

Catalytic Properties of the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ System in Ammonia Oxidation to Nitrogen Oxides

N. I. Zakharchenko

Zhukovskii National Aerospace University, Kharkov, Ukraine

Received January 19, 2001

Abstract—The catalytic properties of the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system in ammonia oxidation are studied at 1073 K. The effect of phase composition on the physicochemical and catalytic properties of the system is determined. The catalytic properties of individual components of the system ($\alpha\text{-Fe}_2\text{O}_3$, $\text{Bi}_2\text{Fe}_4\text{O}_9$, BiFeO_3 , and $\delta\text{-Bi}_2\text{O}_3$) are studied.

INTRODUCTION

Catalytic ammonia oxidation to NO forms the basis for the commercial process of nitric acid manufacturing [1]. A search for non-platinum catalysts (NPC) remains a research challenge because of the high cost, deficiency, and unrecoverable loss of commercial catalysts (platinum, rhodium, and palladium alloys) in technological processes. Iron(III) oxide is one of the promising NPC components used at the second stage of the multistage process of ammonia oxidation [1, 2]. To preserve the high activity and selectivity to NO and to improve on the thermal and chemical stability of Fe_2O_3 , various modifying agents are used such as metal oxides [1–7]. Therefore, the accumulation of experimental data on the catalytic properties of various systems is of both practical and theoretical importance for the creation of the justified methods for the design of catalysts with desired properties. Bismuth(III) oxide is used as a modifying additive for iron oxide catalysts, but the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system has not been studied over a wide range of compositions. Published data on the catalytic properties of the system are scarce and contradictory [1, 3, 4, 6].

This work deals with the catalytic and physicochemical properties of the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system for ammonia oxidation at high temperatures.

EXPERIMENTAL

Catalysts were prepared by the thermal decomposition of the mixtures of hydrated iron ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and bismuth ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) nitrates (analytical purity grade) in an air atmosphere. Nitrates were taken in a calculated amount. The preparation procedure was described earlier [8]. X-ray phase analyses were carried out using an URS-50I diffractometer with FeK_α irradiation. The phase composition of the catalytic system is shown in Table 1.

The specific surface areas (Table 2) were measured using the low-temperature adsorption of nitrogen and

calculated with the BET equation according to the standard procedure [9].

The catalyst selectivities to NO were determined in a flow-type setup with a quartz reactor (2 cm in diameter) according to the procedure described in [10]. The height of the bed of catalyst granules (2×3 mm) was 4–12 cm. The concentration of ammonia in an ammonia–air mixture was ~10 vol %. The contact time was $\tau = 6.59 \times 10^{-2}$ s (under normal conditions), which is an optimal value [5]. The pressure was 0.101 MPa. The temperature of tests was 1073 K, which was close to the optimum for the one-component iron oxide catalyst [8]. The product composition in ammonia oxidation and the thermal decomposition of NO on the catalyst was determined by chromatography according to the known procedure [11] by analyzing the concentrations of NH_3 , O_2 , N_2 , NO, and N_2O in the gaseous mixture before and after the catalyst bed. The sensitivity threshold of the methods was (in vol %): 3.0×10^{-3} for NH_3 , 3.5×10^{-3} for NO, and 5.0×10^{-3} for O_2 , N_2 , and N_2O .

The maximal catalyst capacity with respect to ammonia was determined using the procedure described in [3], which consisted in an increase in the catalyst capacity up to the critical state of “quenching,” that is, thermal balance perturbation in the transition from diffusion to kinetics control.

The figure and Table 2 show the results of studies of the catalytic properties of the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system.

The binding energy of surface oxygen with the individual components of the catalytic system were determined from the temperature dependence of the gas-phase oxygen pressure in the thermodynamic equilibrium with oxygen on oxide surfaces according to the procedure described in [12].

RESULTS AND DISCUSSION

We found only two nitrogen-containing compounds in the products of ammonia oxidation on the studied catalysts under conditions that were far from critical:

NO and N₂. Ammonia breakthrough was not observed. Thus, the overall conversion of the starting compound was 100%. We only observed a change in the NO : N₂ ratio with time. That is, the selectivities to NO and N₂ changed. The thermal dissociation of NO (Table 3) resulted in a decrease in the apparent selectivity to NO:



At this temperature and at the optimal contact time (6.59×10^{-2} s), from 1.0 to 1.6% of NO dissociates.

The selectivity to NO drops due to reaction (I) on individual components as follows (in %):

$\alpha\text{-Fe}_2\text{O}_3$ —1.0,

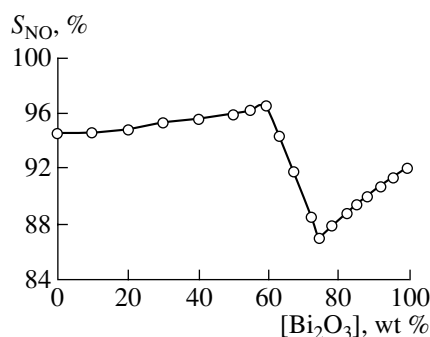
$\text{Bi}_2\text{Fe}_4\text{O}_9$ —1.5,

BiFeO_3 —0.9,

$\delta\text{-Bi}_2\text{O}_3$ —1.3.

With an increase in the feed-flow rate, and a decrease in the contact time to 1.2×10^{-3} s (the critical conditions of catalyst quenching), NO did not dissociate thermally (Table 3). This agrees with data for other NPCs for ammonia oxidation [1].

When the concentration of bismuth is lower than 59.3 wt %, hematite $\alpha\text{-Fe}_2\text{O}_3$ (main signals in X-ray diffraction patterns with interplanar distances of 0.3680, 0.2690, 0.2510, 0.2204, 0.1844, 0.1693, 0.1482, and 0.1452 nm) coexists with bismuth ferrite $\text{Bi}_2\text{Fe}_4\text{O}_9$ (main peaks in X-ray diffraction patterns with interplanar distances of 0.5988, 0.4218, 0.3731, 0.3451, 0.3319, 0.3163, 0.3082, 0.2996, 0.2895, 0.2654, 0.2442, 0.2395, 0.1932, 0.1842, 0.1762, and 0.1624 nm) in the form of two compounds. When the reactant ratio is stoichiometric $\text{Fe}_2\text{O}_3 : \text{Bi}_2\text{O}_3 = 2 : 1$ (59.3 wt % Bi_2O_3), orthorhombic bismuth ferrite is formed. The selectivity to NO on $\text{Bi}_2\text{Fe}_4\text{O}_9$ (96.6%) and its specific surface area ($8.0 \text{ m}^2/\text{g}$) are better than the analogous characteristics for $\alpha\text{-Fe}_2\text{O}_3$ (94.4% and $5.6 \text{ m}^2/\text{g}$, respectively). An increase in the bismuth ferrite concentration in



Dependence of the process selectivity to NO (S_{NO}) on the composition of the $\text{Fe}_2\text{O}_3\text{-Bi}_2\text{O}_3$ system.

$\alpha\text{-Fe}_2\text{O}_3\text{-Bi}_2\text{Fe}_4\text{O}_9$ results in a monotonic increase in the catalyst selectivity to NO (up to 59.3 wt % Bi_2O_3 , see Table 2).

With a concentrations of bismuth oxide ranging from 59.4 to 74.4 wt %, $\text{Bi}_2\text{Fe}_4\text{O}_9$ coexists with another bismuth ferrite phase (BiFeO_3) (the main peaks with interplanar distances of 0.3945, 0.2808, 0.2781, 0.2273, 0.1975, 0.1774, 0.1626, 0.1612, 0.1607, 0.1314, 0.1248, 0.1103, and 0.1053 nm) in the form of two compounds. Bismuth orthoferrite BiFeO_3 is formed at a stoichiometric ratio of the components $\text{Fe}_2\text{O}_3 : \text{Bi}_2\text{O}_3 = 1 : 1$ (74.5 wt % Bi_2O_3). The selectivity to NO (87.0%) on bismuth orthoferrite and its specific surface area ($5.1 \text{ m}^2/\text{g}$) are lower than the corresponding characteristics for $\text{Bi}_2\text{Fe}_4\text{O}_9$. An increase in the concentration of bismuth oxide in the $\text{Bi}_2\text{Fe}_4\text{O}_9\text{-BiFeO}_3$ results in a drastic decrease in the selectivity to NO.

With a concentrations of Bi_2O_3 ranging from 74.6 to 99.9 wt %, the system contains the phases of BiFeO_3 and $\delta\text{-Bi}_2\text{O}_3$ (the main peaks with interplanar distances of 0.3253, 0.2693, 0.2390, 0.1957, 0.1872, 0.1758, 0.1662 nm) as a mixture of two compounds. The selectivity to NO on Bi_2O_3 (92.1%) and the specific surface area ($7.0 \text{ m}^2/\text{g}$) are higher than the analogous character-

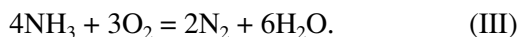
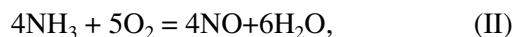
Table 1. Phase composition of the catalytic system $\text{Fe}_2\text{O}_3\text{-Bi}_2\text{O}_3$

[Bi ₂ O ₃], wt %	Phase composition	Characteristics of system components	
		crystalline structure	lattice parameters, nm
0	$\alpha\text{-Fe}_2\text{O}_3$	trigonal, $\alpha\text{-Al}_2\text{O}_3$ -type	$a = 0.5430$
0–59.2	$\alpha\text{-Fe}_2\text{O}_3 + \text{Bi}_2\text{Fe}_4\text{O}_9$	—	—
59.3	$\text{Bi}_2\text{Fe}_4\text{O}_9$	rhombic	$a = 0.7881$ $b = 0.8410$ $c = 0.6010$
59.4–74.4	$\text{Bi}_2\text{Fe}_4\text{O}_9 + \text{BiFeO}_3$	—	—
74.5	BiFeO_3	cubic with rhombohedral distortion, perovskite-like	$a = 0.3955$ $\alpha = 89^\circ 32'$
74.6–99.9	$\text{BiFeO}_3 + \text{Bi}_2\text{O}_3$	—	—
100.0	$\alpha\text{-Bi}_2\text{O}_3$	cubic, CaF_2 -type	$a = 0.5622$

istics for BiFeO_3 . An increase in the concentration of bismuth oxide in the $\text{BiFeO}_3\text{--}\delta\text{-Bi}_2\text{O}_3$ results in an increase in the selectivity of the process to NO.

Thus, the selectivity of ammonia oxidation on the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system depends on the composition and on the ratio between the phases of the two-component catalysts $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_2\text{Fe}_4\text{O}_9\text{--BiFeO}_3$, and $\text{BiFeO}_3\text{--Bi}_2\text{O}_3$.

High-temperature ammonia oxidation on the catalysts occurs via two parallel reactions [1, 13]:



The redox mechanism of the process [13] determines the relationship between the selectivity and the binding strength of oxygen on the catalyst surface [13, 14]. The adsorption heat can be a measure of the binding strength [13, 14]. For the catalysts of the same nature (metals or metal oxides), there are optimal values for the energies of oxygen binding to the surface to obtain the maximal selectivity to NO [13–15]. Deviations from the optimal values of the oxygen binding strength lead to a decrease in the selectivity to NO and an increase in the selectivity to N_2 . The experimental binding energies of oxygen on the catalysts under study are 125.0–143.5 kJ/mol O_2 (the oxidized state of the surface).

Probably, the most active and selective component of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ system in the steady state is characterized by optimal energy characteristics, the maximal number of active sites under given conditions of the reaction, including optimal values of the catalyst–oxygen binding energy for obtaining the maximal selectivity to NO. An increase in the binding energy of adsorbed oxygen relative to the optimal value results in a decrease in the selectivity to NO and an increase in the selectivity to N_2 , because in the formation of the product of deeper oxidation (NO), more oxygen–catalyst bonds should be cleaved than in the case of molecular nitrogen formation [13, 15]. A decrease in the energy of oxygen binding relative to the optimal value results in an increase in the probability of direct ammonia interaction with the catalyst surface (reaction (III)) to form molecular nitrogen. The selectivity to NO decreases in this case [13, 15].

The composition of the system under certain reaction conditions (temperature, pressure, and reactant concentrations) determines a set of energy characteristics of the catalyst surface, its activity, and selectivity.

The maximal values of the catalyst capacity with respect to ammonia are shown in Table 2. The maximal capacities of the catalysts increase with an increase in their specific surface areas: the maximal capacity is observed for $\text{Bi}_2\text{Fe}_4\text{O}_9$ ($8.81 \times 10^3 \text{ m}^3 \text{ NH}_3 \text{ h}^{-1} \text{ m}^{-2}$) and the lowest one is observed for BiFeO_3 ($5.62 \times 10^3 \text{ m}^3 \text{ NH}_3 \text{ h}^{-1} \text{ m}^{-2}$). In terms of the maximal capacity, the high temperature modification $\delta\text{-Bi}_2\text{O}_3$ is the next best after bismuth ferrite ($\text{Bi}_2\text{Fe}_4\text{O}_9$). The maximal

Table 2. Properties of the catalytic system $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$

$[\text{Bi}_2\text{O}_3]$, wt %	Specific surface area, m^2/g	Catalyst selectivity to NO, %*	Maximal capacity with respect to ammonia, $10^3 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}$	Ammonia breakthrough under critical conditions of catalyst “quenching,” rel. %
0	5.6	94.4	6.17	0.38
5.0	5.7	94.5	6.28	0.36
10.0	5.9	94.6	6.50	0.30
20.0	6.2	94.9	6.83	0.25
30.0	6.6	95.3	7.27	0.18
40.0	7.0	95.6	7.71	0.13
50.0	7.5	96.1	8.26	0.07
55.0	7.7	96.3	8.48	0.05
59.3	8.0	96.6	8.81	0.03
63.0	7.2	94.4	7.93	0.10
67.0	6.5	91.8	7.16	0.19
72.0	5.5	88.6	6.06	0.41
74.5	5.1	87.0	5.62	0.51
78.0	5.3	87.9	5.84	0.46
82.0	5.5	88.8	6.06	0.41
85.0	5.7	89.5	6.28	0.36
88.0	5.9	90.1	6.50	0.30
92.0	6.2	90.8	6.83	0.25
96.0	6.6	91.5	7.27	0.18
100.0	7.0	92.1	7.71	0.13

* The contact time τ is $6.59 \times 10^{-2} \text{ s}$.

Table 3. The degree of NO decomposition for different phase compositions of the catalysts in the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system at 1073 K (the composition of the gaseous mixture in vol %: NO, 9.5; N_2 , 71.3; O_2 , 4.6; H_2O , 14.6)

$[\text{Bi}_2\text{O}_3]$, wt %	Degree of NO decomposition (in %) at $\tau = 6.59 \times 10^{-2} \text{ s}$, %*
	6.59×10^{-2}
0 ($\alpha\text{-Fe}_2\text{O}_3$)	1.1
30.0 ($\alpha\text{-Fe}_2\text{O}_3 + \text{Bi}_2\text{Fe}_4\text{O}_9$)	1.3
59.3 ($\text{Bi}_2\text{Fe}_4\text{O}_9$)	1.6
61.0 ($\text{Bi}_2\text{Fe}_4\text{O}_9 + \text{BiFeO}_3$)	1.5
74.5 (BiFeO_3)	1.0
92.0 ($\text{BiFeO}_3 + \delta\text{-Bi}_2\text{O}_3$)	1.2
100.0 ($\delta\text{-Bi}_2\text{O}_3$)	1.4

* When the contact time τ is $1.2 \times 10^{-3} \text{ s}$, the degree of NO decomposition is equal to zero.

capacity depends on the rate of the chemical reaction on the surface, which is determined by the chemical composition of the catalyst. The maximal capacity characterizes the catalyst activity and productivity [1, 16].

Under critical conditions of the process ($\tau = 1.2 \times 10^{-3}$ s), the consecutive reaction of NO decomposition via reaction (I) is not observed (Table 3), but some portion of unreacted ammonia was found after the catalyst bed; that is, ammonia breakthrough takes place (Table 2). With an increase in the specific surface area of the catalyst, ammonia breakthrough declines in agreement with the higher activity of these catalysts. The maximal breakthrough is observed for BiFeO_3 (0.51%), and the minimal breakthrough is observed for $\text{Bi}_2\text{Fe}_4\text{O}_9$ (0.03%).

Thus, of all the components of the $\text{Fe}_2\text{O}_3\text{--Bi}_2\text{O}_3$ system, bismuth ferrite ($\text{Bi}_2\text{Fe}_4\text{O}_9$) can be recommended as an efficient catalyst for ammonia oxidation. Bismuth orthoferrite (BiFeO_3) is insufficiently active and selective in this process. Both bismuth ferrite and hematite are superior to the high-temperature modification of bismuth oxide ($\delta\text{-Bi}_2\text{O}_3$) in the selectivity. Also, $\delta\text{-Bi}_2\text{O}_3$ readily sublimates at $T > 973$ K [17] and melts at 1093 K [18], and this fact prevents its use as a high temperature catalyst for ammonia oxidation. Data on the catalytic properties of the system can be used in the design and use of modified iron oxide catalysts for ammonia oxidation.

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