



Selective catalytic reduction of nitrogen oxide by ammonia on Mn(Fe)-substituted Sr(La) aluminates

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ARTICLE INFO

Article history:

Received 9 December 2008
Received in revised form 16 January 2009
Accepted 16 January 2009
Available online 29 January 2009

Keywords:

Hexaaluminate
XRD
TPR
XPS
Reduction NO

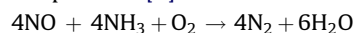
ABSTRACT

Aluminates $\text{SrMn}_2\text{Al}_{10}\text{O}_{19}$, $\text{Sr}_{0.8}\text{La}_{0.2}\text{Mn}_2\text{Al}_{10}\text{O}_{19}$, $\text{LaMn}_2\text{Al}_9\text{O}_{18}$, $\text{LaMnAl}_{10}\text{O}_{18}$ and $\text{SrFeMnAl}_{10}\text{O}_{19}$ prepared by co-precipitation and calcined at 700–1400 °C have been characterized by absorption methods, thermal analysis (TG–DTA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR). It has been shown that calcination at 1100 °C results in the formation of multiphase systems containing mainly hexaaluminate. The specific surface area of the samples calcined at 1100 °C has been ranged from 20 to 25 m²/g, except for the $\text{Sr}_{0.67}\text{Mn}_{2.28}\text{Al}_{10}\text{O}_{19.1}$ hexaaluminate, whose specific surface area was twice as large. TPR–H₂ of the samples calcined at 700 °C proceeded in several steps. The first step was related to the reduction of $\text{Mn}(\text{Fe})_2\text{O}_3$ to $\text{Mn}(\text{Fe})_3\text{O}_4$ at 345–382 °C. The second step was related to the reduction of Mn_3O_4 to MnO. The replacement of the part of Sr ($\text{Sr}_{0.67}\text{Mn}_{2.28}\text{Al}_{10}\text{O}_{19.1}$) by La and of the part of Mn by Fe led to the decrease in T_{TPR} . The amount of H₂ consumed during the reduction of the samples calcined at 700 and 1100 °C increases in the series: $\text{Sr}_{0.67}\text{Mn}_{2.28}\text{Al}_{10}\text{O}_{19.1}$ (1100 °C) < $\text{Sr}_{0.89}\text{Fe}_{0.93}\text{Mn}_{1.03}\text{Al}_{10}\text{O}_{18.8}$ (1100 °C) < $\text{Sr}_{0.89}\text{Fe}_{0.93}\text{Mn}_{1.03}\text{Al}_{10}\text{O}_{18.8}$ (700 °C) < $\text{Sr}_{0.67}\text{Mn}_{2.28}\text{Al}_{10}\text{O}_{19.1}$ (700 °C) < $\text{Sr}_{0.69}\text{La}_{0.33}\text{Mn}_{2.23}\text{Al}_{10}\text{O}_{19.5}$ (700 °C). Surface concentrations of elements in the samples $\text{Sr}_{0.69}\text{La}_{0.33}\text{Mn}_{2.23}\text{Al}_{10}\text{O}_{19.5}$ and $\text{Sr}_{0.89}\text{Fe}_{0.93}\text{Mn}_{1.03}\text{Al}_{10}\text{O}_{18.8}$ differ from the volume chemical contents. The main components on the surface are in oxidized state: Al³⁺, La³⁺ and Fe³⁺, Mn³⁺ and Mn²⁺. Amount of Mn³⁺ ions is 65 and 49%, respectively. Sr is predominantly localized on the surface as SrCO₃. Among hexaaluminates, the most active ($X_{\text{NO}} \approx 78\%$) and selective sample in the selective catalytic reduction (SCR) of NO to N₂ was $\text{Sr}_{0.69}\text{La}_{0.33}\text{Mn}_{2.23}\text{Al}_{10}\text{O}_{19.5}$. This sample was characterized by the highest amount of accessible oxygen and ratio Mn³⁺/Mn²⁺, in which the amount of Mn³⁺ is 65%, determining the red-ox transformation.

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1. Introduction

Nitrogen oxides are one of the major sources of air pollutant. Automobile exhaust gases containing NO_x cause the urban smog, acid rains and contribute to the greenhouse effect. Therefore, their utilization is necessary [1,2]. In the recent years, many methods for the decision of this problem have been reported. Among these processes, the selective catalytic reduction (SCR) of NO_x by NH₃ is the most widespread. The reaction proceeds at a moderate temperature [3]:



A great variety of different catalysts have been tested in this reaction; the most active catalyst is commercial V₂O₅/TiO₂ promoted with WO₃ and/or MoO₃, which is resistant to sulfur

compounds [4–6]. The main disadvantage of this catalyst is its instability under conditions of the working automobile engine, when the operating temperature can rise to 600–800 °C. Therefore, the search of active and stable catalysts for this reaction is continued.

Among the various oxide compositions, hexaaluminate systems of alkaline-earth and rare-earth elements are characterized by high-temperature stability and high activity [7,8]. Their high thermal stability is related to the unique lamellar structure that consists of Al₂O₃-containing spinel block intercalated by mirror planes, in which the largest cations (Ba, Sr, La, etc.) are located [9,10]. The ionic radius and valence of these cations determine the type of the crystal structure of the hexaaluminate: magnetoplumbite or β-alumina [11]. The other feature of hexaaluminates is their ability to form substituted modifications—LaFeMn_xAl_{11-x}O_{19-δ} [12,13]. At the same time, Mn-containing compositions, in particular MnO_x/Al₂O₃ or MnO_x/TiO₂, show high activity in the SCR, but they also are not very stable [14,15]. Therefore, it would be expedient to investigate in the SCR Mn(Fe)-substituted hexaaluminates.

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The aim of the present work was to synthesize the hexaaluminates $\text{Sr}_{1-x}\text{La}_x\text{Mn}_2\text{Al}_{10}\text{O}_{19-\delta}$ ($x = 0; 0.2; 1$), $\text{LaMnAl}_{10}\text{O}_{18}$, $\text{SrFeMnAl}_{10}\text{O}_{19}$ and to study the influence of the nature of alkaline-earth, rare-earth and transition metals on their structure, texture and catalytic properties in the SCR of NO by NH_3 .

2. Experimental

2.1. Catalyst preparation

The hexaaluminates: $\text{SrMn}_2\text{Al}_{10}\text{O}_{19}$ (1SMA), $\text{Sr}_{0.8}\text{La}_{0.2}\text{Mn}_2\text{Al}_{10}\text{O}_{19}$ (2SLMA), $\text{LaMn}_2\text{Al}_9\text{O}_{18}$ (3LMA), $\text{LaMnAl}_{10}\text{O}_{18}$ (4LMA) and $\text{SrFeMnAl}_{10}\text{O}_{19}$ (5SFMA) were prepared via the procedure described elsewhere [9,16]. The procedure is based on the aqueous co-precipitation of soluble nitrates of Al and M ($M = \text{Sr, La, Mn, Fe}$) at $\text{pH} = 7.5\text{--}8$ and temperature of 70°C , with NH_4HCO_3 as a precipitating agent. The slurry was aged at 70°C for 2 h and then filtered. The obtained precipitate was washed and dried in air. The solid was dried at 110°C for 12–14 h and then calcined at 700°C for 4 h in an air flow. The subsequent calcination of the samples was carried out at 1100 and 1400°C for 4 h in a muffler.

The influence of the treatment conditions on the phase structure and textural characteristics of the $\text{LaMnAl}_{10}\text{O}_{18}$ sample were studied.

2.2. Catalyst characterization

The content of the main components was determined by the atomic absorption spectrometry [17] with an accuracy of 0.01–0.03%.

The thermal analysis (TG–DTA) was carried out with a NETZSCH STA 449C in the temperature range from 20 to 1400°C at the heating rate of $10^\circ\text{C}/\text{min}$ in air. The accuracy of determination of weight losses and temperature was $\pm 0.5\%$ and $\pm 5\%$, respectively.

X-ray diffraction (XRD) studies were carried out using a D-500 (Siemens, Germany) diffractometer with Cu K_α ($\lambda = 1.5418 \text{ \AA}$) monochromatic radiation. Diffraction profiles were recorded both in a continuous mode and in a step-by-step scanning mode at $0.05\text{--}0.1^\circ$ in 2θ -step and dwell time of 20–30 s depending on the crystallinity of a sample. The phases were identified by comparison of the measured set of the interfacial distances d_i and the corresponding intensities of the diffraction maximums I_i with those found in the database JCPDS (PCPDF Win. Ver 1.30, JCPDS ICDD, Swarthmore, PA, USA, 1997).

The specific surface area was determined with an accuracy of $\pm 10\%$ by the heat desorption of argon [18].

The temperature-programmed reduction (TPR) of the samples by H_2 was carried out in the flow reactor. During the experiment, water was frozen at temperature -80°C . The temperature was increased from 40 to 900°C at a rate of $10^\circ\text{C}/\text{min}$. The concentration of H_2/Ar was 10 vol.%, flow rate, 40 ml/min, granule size of the catalyst, 0.25–0.5 mm, mass of the catalyst, 0.2 g. The amount of H_2 consumed was determined with a katharometer.

X-ray photoelectron spectroscopy (XPS) was applied for characterization of the surface contents of the elements. XP spectra were recorded on a SPECS electronic spectrometer using both Mg K_α ($h\nu = 1253.6 \text{ eV}$) and Al K_α ($h\nu = 1486.74 \text{ eV}$). The charging on the sample surface is caused by electron photoemission and as a result leads to essential shift of binding energy in a spectrum. A source of electrons with low energy (3 eV) was used for charging compensation. The binding energy was calibrated using the peak of $\text{C}1s$ ($E_b = 284.8 \text{ eV}$). The surface contents of the elements were calculated from the related XPS peak area taking into account section of photoionization of corresponding terms [19].

2.3. Catalyst activity test

The catalyst activity in selective catalytic reduction was tested in accordance with the Light-off test at the following experimental conditions: the reaction gas composition: NO, 350 ppm; NH_3 , 350 ppm; O_2 , 14 vol.%; H_2O , 4.5 vol.%; He, balance; space velocity, $120,000 \text{ h}^{-1}$; catalyst volume, 0.250 cm^3 ; contact time, 0.03 s; heating rate, $10^\circ\text{C}/\text{min}$; temperature range, $100\text{--}600^\circ\text{C}$.

Fig. 1 presents a scheme of the experimental setup designed for testing SCR catalysts. The installation consists of flow-mass controllers for each reaction gas, a mixer, a reactor, a valve system for gas flow commutations, an evaporator for water vapor feeding, a chromatograph and a FTIR spectrometer for analysis of gaseous mixtures.

Ammonia, oxygen, nitric oxide and helium as diluter are taken from corresponding cylinders through flow-mass controllers and solenoid valves and are introduced into the mixer. The second helium flow passes through the evaporator, solenoid valve and then enters to the mixer. The reaction mixture leaving the mixer enters to the switching valve SW-V2 that either directs the mixture to the reactor or passes that over the reactor. The final reaction mixture is analyzed in the first case, and the initial reaction mixture—in the second case. To perform the analysis, the reaction mixture enters through the sampling valve SP-V2 of gas chromatograph to a gas cell of the FTIR spectrometer. The procedure of the reaction mixture analysis is divided into two parts. The first part is GC analysis on nitrogen. The second part is FTIR analysis on nitrogen oxides and ammonia.

3. Results and discussion

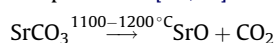
3.1. Chemical and phase composition

According to the chemical analysis, the content of the main components determined experimentally differed from the calculated values; however, this difference was insignificant. Using these data, chemical formulas of hexaaluminate were calculated (Table 1).

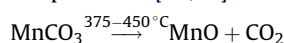
Non-isothermal temperature-programmed treatments of the initial air-dried samples resulted in the appearance of exo- and endoeffects on the TG–DTA curves (Fig. 2). The corresponding temperatures are collected in Table 2. For comparison, data of the thermal analysis for the unsubstituted hexaaluminate $\text{SrAl}_{12}\text{O}_{19}$ (SA) are represented in Table 2. This sample was also prepared by the co-precipitation method.

When the unsubstituted and substituted hexaaluminates were heated from room temperature to 1200 and 1400°C , respectively, they lost about 50% of their weight. The endoeffects observed at $140\text{--}150^\circ\text{C}$ were caused by dehydration of the hexaaluminates. The exoeffect that appeared at 913°C for the unsubstituted sample was probably caused by the crystallization of SrAl_2O_4 (Fig. 2a). For the substituted hexaaluminates, only the endoeffects at $259\text{--}950^\circ\text{C}$, probably due to the decomposition of the corresponding carbonates, were observed.

According to Refs. [20–23], decomposition of the strontium, manganese and iron carbonates proceeds at the different temperatures [20,21]:



The decomposition of MnCO_3 started at about 100°C [21], however, the total decomposition is observed at the higher temperatures [21,22]:



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