzate (motor method)	Concentration of hydrogen in circulating gas, vol %
	Pt	Re					
RB-22u	0.26	0.45	470	86.3	56.1	82.5	87.0
			480	82.2	64.7	86.2	84.5
			490	78.6	70.7	87.6	80.7
KR-108u	0.36	0.36	470	81.5	64.9	86.2	84.4
			480	80.6	69.5	87.5	83.3
			490	77.7	74.2	89.3	82.5
KR-200	0.26	0.42	470	85.3	63.7	86.0	88.4
			480	83.2	70.3	88.1	84.9
			490	79.4	76.4	90.4	82.5
KR-201	0.30	0.30	470	84.2	65.2	86.7	89.2
			480	82.4	71.1	88.7	86.6
			490	78.4	77.0	90.6	84.0

* Loss is assumed to be 2%.

An increase in temperature from 370 to 430°C leads to an increase in the efficiency of purification: the fraction of absorbed sulfur increases from 77.7 to 94.9% (runs 6–8). When purifying a feed containing organosulfur compounds, a critical role belongs to kinetic factors. Therefore, it is necessary to maintain rather high temperature for the decomposition of these compounds on the catalyst/adsorbent.

In general, the purification of the gaseous feed of reforming from sulfur admixtures is carried out at 350–450°C and 1.0–3.5 MPa. The recycle factor of reforming gas is 800–1800 volume fractions per unit feed volume. The space velocity of feed is 6–7 h⁻¹.

Our studies allowed us to develop technical documents for the manufacturing of the AS-31 adsorbent for hydrogen sulfide and the KAS-50 catalyst/adsorbent for sulfur, and provide recommendation for the use. Both adsorbents are produced on an industrial scale. The AS-31 adsorbent is used at reforming plants of AO Slavneft in Yroslavl and at the Habarovsk Oil Refinery. KAS-50 is used at the reforming plant of the Surgutgazprom Condensate Stabilization Factory in Surgut.

In 1994–1995, the All-Russia Research Institute of Petrochemistry developed the catalysts KR-108u and RB-22u for reforming, which preformed well at several reforming plants of Angarsk and Saratov Oil Refineries. However, their activity was lower than the activity of the best foreign samples (R-56, RG-482, and E-601). Therefore, we developed new catalysts KR-200 and KR-201, which are more active than RB-22u and KR-108u (Table 4). On the catalyst with a high concentration of rhenium KR-200, reformate with a concentration of aromatic hydrocarbons of 70 wt % and an octane number of 88 (motor method) can be obtained at a 10°C lower temperature than on RB-22u, which is close to it in the composition. For the KR-201 catalyst with equal concentrations of rhenium and platinum, the same result is obtained at a 4°C lower temperature than

on KR-108u, although the concentrations of rhenium and platinum are higher in the latter case. These results are due to the optimal distribution of platinum, rhenium, and halide over the bulk of support granule.

The results of our work can be summarized as follows:

1. We developed the technology for the purification of hydrogen-containing gas of reforming from hydrogen sulfide. The aluminum–zinc adsorbent AS-31 prepared by co-precipitation of zinc and aluminum oxide from their salts is capable of adsorbing hydrogen sulfide at natural parameters of hydrogen-containing gas of reforming (20–120°C and 4 MPa). It can be recovered many times by heating in a flow of this gas or nitrogen. The sulfur capacity of the adsorbent is at a level of 0.5–1.0%. The new AKD-981 adsorbent forms weak adsorption complexes with hydrogen. Its recoverability is 2–3 times higher than that of the AS-31 catalyst.

2. We developed the technology of sulfur compound absorption from the gas feed of catalytic reforming at 350–450°C. The adsorbent/catalyst KAS-50 used for that purpose is prepared by mixing manganese dioxide with aluminum hydroxide, and its sulfur capacity is at a level of 20%.

3. Based on thermochemical calculations, we proposed the method for the consecutive transformation of MnO_2 into MnO, which does not include highly exothermic steps. We experimentally determined conditions for the maximal sulfur capacity and the best quality of purification.

4. We showed that the nature of a sulfur-containing compound affects the characteristics of purification from sulfur: hydrogen sulfide and sulfur, which is present in mercaptans and organic polysulfides, are almost completely absorbed, although the extent of thiophene sulfur absorption is only 10–15%.

5. We developed new KR-200 and KR-201 catalysts for reforming, which are more active than their predecessors used in the industry.

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