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Supported honeycomb monolith catalysts for high-temperature ammonia decomposition and H_2S removal

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Abstract

Catalysts that have potential in simultaneous removal of H_2S and NH_3 decomposition were developed. The monolith supports of high surface area and acceptable mechanical strength based on titania and silica–alumina precursors were prepared and tested. Preparation routine and composition of Mn, Fe and Cu oxides supported honeycomb catalysts have been optimized. Impregnated and washcoated monolith catalysts were tested in ammonia high-temperature decomposition. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Processes, which allow the simultaneous removal of hydrogen sulfide and ammonia from hot fuel gas, using one sorbent/catalyst are of primary interest. The development of the sorbent/catalysts in the form of monolith increases their technical merit due to ease of operation and regeneration owing to low pressure drop, small dust and attrition sensitivity. The oxides of transition metal Fe_2O_3, CuO, Cr_2O_3, which are the most active catalysts for ammonia decomposition [1], and manganese oxides, which are very attractive for regenerative sulfur removal [3,4], should be considered as the most promising candidates for active components of such sorbent/catalysts. However, bulk catalysts are subject to poisoning by sulfur compounds, have low thermal stability, and their selectivity decreases as temperature increases. Titania is widely used as a support to improve thermal, mechanical and chemical properties of catalyst and sorbents but its application in the form of honeycomb support is rather limited. In this work, oxides of Mn, Fe and Cu were used to prepare monolith catalysts based on titania honeycomb support and titania washcoating on alumina–silica monolith. Physico-chemical properties of the synthesized supports and catalysts, as well as the results of their testing in ammonia decomposition are described.

2. Experimental

2.1. Preparation of the monolith support

The monolith supports were prepared by extrusion of the masses based on titanium dioxide (anatase) or

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silica–alumina precursors followed by drying at 110°C and calcination at 700°C. To provide absence of defects during drying, Ca and Na forms of montmorillonite were used as a binder. Die with diameter of 20 mm, size of square channels 2 × 2 mm, was used for the extrusion.

2.2. Preparation of the impregnated monolith catalysts

The impregnated catalysts were prepared by wet impregnation of the TiO_2 monolith supports with aqueous solution of manganese nitrate or acetate (2 M) with subsequent drying at 110°C and calcination at 500, 700 and 900°C. To obtain higher manganese loading, the impregnation–drying–calcination procedure was repeated.

The Cu- and Fe-containing catalysts were prepared by impregnation of the monolith support with aqueous solution of copper nitrate (3 M), iron nitrate (2 M) or iron (III) ammonium oxalate (1 M). The prepared samples were calcined at 500°C.

2.3. Preparation of the washcoated monolith catalysts

Washcoated catalysts were prepared using the SiO_2/Al_2O_3 monolith supports. The mixtures of TiO_2 and γ-Al_2O_3 (as a binder) were applied as a precursor of washcoating layer. Active component (Mn) was introduced into the washcoating by two methods:

1. Impregnation of TiO_2 with solution of $Mn(NO_3)_2$, drying and calcination at 500°C; subsequently, a suspension of the Mn_2O_3/TiO_2 and binder mixture was prepared.
2. Bulk MnO_2 or Mn_2O_3 obtained by the decomposition of $Mn(NO_3)_2$ were mixed with TiO_2 and binder and a suspension base 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.

2.4. Activity test procedure

Ammonia decomposition was carried out in a flow reactor within the temperature range 400–1000°C and space velocities of 500–2000 h^{-1}. Ammonia concentration in initial gas mixture was 1 vol.%. Gas flow was balanced by helium.

3. Results and discussion

3.1. Preparation and study of monolith supports

It has been found that the best binder providing high mechanical strength and absence of defects is the pillared clay of montmorillonite type (Ca- or Na-forms). The properties of the monolith supports with optimal ratio between binder and TiO_2 and silica–alumina, respectively, are given in Table 1. It is seen that the increase of the calcination temperature leads to an increase in the mechanical strength of the monolith supports and decrease in S_{BET} and the pore volume. Taking into account the conditions of the catalysts preparation (impregnation method) and activity

Table 1
Properties of the monoliths support

Composition of the monolithsᵃ	T (°C)	S_{BET} (m^2/g)	Phase composition	Mechanical strength (kg/cm^2)	Pore volume (water) (cm^3/g)
63% TiO_2 + 35% Ca-f + 2% MSF	700	86	TiO_2 (anatase) $D \sim 200$ Å + $Al_2O_3 \cdot SiO_2$	8	0.41
	900	16	TiO_2 (anatase) $D \sim 400$ Å + $Al_2O_3 \cdot SiO_2$	28	0.22
75% silica–alumina (clay) + 25% Ca-f	700	33	$Al_2O_3 \cdot SiO_2 + \alpha$-$SiO_2$	19.5	0.11
	900	0.5	$Al_2O_3 \cdot SiO_2 + \alpha$-$SiO_2$	24.0	0.08

[a] Ca-f means the pillared clay of montmorillonite type in Ca-form; MSF — mullite-silica fibers; silica–alumina (clay) — pure clay *Obskaya*.

testing, a temperature of 700°C seems to be optimal for monolith supports calcination. After calcination at this temperature, the synthesized monolith materials still possess relatively high surface area and acceptable mechanical strength that allows their application as supports for monolith catalysts.

3.2. Impregnated monolith catalysts

The dependence of the properties of the catalysts and their activity on the nature of the active component, loading of the active component, duration of the impregnation step of the monolith supports, type of the support and calcination temperature have been studied.

It has been found that after calcination at 500°C, manganese oxide is present as dispersed MnO_2. Increasing the calcination temperature to 700°C leads to the formation of orthorhombic β-Mn_2O_3 and the appearance of rutile phase due to monolith support transformation. For the catalysts with a high manganese oxide loading prepared on the support composed of pillared clay of montmonrillonite type in Ca-form (Ca-f), calcination at 900°C results in an interaction between manganese and clay. A structure like $MnMn_6SiO_{12}$ with substitution of part of Mn-cations by Al^{3+} or Si^{4+} is formed. Titanium dioxide is present as a rutile phase. It should be noted that pure titanium dioxide transforms to rutile phase only at 1050°C. Low temperature formation of rutile may be explained by the decrease of thermal stability of bulk titanium dioxide in the presence of manganese as it was observed for alumina in Mn–alumina systems [2].

For the samples containing Cu or Fe oxides only a minor interaction between active components and the supports is observed.

3.3. Washcoated monolith catalysts

To optimize compositions of the washcoated monolith catalysts, bulk samples of washcoating precursors have been prepared and tested. For washcoating precursors containing manganese oxide, increasing the calcination temperature from 500 to 700°C leads to the formation of orthorhombic β-Mn_2O_3. For the samples of TiO_2 impregnated with manganese salt the appearance of rutile phase is observed even at 700°C. For the samples where manganese was introduced as an individual bulk oxide, rutile phase forms only at 900°C. For the samples calcined at 900°C, the product of interaction between manganese and titanium dioxide is also present. A solid solution of hexagonal structure like $MnTiO_3$ is formed. It should be noted that phase composition of the bulk Mn-oxide containing washcoating materials prepared by impregnation of TiO_2 is similar to the composition detected for impregnated monolith catalysts calcined at the same temperature.

3.4. Testing of the catalyst activity

3.4.1. Impregnated monolith catalysts

Activities of the impregnated monolith catalysts are also given in Table 2. Increasing the manganese content from 5 to 20 wt.% leads to high activity of the catalyst (>80% conversion at 850°C). It is seen that the catalysts with optimal manganese oxide content calcined at 500 and 700°C demonstrate rather high activity. The conversion of NH_3 is 80% at 800°C, although there is some decline in the activity at further increase of reaction temperature up to 900°C. The sample calcined at 900°C demonstrates high conversion only at temperature above 900°C (Fig. 1).

The iron and copper containing catalysts prepared by impregnation exhibit higher activity and stable performance at higher temperatures in comparison with samples containing only manganese oxides. Thus, $T_{50\%}$ (temperature at 50% conversion) decreases almost for 80°C and the conversion of ammonia close to 95% can be attained in the temperature range of 750–800°C (Fig. 2).

In order to combine high activity of the systems based on iron and copper oxides in the reaction of ammonia decomposition with high activity of manganese containing catalysts in the regenerative hydrogen sulfide removal [3,4], samples which contain both active components (Fe–Mn and Cu–Mn) were synthesized by impregnation of monolith support. Activities of these mixed monolith catalysts are also listed in Table 2. It has been found that the combination of manganese oxide with iron oxide results in the most active catalyst.

The impregnated Mn-containing catalysts lose their activity at 800–900°C. This may occur due to chemical

Table 2
Activity of prepared catalysts in ammonia decomposition reaction

N	Catalyst composition/$T_{\text{calcination}}$ (°C)	Conversion of NH_3 at different T (°C), %					$T_{\text{max conv.}}$ (°C)/% conv.
		500	600	700	800	900	
Impregnated monolith catalysts							
1	15% MnO_2(64% TiO_2 + 36% Ca-f)/500	15	35	35	75	55	875/80
2	15% MnO_2(64% TiO_2 + 36% Ca-f)/700	15	30	15	58	57	850/70
3	15% MnO_2(64% TiO_2 + 36% Ca-f)/900	10	5	16	16	35	965/82
4	20% MnO_2(64% TiO_2 + 36% Ca-f)/500	10	40	27	80	60	800/80
5	20% MnO_2(64% TiO_2 + 36% Ca-f)/700	25	40	30	80	55	850/85
6	7.5% CuO(64% TiO_2 + 36% Ca-f)/500	15	22	60	95	–	800/95
7	14% CuO(64% TiO_2 + 36% Ca-f)/500	10	20	70	95	–	780/95
8	8% Fe_2O_3(64% TiO_2 + 36% Ca-f)/500	15	15	65	95	–	800/95
Mixed impregnated monolith catalysts							
9	(7.5% CuO + 15% MnO_2)64% TiO_2 + 36% Ca-f/500	10	15	55	90	–	750/90
10	(8% Fe_2O_3 – 15% MnO_2)64% TiO_2 + 36% Ca-f/500	15	62	85	98	–	750/98
Washcoated monolith composition							
11	[80% (12% MnO_2/TiO_2) + 20% Al_2O_3]/500	5	0	20	80	100	900/100
12	[80% (12% MnO_2/TiO_2) + 20% Al_2O_3]/700	10	10	10	90	100	850/100
13	70% TiO_2 + 10% MnO_2 + 20% Al_2O_3/500	10	10	5	75	100	900/100
14	70% TiO_2 + 10% MnO_2 + 20% Al_2O_3/700	0	0	10	90	100	810/100
15	70% TiO_2 + 10% MnO_2 + 20% Al_2O_3/900	5	10	20	40	100	900/100
16	60% TiO_2 + 20% MnO_2 + 20% Al_2O_3/500	5	40	20	95	100	850/100
17	60% TiO_2 + 20% MnO_2 + 20% Al_2O_3/700	10	40	15	80	100	875/100
18	70% TiO_2 + 10% Mn_2O_3 + 20% Al_2O_3/500	10	19	20	80	100	850/100
19	70% TiO_2 + 10% Mn_2O_3 + 20% Al_2O_3/700	25	10	10	60	100	900/100

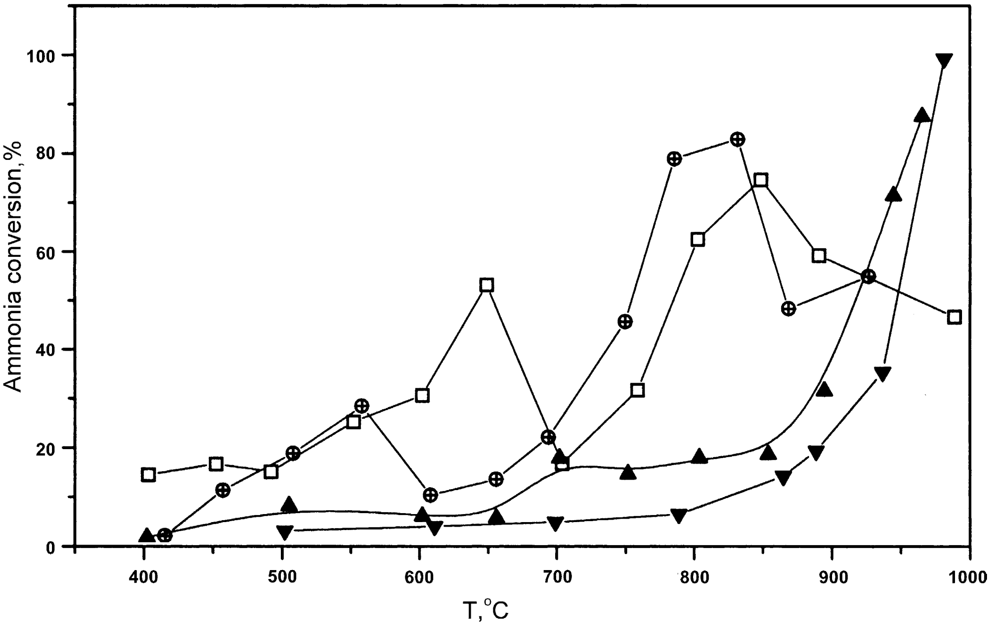

Fig. 1. Ammonia conversion vs temperature over impregnated monolith catalyst 15% MnO_2/(TiO_2 + Ca-f) calcined at: 500°C (⊕); 700°C (□), 900°C (▲); 1000°C (▼).

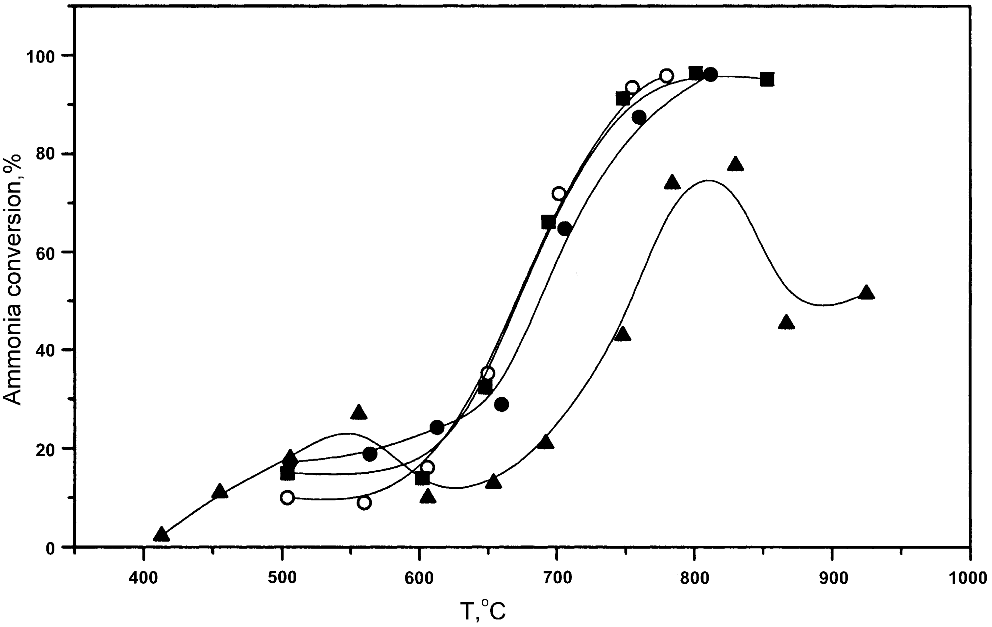

Fig. 2. Ammonia conversion vs temperature over impregnated monolith catalysts: 15% $MnO_2/(TiO_2 + Ca\text{-}f)$ (N1) (▲); 8% $Fe_2O_3/(TiO_2 + Ca\text{-}f)$ (N8) (■); 7.5% $CuO/(TiO_2 + Ca\text{-}f)$ (N6) (●); 14% $CuO/(TiO_2 + Ca\text{-}f)$ (N7) (○).

interaction on Mn oxides and the support resulting in the formation of inactive phases containing Mn cations in silica–alumina or titanium oxide structure. Samples of catalyst preliminarily treated at high temperature (900°C) do not lose their activity after 800°C. This is the subject for future study.

3.4.2. Washcoated monolith catalysts

The catalytic activity of the bulk samples of washcoating precursors was tested at the same conditions as above mentioned for impregnated catalysts.

High conversion of ammonia on the manganese-containing washcoating material is observed at lower temperature than that for the impregnated catalysts. Thus, 100% of ammonia conversion is achieved at 850–900°C for all bulk samples of washcoating precursors. The most active is the bulk washcoating composition 70% TiO_2 + 10% MnO_2 + 20% Al_2O_3 in which MnO_2 is introduced as a bulk oxide.

XRD data of the samples after the catalytic tests shows that NH_3 decomposition on oxide systems is accompanied by partial or complete reduction of active component and its interaction with the support.

4. Conclusions

Titania and silica–alumina monolith type supports have been prepared successfully. Optimal ratio between main oxide component, titania and silica–alumina, respectively, and binder as well as calcination temperature resulted in high surface area and acceptable mechanical strength of the monolith support has been determined.

Individual and mixed Cu, Fe, and Mn-supported monolith catalysts have been synthesized using impregnation and washcoating techniques. For impregnated monolith catalysts containing individual oxides, the most active compositions of active phase are the following:

- 14% CuO, calcined at 500°C (95% of NH_3 conversion at 780–800°C);
- 8% Fe_2O_3, calcined at 500°C (95% of NH_3 conversion at 780–800°C);
- 15–20% MnO_2, calcined at 700°C (80–85% of NH_3 conversion at 800–850°C).

For mixed monolith catalysts, the most active are the catalysts containing:

- 8% Fe_2O_3 + 15% MnO_2, calcined at 500°C (98% of NH_3 conversion at 750°C);
- 7.5% CuO + 15% MnO_2, calcined at 500°C (90% of NH_3 conversion at 800°C).

Among washcoated monolith catalysts, the catalyst with washcoat prepared from a mixture of 70% TiO_2 + 10% MnO_2 + 20% Al_2O_3 (MnO_2 introduced as the bulk oxide) and calcined at 700°C has the highest catalytic activity (100% of NH_3 conversion at 810°C).

Mixed impregnated monolith catalysts based on Fe_2O_3/MnO_2 active seems to be the most preferable among the studied systems since they possess the highest catalytic activity at lower temperature and are expected to be perfect sorbent for H_2S removal. The synthesized catalysts combine satisfactory high catalytic activity in ammonia decomposition with acceptable mechanical strength of monolith supports.

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