

Manganese Oxide Monolith Catalysts Modified by Fe and Cu for High-Temperature Ammonia Decomposition and H₂S Removal

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Abstract

Monolith sorbents/catalysts that have potential in simultaneous removal of H₂S and NH₃ from hot fuel gas were developed. Preparation methodology and composition of supported honeycomb sorbents/catalysts, based on manganese oxides modified by Fe and Cu oxides, have been optimized. Impregnated and washcoated monolith catalysts were tested in ammonia high temperature decomposition and H₂S sorption. Approaches for improving the thermal stability and catalytic activity under reaction conditions are described.

INTRODUCTION

An effective direct usage (*e. g.* high temperature turbines) of the gases, obtained in the Integrated Gasification Combined Cycle, is substantially limited, since those gases contain undesirable impurities, first of all, ammonia (up to 0.3 % vol. [1]) and hydrogen sulfide (0.1–1.5 % vol. [2]). Development of an effective monolith sorbents/catalysts that allow the high temperature abatement of ammonia via its decomposition toward N₂ and H₂ and simultaneous H₂S sorption is the most promising way to solve this problem.

It is known, that the most important processes for high temperature regenerative H₂S removal use sorbents on the base of single or mixed-metal oxides, such as: ZnO [3], zinc ferrite [4], zinc titanate [3, 5], CuO [6, 7], MnO/ γ -Al₂O₃ [2, 8] and FeO [9] or FeO/ γ -Al₂O₃ [2]. The sorbents usually provide H₂S removal from the fuel gas to levels less than 20 ppm due to the sulfidation reaction. The gases, con-

taining steam [2, 8, 9] (in this case H₂S is desorbing in a high concentration), or O₂/N₂ mixture [3–7] (in this case SO₂ is formed) are used for the regeneration of these sorbents. Both the sorption and regeneration steps are carried out at high temperatures of the sorbents of about 700–1100 °C. The main disadvantages of ZnO-containing sorbents are the loss of surface area at high regeneration temperatures and formation of zinc sulfate at low regeneration temperatures [3, 4]. Also, when these sorbent materials are used for the purification of strongly reducing gas streams, during sorption, ZnO is reduced into the metallic state, followed by vaporization of elemental zinc at temperatures above 600 °C [5]. Manganese and iron oxides sorbents are preferable, since they can be regenerated by steam [2, 8, 9]. Besides, the regeneration of MnS with steam at 850 °C proceeds more easier in the presence of γ -Al₂O₃, and results in the formation of bulk manganese aluminate (MnAl₂O₄), instead of MnO [8]. Remarkably, MnAl₂O₄ converts again into MnS

and γ -Al₂O₃ during subsequent sulfidation. Therefore, deposition of manganese oxides on γ -Al₂O₃ allows lowering the regeneration temperatures of these sorbents.

On the other hand, transition metal oxides – Fe₂O₃, CuO, Cr₂O₃, MnO_x [10–13] are known to be the most active catalysts for ammonia decomposition. However, these bulk catalysts have low thermal stability and their selectivity in the reaction drops with temperature elevation. Deposition of these oxides on the supports allows to raise substantially their thermal stability under the reaction conditions [10]. Titania-supported copper-manganese oxides with Cu–Mn loading 12 % mass and molar ratio of Cu : Mn = 20 : 80 are the most active and selective in N₂ formation in the reaction of selective oxidation of ammonia to nitrogen (600 ppm NH₃, 6 % O₂) [14]. The catalytic materials containing transition metals of VIII group or their oxides are often used for the NH₃ decomposition in the oxygen-free atmosphere [10]. Various materials were proposed for hot gas cleaning from NH₃ at high temperatures. The proposed Ni-based catalysts either in granulated [15] or in monolithic form [16] are the most promising systems for high temperature (at 900 °C) NH₃ decomposition, but these catalysts are deactivated by H₂S (100 ppm [16]), especially at high pressures and low temperatures. Limestone calcined at high temperatures is also active in decomposition of NH₃ (1 % vol. in He) at above 800 °C. But CaO loses its catalytic selectivity in the atmosphere reproducing the hot coal gases (H₂–CO–CO₂), especially with increasing pressure [17]. The decomposition of ammonia is observed at 900 °C on alumina for a simulated fuel gas mixture (50 % conversion [18]), and on SiC and dolomite in the product gas from fluidized-bed gasifier [16].

Published data allow to conclude that the oxides of transition metals Mn, Fe and Cu are the most perspective candidates for active components of the sorbents/catalysts for simultaneous cleaning of the hot coal gas from hydrogen sulfide and ammonia. Commercial Ni- or Al-based catalysts, used for high temperature ammonia decomposition, can not be applied for simultaneous cleaning of hot coal gases from NH₃ and H₂S due to the low or negligible sorption capacity by H₂S and also due to the prob-

lems with regeneration. Development of the sorbents/catalysts in the form of monolith increases their technical merit due to the easy operation, regeneration, low pressure drop, small dust and attrition sensitivity. Titania is widely used as a support to improve thermal, mechanical and chemical properties of the catalysts and sorbents [19], but its application in the form of honeycomb support is rather limited [13].

Individual Mn, Fe and Cu salts were used as the precursors to prepare monolith sorbents/catalysts based on titania honeycomb support and aluminosilicate monolith washcoated with titania [13]. The monolith sorbents/catalysts combine high catalytic activity in the ammonia decomposition with acceptable mechanical strength of the monolith supports. It was shown [13], that the iron- and copper-containing catalysts, prepared by the impregnation, exhibit higher activity and stable performance at high temperatures in comparison with the manganese oxides-containing samples. So that 95 % and 80 % of NH₃ conversion is achieved at 780–800 °C, respectively, on monolith sorbents/catalysts, containing individual Fe, Cu and Mn oxides. Supported manganese oxide catalysts above 700 °C show a high initial activity, but lose their activity in the temperature range 800–900 °C due to a strong interaction with the monolith support material [20]. There are two ways to stabilize the monolith catalysts: modification of the monolith support, and introduction of modifying elements into the supported active component.

This work is devoted to the study of physicochemical properties of the manganese oxides-supported monolith sorbents/catalysts modified by Fe and Cu, and to their testing in ammonia decomposition and H₂S sorption.

EXPERIMENTAL

Catalysts preparation

The monolith supports were prepared by extrusion of the masses based on titanium dioxide (anatase) or aluminosilicate precursors followed by drying at 110 °C and calcination at 700 °C in accordance with [13]. Ca-forms of

TABLE 1

Properties of the monolith supports

Sample	Composition of the monoliths	T, °C	S _{sp} , m ² /g	Phase composition	Mechanical strength, kg/cm ²
MS-1	63 % TiO ₂ + 35 % Ca-f ^a + 2 % MSF ^c	700	86	TiO ₂ (anatase) Ca-montm ^b	8
MS-2	75 % aluminosilicate (clay) ^d + 25 % Ca-f ^a	700	33	Al ₂ O ₃ · SiO ₂ + α-SiO ₂	19.5

^aCa-f means the Ca-form of montmorillonite with general formula Ca_{0.2}(Al,Mg)₂Si₄O₁₀(OH)₂ · 4H₂O.

^bProduct of Ca-montmorillonite dehydration.

^cMSF – mullite-silica fibers with diameter 0.25 mm and length 10 mm, made in Russia, State Standard (GOST) 23 619–79.

^dObskaya clay – clay from Ob'river region (Russia), after calcination at 500 °C represents aluminosilicate.

montmorillonite (denoted as Ca-f) were used as a binder for preparation of the extrusion masses. The mullite-silica fibers (2 % mass) were added to the extrusion mass for improvement of the mechanical strength of titania-based monolith. Monolith supports have diameter 18 mm, square channels 1.5×1.5 mm, wall thickness 1 mm. The physico-chemical properties of the samples are given in Table 1.

Preparation of the impregnated monolith catalysts. The impregnated catalysts were prepared by wet impregnation of the TiO₂-monolith supports (MS-1) with the aqueous solution of manganese nitrate (110 mg Mn/ml) with subsequent drying at 110 °C and calcination at 500, 700 and 900 °C. To obtain manganese loading equal to 15 % mass (hereafter calculated for MnO₂), the impregnation-drying-calcination procedure was repeated three times.

The manganese-containing catalysts modified by Fe₂O₃ were prepared by impregnation of the Mn-catalyst by aqueous solution of the iron nitrate (112 mg Fe/ml) or iron (III) ammonium oxalate (56 mg Fe/ml), with subsequent drying at 110 °C and calcination at 500, 700, 900 °C. Iron loading was 4–8 % mass (hereafter calculated for Fe₂O₃).

The manganese-containing catalysts modified by CuO were prepared by impregnation of the Mn-catalyst by aqueous solution of the copper nitrate (192 mg Cu/ml), with subsequent drying at 110 °C and calcination at 500, 700, 900 °C. Copper loading was 4–8 % mass (hereafter calculated for CuO).

Preparation of the washcoated monolith catalysts. Washcoated catalysts were prepared using the aluminosilicate monolith supports (MS-2). Bulk MnO₂ or Mn₂O₃, obtained by the decomposition of Mn(NO₃)₂, were mixed with TiO₂ and γ-Al₂O₃ (as a binder), and a suspension based on this mixture was prepared. After the suspension had been deposited on the monolith support, the catalysts were dried and calcined at 500, 700 and 900 °C. Active component – Fe and Cu oxides were introduced into the washcoating by impregnation with Fe or Cu nitrate solutions.

Preparation of the model catalysts. The model Mn-containing catalysts on granulated TiO₂ (anatase) and Ca-montmorillonite were prepared by procedure written above. Mn loading in these catalysts was 15 % mass.

The bulk MnO₂, Mn₂O₃, MnO were prepared by the decomposition of manganese nitrate at temperatures 300, 700 and 900 °C respectively.

The bulk MnTiO₃ and FeTiO₃ were prepared by the mechanical mixing of equimolar quantities of Mn(NO₃)₂ · 4H₂O or Fe(NO₃)₃ · 9H₂O and TiO₂ (anatase), with subsequent calcination at 800 °C/8h in air and 900 °C/2h in gas mixture 1 % vol. NH₃ + helium.

Activity test

Reaction of ammonia decomposition was studied in a flow reactor within temperature range of 400–1000 °C and space velocity of 1000 h⁻¹. Ammonia concentration in the initial

gas mixture was 1 % vol. in helium. Catalytic activity was defined as ammonia conversion (X , %) at the given temperature.

The study of hydrogen sulfide sorption was carried out in a flow reactor at the temperature 700 °C and space velocity 3600 h⁻¹; hydrogen sulfide concentration in initial gas mixture was 2.8 % vol. in argon. The sorption capacity was determined as the amount of sorbed H₂S in mmol of H₂S per 1 g of the catalyst, or in % mass.

XRD (X-ray diffraction) characterization of catalyst samples was conducted with HZG-4 diffractometer (Germany) using the CuK_α radiation. The patterns were recorded over a range of 2θ angles from 10° to 60° with the sweep rate 1°/min.

Formation of sulfur compounds on the catalyst surface after hydrogen sulfide sorption was studied using a MAP-3 microanalyzer. The probe diameter was 1–2 mm, the working voltage was 25 kW. The AlK_α, TiK_α, CuK_α, and SK_α were analytical lines.

RESULTS AND DISCUSSION

Testing of the catalyst activity in ammonia decomposition

The dependencies of properties of the catalysts and their activity on the nature of active component (Mn, Fe, Cu), loading of the active component (5–20 % mass), type of the support and calcination temperature have been studied earlier [13].

It was found [13, 20], that manganese oxides deposited on the TiO₂-monolith support (MS-1) and calcined at 700 °C have rather high activity in NH₃ decomposition (Sample No. 2, Table 2). At 740 °C the NH₃ conversion is more than 80 %. Considerable decrease of the activity for the samples is observed upon their exposure to the reaction mixture at temperatures above 750–800 °C. Then, NH₃ conversion over these catalysts, preliminary calcined at 500 and 700 °C, decreases from 70–80 % to 55 % when the reaction temperature is above 850 °C. The

TABLE 2

The properties of Mn-containing (15 % mass) catalysts in ammonia decomposition

No.	Catalyst/calcination T , °C	Properties of fresh catalyst		NH ₃ conversion, %, at temperature, °C		Properties after reaction	
		S_{sp} , m ² /g	XRD composition	800	900	S_{sp} , m ² /g	XRD composition
1	MnO ₂ /(TiO ₂ + Ca-f ^a)/500	93	Anatase, MnO ₂	75	55	11	Anatase + rutile = 3 : 1 Mn(Ti,Al,Mn)O ₃ ^b
2	The same/700	42	Anatase, β-Mn ₂ O ₃	60	60	6.8	Anatase + rutile = 2 : 3 Mn(Ti,Al,Mn)O ₃ ^b
3	»/900	0.8	Rutile, MnMn ₆ SiO ₁₂ ^c	15	35	0.7	Rutile + MnMn ₆ SiO ₁₂ Mn(Ti,Al,Mn)O ₃ ^b
4	MnO ₂ /Ca-f/700	3.6	α-SiO ₂ , Ca-montm ^d , β-Mn ₂ O ₃	45	55	0.6	α-SiO ₂ , Ca(Al,Si) ₂ Si ₂ O ₈ , MnMn ₆ SiO ₁₂
5	The same/900	0.7	Ca(Al,Si) ₂ Si ₂ O ₈ + MnMn ₆ SiO ₁₂ ^c	40	60	0.2	α-SiO ₂ + Ca(Al,Si) ₂ Si ₂ O ₈ , MnMn ₆ SiO ₁₂ ^c
6	MnO ₂ /TiO ₂ /700	11	Anatase (~85%), rutile (~15%), β-Mn ₂ O ₃	85	100	4.1	Rutile, MnTiO ₃
7	The same/900	0.8	Rutile, MnTiO ₃	50	95	0.5	Rutile, MnTiO ₃

^aCa-f means Ca-form of montmorillonite.

^bHexagonal structure, like MnTiO₃.

^cStructure, like MnMn₆SiO₁₂, with substitution of the part of Mn-cations by Si⁴⁺.

^dProduct of Ca-montmorillonite dehydration.

catalysts with 15 % mass Mn, prepared on TiO_2 -monolith and preliminary calcined at 900 °C (Sample No. 3, Table 2), demonstrate high conversion (up to 90 %) only at the reaction temperature above 950 °C.

Deactivation of the manganese oxide-containing catalysts calcined at 500 and 700 °C may be explained by the chemical interaction of the Mn oxides and the support materials resulting in the formation of inactive phases of Mn cations with the Ca-montmorillonite (binder) or the titanium dioxide. Comparison of the initial phase composition of these catalysts (see Table 2) and those after ammonia decomposition, done using XRD shows, that at the reaction conditions MnO_2 and $\beta\text{-Mn}_2\text{O}_3$ (initial active phase in samples No. 1, 2) were partially reduced with the formation of interaction phase of manganese oxides with TiO_2 . This interaction phase is a solid solution on the basis of hexagonal structure of MnTiO_3 with partial substitution of Ti^{+4} by Mn^{+3} or Al^{+3} (from binder).

The phases similar to MnTiO_3 are formed after the calcination at 900 °C of the catalysts based on TiO_2 -monolith with Ca-montmorillonite, and these catalysts are active only at the high temperatures (Sample No. 3, Table 2). Taking into account all the presented above, it is believed that $\beta\text{-Mn}_2\text{O}_3$ phase is more active than MnTiO_3 phase in ammonia decomposition.

To elucidate the nature of catalyst deactivation due to the interaction of the catalytically active Mn species with the material of monolith support, the samples of bulk MnO_2 , Mn_2O_3 , MnO , MnTiO_3 and special series of the samples, supported on granulated Ca-montmorillonite and TiO_2 (anatase), were prepared.

The manganese oxides supported on granulated Ca-montmorillonite (Sample No. 4, Table 2) after the operation at 900 °C lose their activity to 55 %. According to the XRD data, the active manganese oxide, $\beta\text{-Mn}_2\text{O}_3$, interacts with the support forming a solid solution similar to $\text{MnMn}_6\text{SiO}_{12}$. Because of the complicated composition of the products, which are formed upon the thermal decomposition of manganese oxides supported on Ca-montmorillonite, it is impossible to state exactly, that nature of montmorillonite affects on the deactivation of monolith catalysts at the reaction condition.

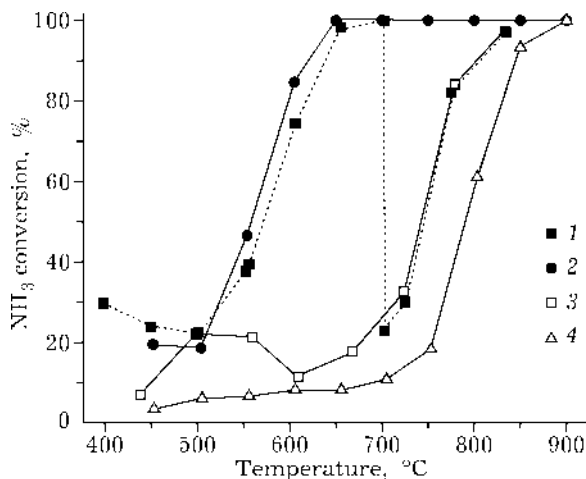


Fig. 1. Ammonia conversion vs. temperature over bulk MnO_2 (1), Mn_2O_3 (2), MnO (3), MnTiO_3 (4).

For the impregnated 15 % $\text{Mn}_2\text{O}_3/\text{TiO}_2$ catalysts (Sample No. 6, Table 2), the NH_3 decomposition attains 100 % conversion at 855 °C. Operation of this catalyst under reaction mixture at 850 °C within 1–2 h leads to the transformation of active manganese oxide $\beta\text{-Mn}_2\text{O}_3$ into MnTiO_3 .

It should be underlined, that the ammonia conversion curves for bulk MnO_2 and Mn_2O_3 , prepared by decomposition of manganese nitrate, are similar in the temperature range of 500–700 °C (Fig. 1). The conversion on these oxides reaches maximum value at 700 °C (100 %), but for MnO_2 decreases to 20 % within 2 h of operation at this temperature. At the reaction temperatures above 700 °C, the ammonia conversion curve for bulk MnO_2 is similar to that of MnO . 100 % NH_3 conversion is achieved at 830 °C. For bulk Mn_2O_3 , ammonia conversion remains high (~100 %) up to 900 °C (in contrast to the commercial sample Mn_2O_3 [20]). In accordance with the XRD data for both precursors, the manganese oxides are reduced to MnO and Mn_3O_4 . In comparison with MnO , the ammonia conversion curve for bulk MnTiO_3 is shifting by 50 °C into the high-temperature region. Therefore, the reduced forms of manganese oxide, such as MnO and MnTiO_3 (or solid solution on the basis of MnTiO_3), which are thermodynamically stable at high temperatures, can be considered as the active components in NH_3 decomposition at temperatures above 700 °C.

There are two ways to stabilize the monolith catalysts: (1) modification of the monolith

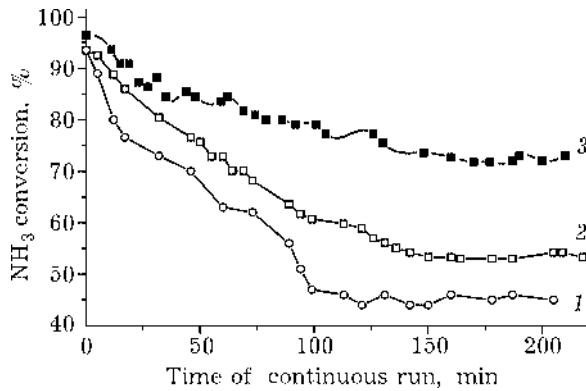


Fig. 2. Stability of 15 % MnO₂ (1), (5 % Fe₂O₃ + 15 % MnO₂) (2), (8 % Fe₂O₃ + 15 % MnO₂) (3) catalysts prepared on MS-1 upon ammonia decomposition at 860 °C.

support, (2) introduction of modifying elements in the supported active component. In this work the second way is considered. To stabilize the impregnated manganese-containing catalysts, 4–8 % mass of iron oxide were introduced into the supported active component. The modified catalyst with 7–8 % mass of Fe₂O₃ demonstrates high activity and stability at elevated temperatures. It is seen from Fig. 2, that ammonia conversion over the manganese-containing catalyst, modified by 8 % mass Fe₂O₃, is reduced from 94 to 73 % at 860 °C. For comparison, ammonia conversion for the unmodified catalyst is decreased to 46 % at this temperature. According to XRD data (Table 3)

TABLE 3

Properties of Mn-Fe-containing monolith catalysts

No.	Catalyst/calcination T, °C	Initial properties		Steady state activity in NH ₃ decomposition		Properties after reaction	
		<i>S</i> _{sp} , m ² /g	Phase composition	<i>T</i> _{50 %} , °C	<i>T</i> _{max} conv., °C (conv., %)	<i>S</i> _{sp} , m ² /g	Phase composition
<i>Impregnated catalysts^a</i>							
1	8 % Fe ₂ O ₃ (N) + 15 % MnO ₂ /500	58	Anatase, β-Mn ₂ O ₃ , <i>D</i> < 5 nm, α-Fe ₂ O ₃ , <i>D</i> < 5 nm	690	790 (90)	6.0	Rutile, anatase (tr), (Fe,Mn)TiO ₃ ^c
2	8 % Fe ₂ O ₃ (O) + 15 % MnO ₂ /500	49	Anatase, β-Mn ₂ O ₃ , <i>D</i> < 5 nm, α-Fe ₂ O ₃ , <i>D</i> < 5 nm	720	760 (85)	7.2	Rutile, anatase (tr), (Fe,Mn)TiO ₃ ^c
3	The same/700	33	Anatase, β-Mn ₂ O ₃ , <i>D</i> < 20 nm, Fe(Fe,Mn,Ti)O ₃ ^b	725	845 (80)	3.2	Rutile, anatase (tr), (Fe,Mn)TiO ₃ ^c
4	»/900	0.2	Rutile, (Fe,Mn)TiO ₃ ^c , MnMn ₆ SiO ₁₂	810	985 (95)	<1	Rutile, (Fe,Mn)TiO ₃ ^c
<i>Washcoating composition</i>							
5	60 % TiO ₂ + 17 % Al ₂ O ₃ + 15 % MnO ₂ + 8 % Fe ₂ O ₃ /500	155	Anatase, MnO ₂ , α-Fe ₂ O ₃ , Fe(Fe,Al)O ₃ ^b	550	800 (100)	24	Rutile (70 %), anatase (30 %), FeTiO ₃ , (Mn,Fe)(Al,Ti)O ₃ ^c
6	The same/700	73	Anatase, Mn ₂ O ₃ , α-Fe ₂ O ₃ Fe(Fe,Mn,Al)O ₃ ^b	575	750 (100)	19	Rutile (70 %), anatase (30 %), FeTiO ₃ , (Mn,Fe)(Al,Ti)O ₃ ^c

^aFor the preparation of impregnated catalysts was used monolith support MS-1. Samples 1 and 2–4 were prepared by impregnation of Mn-catalyst by Fe-nitric solution and by Fe-ammonia-oxalate solution, respectively.

^bHexagonal structure, like α-Fe₂O₃.

^cHexagonal structure, like MnTiO₃.

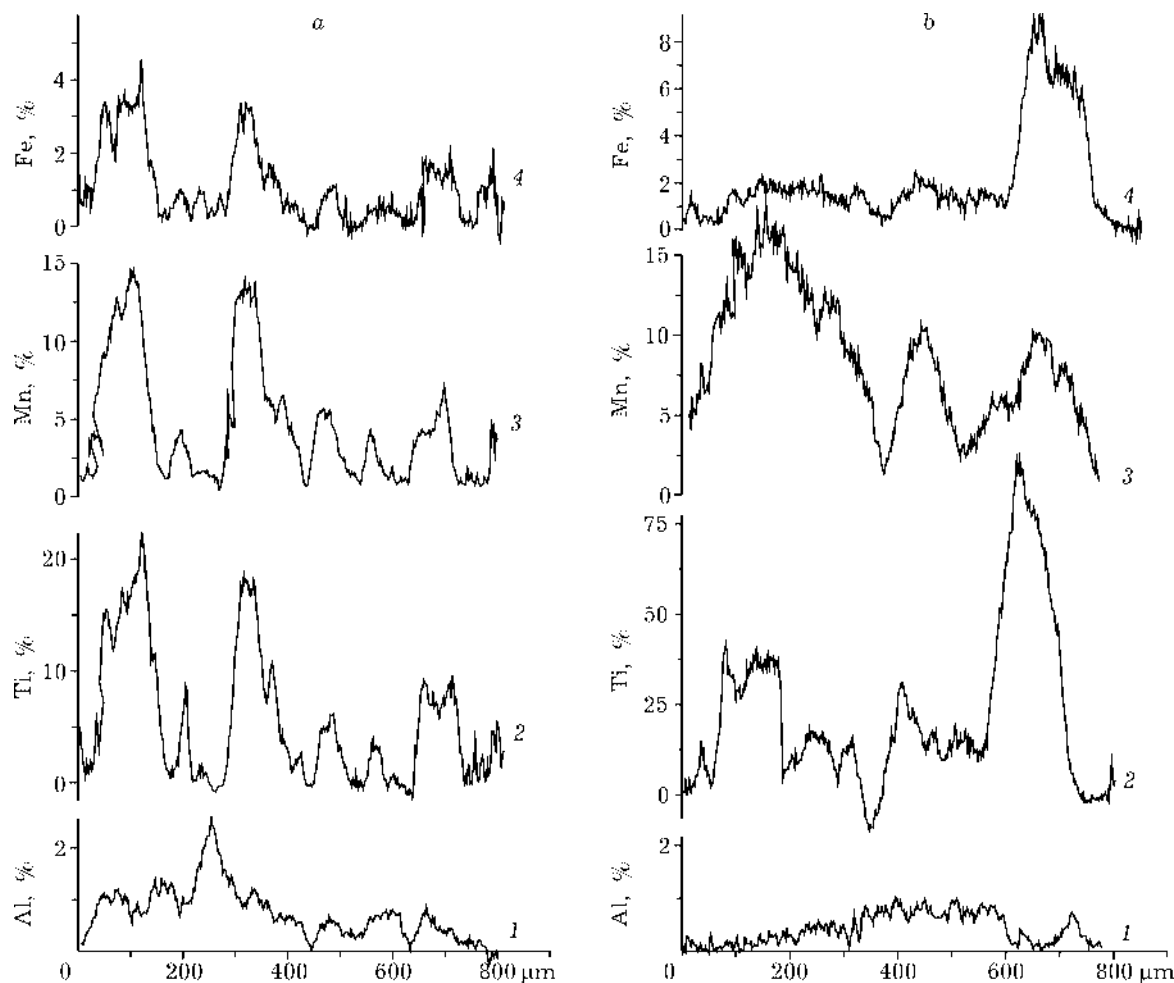


Fig. 3. Intensity of AlK_α (1), TiK_α (2), MnK_α (3) and FeK_α (4) radiation for 8 % Fe_2O_3 + 15 % Mn_2O_3 catalyst prepared on MS-1: initial (a) and after NH_3 decomposition testing (b).

interaction of Fe_2O_3 and Mn_2O_3 with the support material, namely TiO_2 , resulting in the formation of solid solution with the hexagonal structure similar to $(\text{Fe}, \text{Mn})\text{TiO}_3$ is observed for all the studied modified catalysts after testing in NH_3 decomposition.

The symbiosis of TiK_α , MnK_α and FeK_α profiles, which were obtained for the modified catalyst using X-ray microanalysis, indicates the interaction of Mn and Fe oxides with TiO_2 (Fig. 3). It should be emphasized, that the interaction of these components occurs in the initial catalyst (see Fig. 3, a), and is strengthened in catalyst after ammonia decomposition test (see Fig. 3, b).

As it is illustrated in Fig. 4, the specially prepared bulk FeTiO_3 demonstrates higher catalytic activity and stability in ammonia decomposition at temperatures above 600 °C than

bulk MnTiO_3 . For instance, temperatures at which 50 % ammonia conversion is achieved are 540 and 790 °C, respectively, for FeTiO_3 and MnTiO_3 . It should be pointed out that, as

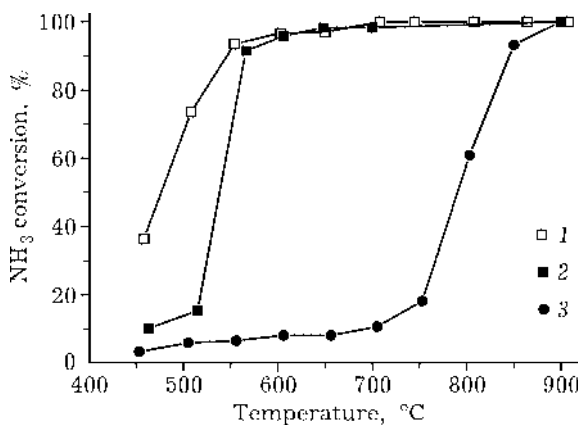


Fig. 4. Ammonia conversion vs. temperature over bulk $\alpha\text{-Fe}_2\text{O}_3$ (1), FeTiO_3 (2), MnTiO_3 (3).

TABLE 4
Properties of Mn-Cu-containing monolith catalysts

No.	Catalyst/calcination <i>T</i> , °C	Initial properties		Steady State Activity in NH ₃ decomposition		Properties after reaction	
		<i>S</i> _{sp} , m ² /g	Phase composition	<i>T</i> _{50 %} , °C	<i>T</i> _{max conv.} , °C (conv., %)	<i>S</i> _{sp} , m ² /g	Phase composition
<i>Impregnated catalysts^a</i>							
1	8 % CuO (N) + 15 % MnO ₂ /500	56	Anatase, MnO ₂ , <i>D</i> < 30 nm, CuO, <i>D</i> < 20 nm	690	790 (90)	5.6	Anatase, MnTiO ₃ , Cu ⁰ , <i>D</i> > 40 nm
2	The same/700	23	Anatase, β-Mn ₂ O ₃ , CuMn ₂ O ₄ , CuO	700	820 (90)	5.5	Anatase, MnTiO ₃ , Cu ⁰ , <i>D</i> > 40 nm
3	The same/900	3	Rutile, MnTiO ₃ , CuMn ₂ O ₄	800	900 (75)	2.4	Rutile, MnTiO ₃ , Cu ⁰ , <i>D</i> > 50 nm
<i>Washcoating composition^b</i>							
4	60 % TiO ₂ + 17 % Al ₂ O ₃ + 15 % MnO ₂ + 8 % CuO/700	54	Anatase, γ-Al ₂ O ₃ , β-Mn ₂ O ₃ , (Cu,Mn)[Al] ₂ O ₄ ^c	725	775 (100)	27	Anatase, MnTiO ₃ , CuO
5	The same/900	15	Rutile, α-Al ₂ O ₃ , (Cu, Mn)[Al] ₂ O ₄ ^c	560	700 (100)	1.8	Rutile + α-Al ₂ O ₃ , Mn(Mn,Ti)O ₃ ^d , (Cu,Mn)[Al] ₂ O ₄ ^c , Cu ⁰

^aFor the preparation of impregnated catalysts was used monolith support MS-1. Samples No. 1–3 were prepared by impregnation of Mn-catalyst by Cu-nitric solution.

^bFor Samples No. 4, 5, CuO was introduced via impregnation of 60 % TiO₂ + 17 % Al₂O₃ + 15 % MnO₂ by Cu-nitric solution.

^cStructure, like CuMn₂O₄.

^dHexagonal structure, like MnTiO₃.

it is shown in Fig. 4, catalytic activities of bulk FeTiO₃ and pure α-Fe₂O₃ are the same at temperatures above 600 °C. Accordingly, it is believed that high activity and stability of the modified catalysts at elevated temperatures are provided by the formation of phase FeTiO₃ under the reaction conditions.

The main goal of this work is the development of optimal catalysts for the simultaneous ammonia and H₂S removal from hot coal gases. In order to combine high efficiency of the systems on the basis of iron and copper oxides in ammonia decomposition, and high activity of the manganese-containing catalysts in regenerative hydrogen sulfide removal, the samples with two active components were synthesized by the impregnation of monolith support. The properties of catalysts based on Fe–

Mn- or Cu–Mn-oxides are presented in Tables 3 and 4. Temperature at which 90 % NH₃ conversion is achieved on the Cu–Mn-oxides impregnated catalysts was about 790–810 °C. System on the basis of manganese oxide doped with iron oxide (8 % mass) is the most active catalyst.

It should be noted, that XRD data of all the spent catalysts show that NH₃ decomposition on the oxide systems is accompanied by the partial or complete reduction of the active component, and its interaction with the support, resulting in the formation of hexagonal structures like MnTiO₃ or FeTiO₃ (see Tables 3 and 4). In the case of Cu oxide-containing catalysts, reduction of the CuO and spinel structure like CuMn₂O₄ into metallic state (Cu⁰) at the reaction conditions was observed.

Washcoated monolith catalysts

To optimize compositions of the washcoated monolith catalysts, bulk samples of the washcoating precursors have been prepared and tested. As it is indicated in [13], the activity of manganese oxide-containing washcoating materials and of washcoated catalysts is rather high. For example, 100 % of NH_3 conversion is achieved at 850–900 °C for all the bulk samples of washcoating precursors. The most active among the bulk manganese-containing washcoating compositions was the sample, in which MnO_2 was introduced as a bulk oxide. For the manganese-containing washcoating material, higher conversion of ammonia is observed at lower temperatures than that for the impregnated catalysts.

Our intentions were to improve these compositions by modifying them with iron or copper oxides. The modification of manganese-containing washcoating composition 65 % TiO_2 + 15 % MnO_2 + 20 % Al_2O_3 by Fe_2O_3 leads to the substantial increasing of its activity. For example, the temperature of attaining of 100 % NH_3 conversion ($T_{100\%}$) was 870 and 720 °C for unmodified and modified catalysts, respectively (Fig. 5). The effect of CuO additives on the activity of washcoating composition 65 % TiO_2 + 15 % MnO_2 + 20 % Al_2O_3 was weaker ($T_{100\%}$ = 780 °C, see Fig. 5).

The effect of Fe_2O_3 and CuO additives on the activities of washcoated catalysts prepared

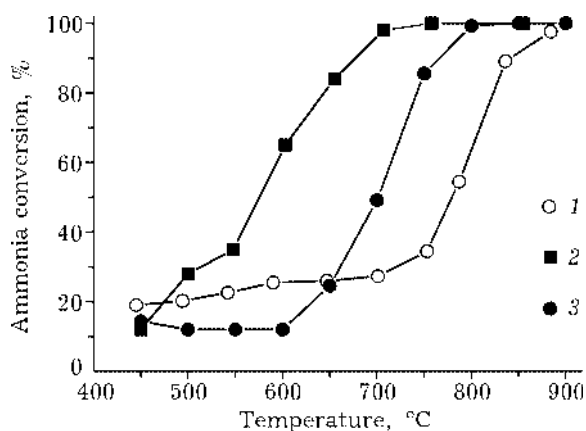


Fig. 5. Ammonia conversion vs. temperature over bulk washcoating materials calcined at 700 °C: 1 – 15 % Mn_2O_3 + 20 % Al_2O_3 + 65 % TiO_2 ; 2 – 8 % Fe_2O_3 + 15 % Mn_2O_3 + 17 % Al_2O_3 + 60 % TiO_2 ; 3 – 8 % CuO + 15 % Mn_2O_3 + 17 % Al_2O_3 + 60 % TiO_2 .

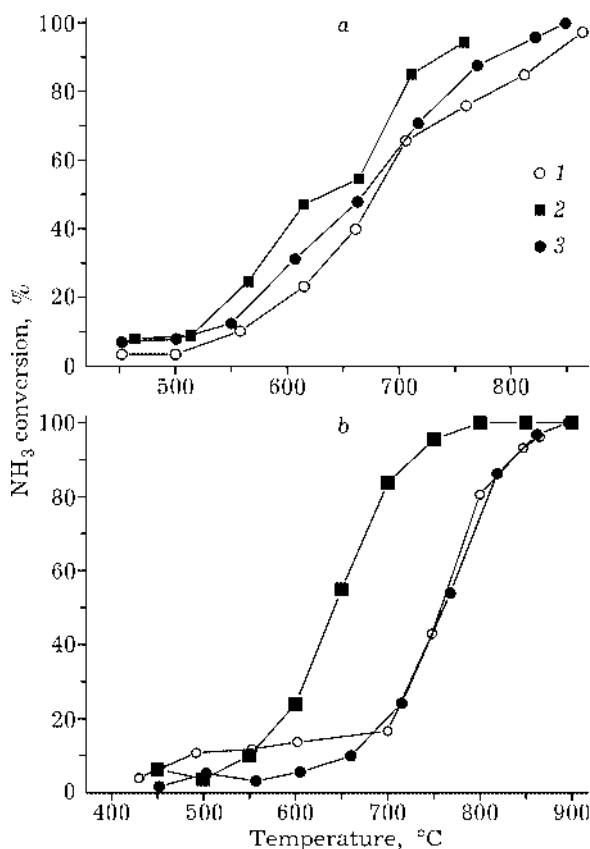


Fig. 6. Ammonia conversion vs. temperature over washcoated monolith catalysts based on aluminosilicate (a) and cordierite (b) after calcination at 700 °C: 1 – 15 % Mn_2O_3 + 20 % Al_2O_3 + 65 % TiO_2 ; 2 – 8 % Fe_2O_3 + 15 % Mn_2O_3 + 17 % Al_2O_3 + 60 % TiO_2 ; 3 – 8 % CuO + 15 % Mn_2O_3 + 17 % Al_2O_3 + 60 % TiO_2 .

on aluminosilicate (MS-2) or cordierite (Corning, 400 cell/inch) monolith was less pronounced (Fig. 6). For example, temperature of 95 % NH_3 conversion was 870, 760 and 820 °C for unmodified, modified by Fe_2O_3 and CuO catalysts, respectively, in case of MS-2 monolith. The modification effect of CuO additives was smoother when using the cordierite (see Fig. 6, b).

Testing of the catalyst in hydrogen sulfide sorption

The samples chosen in accordance with the results of catalytic activity tests in the ammonia decomposition have been tested in the hydrogen sulfide sorption. All experimental data are presented in Table 5. The sorption capacities of pure monolith support MS-1 and impregnated catalyst containing only 15 % MnO_2 are presented in Table 5 for comparison. The

TABLE 5

Properties of monolith catalysts in the H₂S sorption

Catalyst/calcination T, °C	Testing H ₂ S sorption at 700 °C			Testing in NH ₃ decomposition after H ₂ S sorption		
	Sorption capacity, mmol/g (% mass)	S _{sp} , m ² /g	XRD phase	T _{50 % before} , °C	T _{50% after} , °C	XRD phase
MS-1/ 700	0.4 (1.3)	62	Anatase, α-SiO ₂ (tr), Ca-montm ^a (tr)	725	640	Anatase, α-SiO ₂ (tr)
15 % MnO ₂ / ^b 700	1.7 (5.8)	18	Anatase+rutile, MnS	780	710	Anatase+rutile, MnS
8 % Fe ₂ O ₃ + 15 % MnO ₂ / ^b 700	2.1 (6.8)	15	Anatase+rutile, MnS, Fe _{1-x} S	725	670	Anatase+rutile, MnS, Fe _{1-x} S
8 % Fe ₂ O ₃ + 15 % MnO ₂ / ^b 700 after NH ₃ test	0.4 (1.4)	1.5	Rutile, MnS	–	–	–
8 % CuO + 15 % MnO ₂ / ^b 700	2.7 (6.1)	5.4	Anatase+rutile, MnS, CuS, Cu ₂ S	740	750	Anatase + rutile, MnS, CuS
8 % CuO + 15 % MnO ₂ / ^b 700 after NH ₃ test	(0.20)	5.5	Rutile, MnS	–	–	–
60 % TiO ₂ + 17 % Al ₂ O ₃ + 15 % MnO ₂ + 8 % Fe ₂ O ₃ / ^c 500	1.9 (6.0)	34	Anatase, MnS, Fe _{1-x} S	575	625	Anatase, MnS, Fe _{1-x} S
60 % TiO ₂ + 17 % Al ₂ O ₃ + 15 % MnO ₂ + 8 % CuO/ ^c 700	1.4 (4.4)	54	Anatase, MnS, γ*-Al ₂ O ₃	725	710	50 % Anatase, 50 % rutile, MnS, γ*-Al ₂ O ₃

^aCa-montmorillonite.^bImpregnated catalysts on the basis of monoliths support MS-1.^cBulk washcoating material.

sorption capacity of original monolith support MS-1 achieved 1.3 % mass, which can be explained by the presence of 2 % mass CaO and 1.8 % mass Fe₂O₃ as admixtures in Ca-montmorillonite, used as the binder. It has been found, that the sorption capacity of impregnated Mn-containing catalysts on TiO₂-monolith support depends on the Mn content. The increasing of Mn content from 5 to 20 % mass leads to the proportional rise of sorption capacity from 1.6 to 6.3 % mass.

The sorption capacities of the impregnated catalyst and bulk washcoating material, containing simultaneously 15 % MnO₂ and 8 % Fe₂O₃, were 6.8 and 6.0 % mass, respectively. These data are in a good correlation with those previously reported by Bakker [3]. By means

of the XRD analysis formation of the MnS and Fe_{1-x}S_x phases was detected.

Sorption capacity of the Mn-containing catalyst modified by 8 % mass CuO was similar to unmodified catalyst. The sorption capacities of the impregnated catalyst and bulk washcoating material, containing simultaneously 15 % MnO₂ and 8 % CuO, were 6.1 and 4.4 % mass, respectively. By means of the XRD analysis, formation of the MnS, Cu₂S and CuS phases was detected for the impregnated catalyst.

The sulfidation degree of supported oxides, calculated from the stoichiometric reaction for all the studied catalysts, was estimated to be around 70 %. Thus, it is believed that part of the active component may remain in the forms

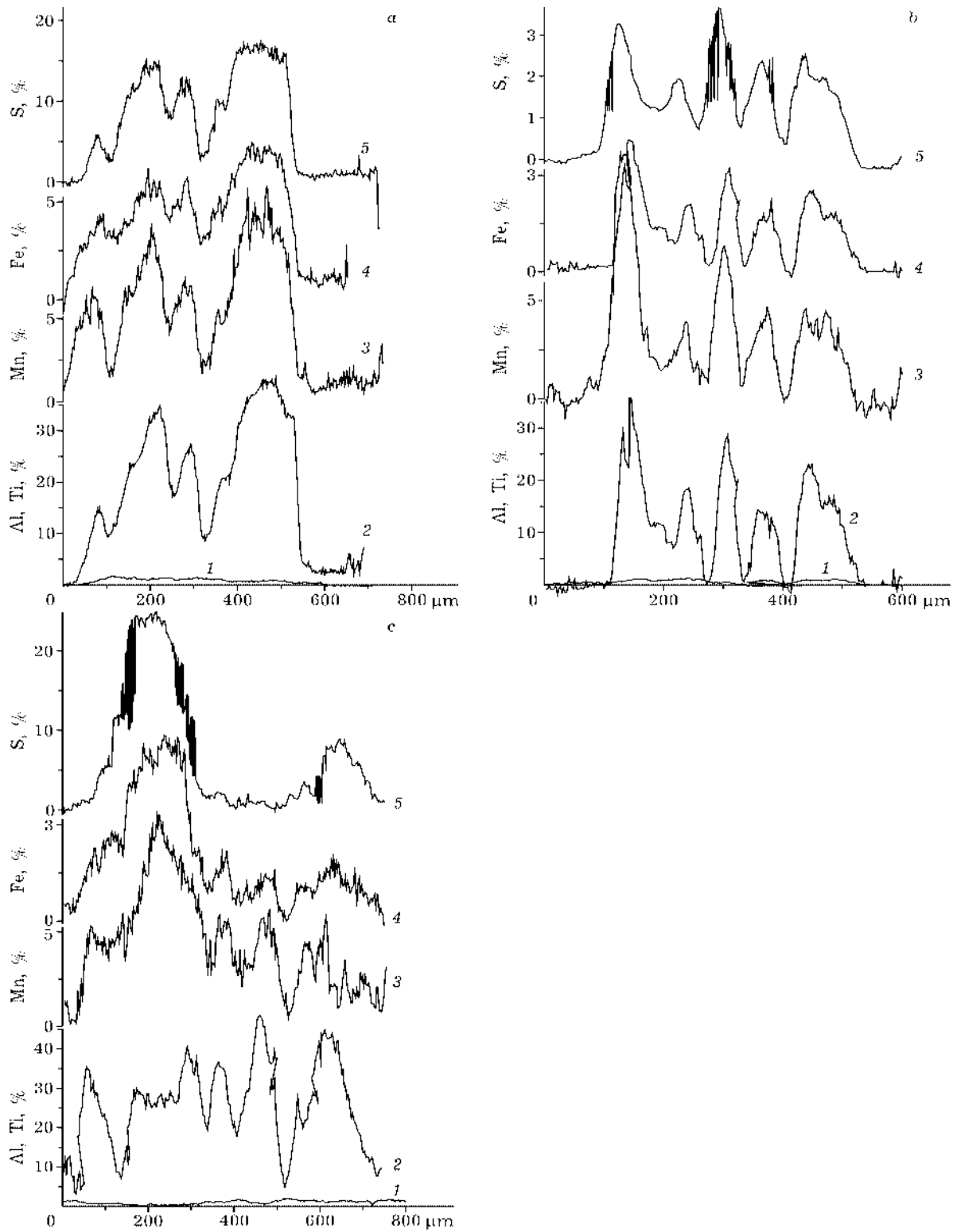


Fig.7. Intensity of AlK_{α} (1), TiK_{α} (2), MnK_{α} (3), FeK_{α} (4) and SK_{α} (5) radiation for 8 % Fe_2O_3 + 15 % MnO_2 catalyst prepared on MS-1: a - after H_2S sorption test; b - after subsequent testing in H_2S sorption and NH_3 decomposition; c - after subsequent testing in NH_3 decomposition and H_2S sorption.

of Mn, Fe and Cu oxides, although this fact was not confirmed by the XRD analysis.

The increase of calcination temperature of Mn-containing catalyst modified by Fe_2O_3 up to 900 °C leads to the substantial reduction of H_2S sorption capacity. Similar decrease of the sorption capacity (to 1.4 % mass) was observed for this catalyst after testing in NH_3 decomposition. It should be noted, that sorption capacity of the catalyst modified by CuO after testing in NH_3 decomposition was close to zero.

Testing of the catalyst in ammonia decomposition after hydrogen sulfide sorption

The catalysts after hydrogen sulfide sorption were tested consequently in ammonia decomposition reaction. As it can be seen from the data of Table 5 samples exhibited the activity equal to the activity of fresh catalysts, or even higher. These results can be explained in terms of formation of partially reduced iron and manganese cations, which are known to be more active in ammonia decomposition [1].

The Mn-containing catalyst modified by Fe_2O_3 after testing in H_2S sorption was studied by X-ray spectral microanalysis. The investigation of modified catalyst demonstrated that the catalyst after H_2S sorption test contains about 20 % mass S. In this case sulfur is chemically bonded with Mn and Fe cations, that is proved by the symbasis of SK_α , MnK_α , FeK_α profiles (Fig. 7, a). The catalyst after subsequent testing in H_2S sorption and NH_3 decomposition contains negligible amount of sulfur chemically bonded with Mn and Fe cations (see Fig. 7, b). The catalyst after subsequent testing in NH_3 decomposition and H_2S sorption contains negligible amounts of both the sulfur chemically bonded with Mn and Fe cations and of the elemental sulfur (see Fig. 7, c). Thus, two parallel reactions: H_2S sorption and decomposition take place on this case.

CONCLUSIONS

The introduction of 4–8 % mass Fe or Cu oxides into Mn-containing catalyst allows to

improve thermal stability at high reaction temperatures and catalytic performance.

Under the reaction conditions the manganese oxides (MnO_2 and $\beta\text{-Mn}_2\text{O}_3$) interact with support (TiO_2), which results in the formation of pure or partially substituted hexagonal structures, like MnTiO_3 . The similar phenomenon was observed for the Fe oxide-containing catalysts, where $\alpha\text{-Fe}_2\text{O}_3$ transformed to FeTiO_3 . In the case of Cu oxide-containing catalysts, reduction of CuO into metallic state (Cu^0) under the reaction conditions was observed. The investigation of bulk MnTiO_3 , FeTiO_3 and the special series of samples supported on granulated Ca-montmorillonite and TiO_2 allows to understand the reason of high temperature deactivation of the impregnated manganese oxide catalyst. It has been found, that bulk FeTiO_3 has higher catalytic activity and stability in the ammonia decomposition at temperatures above 600 °C, than bulk MnTiO_3 . The obtained data indicate, that high activity and stability of the modified catalysts at elevated temperatures is provided by the formation of active phase $(\text{Fe,Mn})\text{TiO}_3$.

The monolith catalysts based on $\text{Fe}_2\text{O}_3 + \text{MnO}_2$ active component seem to be the most preferable among studied systems, since they possess the highest catalytic activity at lower temperatures and are the best sorbents for H_2S removal.

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