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CATALYSIS

Fe_2O_3–Li_2O Catalysts for Ammonia Oxidation

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Abstract—The catalytic properties of the Fe_2O_3–Li_2O system in ammonia oxidation were studied in the high-temperature region. The influence of the phase composition of the system on the physicochemical and catalytic properties of the catalysts were revealed. The catalytic properties of lithium ferrite, which is the most active and selective component of the Fe_2O_3–Li_2O system, were studied. The mechanism of lithium ferrite deactivation at 1273 K is considered.

Catalytic oxidation of ammonia to nitrogen(II) oxide is the basic reaction for industrial production of nitric acid [1]. Owing to the high cost, deficiency, and irrecoverable loss of industrial catalysts (platinum, rhodium, and palladium alloys) in technological processes, a search for new efficient non-platinum catalysts (NPC) is urgent. Iron(III) oxide is a promising support for NPC, used industrially as a component in the second stage of a combined system for ammonia oxidation [1, 2]. To preserve the high activity and selectivity with respect to nitrogen(II) oxide and to enhance the thermal and chemical resistance of iron(III) oxide, various modifying additives are used, and metal oxides in particular [1–6]. The available data on catalysts for ammonia oxidation are empirical, because the modern theory of catalysis allows no unambiguous prediction of a set of properties for catalysts with various compositions, preparation procedures, and chemical prehistories. Accumulation of data on the catalytic properties of the systems is of practical and theoretical interest for the development of scientifically substantiated methods for creating catalysts with prescribed properties.

Lithium oxide (Li_2O) is used as modifying additive to iron oxide–containing catalysts, but the system Fe_2O_3–Li_2O has not been studied in a wide composition range [1, 3, 5–6]. The present work is concerned with the catalytic and physicochemical properties of the Fe_2O_3–Li_2O system in ammonia oxidation.

The catalyst was prepared by thermal decomposition in air of ferric nitrate hydrate $Fe(NO_3)_3 \cdot 9H_2O$ and lithium nitrate hydrate $Li(NO_3) \cdot 3H_2O$ (both analytically pure) mixed in a calculated ratio [7]. An X-ray phase analysis was performed on a URS-50I diffractometer in Fe_{K_α}-radiation. The phase composition of the Fe_2O_3–Li_2O catalytic system is presented in Table 1.

Table 1. Phase composition of the Fe_2O_3–Li_2O catalytic system

C_{Li_2O}, wt %	Phase composition	Properties of system components	
		crystal structure	unit cell parameter a, nm
0	α-Fe_2O_3	Trigonal α-Al_2O_3	0.5430
0–3.5	α-Fe_2O_3 + α-$Li_{0.5}Fe_{2.5}O_4$	–	–
3.6	α-$Li_{0.5}Fe_{2.5}O_4$	Cubic $MgAl_2O_4$	0.8330
3.7–15.7	α-$Li_{0.5}Fe_{2.5}O_4$ + α-$LiFeO_2$	–	–
15.8	α-$LiFeO_2$	Cubic NaCl	0.4156
15.9–48.2	α-$LiFeO_2$ + Li_5FeO_4	–	–
48.3	Li_5FeO_4	Rhombic Na_2O	0.9218
48.4–99.9	Li_5FeO_4 + Li_2O	–	–
100.0	Li_2O	Cubic antifluorite CaF_2	0.4628

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Table 2. Properties of the Fe_2O_3–Li_2O catalytic system

C_{Li_2O}, wt %	S_{sp}, $m^2\ g^{-1}$	S_{NO}, % ($\tau = 6.77 \times 10^{-2}$ s)	$X \times 10^{-3}$, $m^3\ h^{-1}\ m^{-2}$	Y, rel. %	C_{Li_2O}, wt %	S_{sp}, $m^2\ g^{-1}$	S_{NO}, % ($\tau = 6.77 \times 10^{-2}$ s)	$X \times 10^{-3}$, $m^3\ h^{-1}\ m^{-2}$	Y, rel. %
0	5.9	94.7	6.50	0.30	30.0	2.2	24.3	2.42	1.33
2.0	6.4	95.0	7.05	0.26	35.0	1.9	19.1	2.09	1.41
3.0	6.8	95.3	7.49	0.24	40.0	1.7	15.5	1.87	1.48
3.6	7.1	95.5	7.82	0.21	45.0	1.6	12.2	1.76	1.50
4.0	6.9	92.9	7.60	0.23	48.3	1.5	11.2	1.65	1.53
5.0	6.6	85.5	7.27	0.25	50.0	1.4	9.2	1.54	1.55
6.0	6.3	78.6	6.94	0.27	53.0	1.3	6.8	1.43	1.58
8.0	5.7	70.2	6.28	0.40	56.0	1.2	5.5	1.32	1.64
10.0	5.0	62.9	5.50	0.55	60.0	1.0	3.8	1.10	1.71
13.0	4.2	55.7	4.63	0.75	65.0	0.9	2.6	0.99	1.73
15.0	3.6	52.0	3.97	0.91	70.0	0.8	1.9	0.88	1.78
15.8	3.5	51.0	3.86	0.93	80.0	0.6	1.1	0.67	1.87
18.0	3.1	42.1	3.42	1.02	90.0	0.5	0.7	0.55	1.92
20.0	2.9	37.7	3.19	1.10	100.0	0.4	0.4	0.44	1.97
25.0	2.5	30.2	2.75	1.22					

Note: X is the limiting AAM load, Y is ammonia breakthrough under the critical process conditions, and S_{NO} is selectivity by NO.

The specific surface area S_{sp} of the catalysts was measured by low-temperature adsorption of nitrogen and calculated by the BET equation (Table 2).

The catalyst selectivity by NO was determined on a flow-through installation with a quartz reactor 2×10^{-2} m in diameter [8]. The catalyst bed $(4–12) \times 10^{-2}$ m in height was composed of $(2 \times 3) \times 10^{-3}$-m granules; the ammonia concentration in the ammonia–air mixture (AAM) was about 10 vol %; the time of contact was 6.77×10^{-2} s, and the optimal pressure, according to previously obtained data [4], was 0.101 MPa. The test temperature corresponded to the maximum selectivity of a single-component iron oxide catalyst (1053 K) [7]. The compositions of the products of ammonia oxidation and thermal decomposition of nitrogen(II) oxide on the catalysts were determined by chromatographic analysis of the gas mixture for NH_3, O_2, N_2, NO, and N_2O before and after catalyst introduction, as in [9]. The sensitivity of analysis was (in 10^{-3} vol %): 3.0 for NH_3, 3.5 for NO, and 5.0 for O_2, N_2, and N_2O.

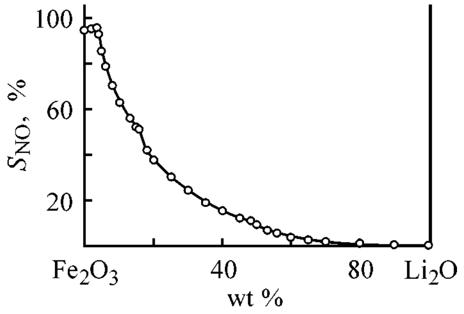

Fig. 1. Catalyst selectivity S_{NO} vs. composition of the Fe_2O_3–Li_2O system.

The limiting AAM load was determined by a procedure [3] consisting in that the catalyst is loaded to a critical state (dying), with the heat balance of a catalyst disturbed when the reaction passes from the diffusion to the kinetic region.

The results obtained in studying the catalytic properties of the Fe_2O_3–Li_2O system are presented in the Fig. 1 and Table 2.

Only two nitrogen compounds, N_2 and NO, were found among the reaction products of ammonia oxidation on the catalysts studied; under conditions far from critical no ammonia “breakthrough” occurred. Thus, the overall conversion of the initial substance is 100% and the only variable parameter of the catalytic process is the ratio between nitrogen(II) oxide and molecular nitrogen, i.e., the selectivity by NO (or by nitrogen). Thermal dissociation of NO may diminish the observed selectivity by nitrogen(II) oxide:

$$2NO = N_2 + O_2. \qquad (1)$$

Experimental data on the degree of thermal dissociation of nitrogen(II) oxide on the catalysts of the system studied are presented in Table 3.

At the testing temperature and the optimal time of contact (6.77×10^{-2} s), nitrogen(II) oxide undergoes thermal dissociation in trace amounts (Li_2O and a mixture of Li_5FeO_4 with Li_2O) to 1.2% (on $Li_{0.5}Fe_{2.5}O_4$). The thermal dissociation of NO on lithium oxide does not virtually occur. At higher reagent flow velocities, i.e., with the time of contact decreasing to 1.2×10^{-3} s (critical conditions of catalyst dying), no thermal dissociation of nitrogen(II) oxide occurs, which is consistent with data on other NPC catalysts for ammonia oxidation [1, 10].

At lithium oxide concentrations of up to 3.6%, iron(III) oxide with a structure of α-Fe_2O_3 hematite (reflections with interplanar spacings of 0.3680, 0.2690, 0.2510, 0.2204, 0.1844, 0.1693, 0.1482, and 0.1452 nm) coexists with lithium ferrite α-$Li_{0.5}Fe_{2.5}O_4$ (main reflections with interplanar spacings of 0.589, 0.478, 0.374, 0.340, 0.2946, 0.2769, 0.2514, 0.2084, 0.1703, 0.1605, 0.1474, 0.1273, 0.1204, and 0.1115 nm) as a binary mixture. At the stoichiometric ratio $Li_2O : Fe_2O_3 = 1 : 5$ (3.6 wt % Li_2O) lithium ferrite is formed with a structure of the $Fe^{3+}[Li^{+}_{0.5}Fe^{3+}_{1.5}]O_4$ inverted spinel. The specific surface area of lithium ferrite (7.1 $m^2 g^{-1}$) slightly exceeds that of iron(III) oxide (5.9 $m^2 g^{-1}$). The selectivity of lithium ferrite by nitrogen(II) oxide is 95.5, i.e., exceeds the similar characteristic for α-Fe_2O_3 (94.7%). When the concentration of lithium ferrite, possessing the higher selectivity and specific surface area, is raised, the selectivity of catalysts of the α-Fe_2O_3–α-$Li_{0.5}Fe_{2.5}O_4$ system grows.

In the lithium oxide concentration range 3.7–15.7%, the ferrite phase α-$Li_{0.5}Fe_{2.5}O_4$ coexists with the α-modification of lithium metaferrite α-$LiFeO_2$ (main reflections with interplanar spacings of 0.239, 0.2073, 0.1467, 0.1252, 0.1200, 0.1089, 0.0925, 0.0845, 0.0640, and 0.0657 nm) as a binary mixture. The selectivity and the specific surface area of lithium metaferrite (51.0% and 3.5 $m^2 g^{-1}$) are considerably lower than the similar characteristics for α-$Li_{0.5}Fe_{2.5}O_4$. The increase in the concentration of the low-active phase of lithium metaferrite in the α-$Li_{0.5}Fe_{2.5}O_4$–α-$LiFeO_2$ system leads to an abrupt monotonic decrease in the selectivity of catalysts by nitrogen(II) oxide.

X-ray phase analysis shows that, at lithium oxide concentrations of 15.9–48.2%, lithium metaferrite α-$LiFeO_2$ coexists with the Li_5FeO_4 phase as a binary mixture. Li_5FeO_4 ranks far below α-$LiFeO_2$, and especially α-$Li_{0.5}Fe_{2.5}O_4$, in selectivity and specific surface area (11.2% and 1.5 $m^2 g^{-1}$). Raising the concentration of the low-active Li_5FeO_4 phase in the α-$LiFeO_2$–Li_5FeO_4 system drastically decreases the selectivity of catalysts by NO.

Table 3. Degree of NO decomposition on Fe_2O_3–Li_2O catalysts at 1053 K [Gas mixture composition (vol %): 9.5 NO, 71.3 N_2, 4.6 O_2, and 14.6 H_2O (vapor) ($\tau = 6.77 \times 10^{-2}$)]

C_{Li_2O}, wt %	Phase composition	γ,* %
0	α-Fe_2O_3	1.0
2.0	α-$Fe_2O_3 + \alpha$-$Li_{0.5}Fe_{2.5}O_4$	1.1
3.6	α-$Li_{0.5}Fe_{2.5}O_4$	1.2
10.0	α-$Li_{0.5}Fe_{2.5}O_4 + \alpha$-$LiFeO_2$	0.7
15.8	α-$LiFeO_2$	0.5
35.0	α-$LiFeO_2 + Li_5FeO_4$	0.2
48.3	Li_5FeO_4	0.1
70.0	$Li_5FeO_4 + Li_2O$	<0.1
100.0	Li_2O	<<0.1**

* Degree of NO decomposition.
** Virtually absent.

At lithium oxide concentrations exceeding 48.3%, Li_5FeO_4 coexists with the phase of lithium oxide as a mixture of two compounds. The selectivity and the specific surface area of lithium oxide (0.4% and 0.4 $m^2 g^{-1}$) are lower than those of Li_5FeO_4 and all other system components. Raising the lithium oxide concentration in the Li_5FeO_4–Li_2O system leads to a monotonic decrease in the selectivity of catalysts by nitrogen(II) oxide. Thus, the selectivity of the system depends on its composition, in particular, on the ratio of phases in the two-component catalyst.

In the Fe_2O_3–Li_2O catalytic system, the only component of practical interest is lithium ferrite α-$Li_{0.5}Fe_{2.5}O_4$, the most active and selective compound surpassing even α-Fe_2O_3 in its characteristics. The other system components are low-active (α-$LiFeO_2$ and Li_5FeO_4) or virtually inactive (Li_2O).

The high-temperature oxidation of ammonia on catalysts occurs by two parallel reactions [1, 11]:

$$4NH_3 + 5O_2 = 4NO + 6H_2O, \quad (2)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O. \quad (3)$$

The redox mechanism of the reactions [11] is responsible for the correlation between the selectivity and strength of binding of chemisorbed oxygen to the catalysts [12]. The measure of the strength of oxygen binding to the catalyst is the heat of its chemisorption [11, 12]. For catalysts of certain nature (metals and

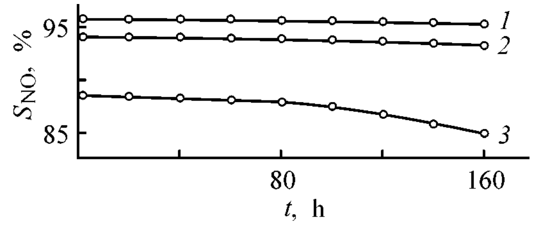

Fig. 2. Selectivity S_{NO} of lithium ferrite vs. operation time t. The linear velocity of AAM flow is 0.8 m s^{-1} (operation conditions). Temperature (K): (*1*) 1073, (*2*) 1173, and (*3*) 1273.

metal oxides) there exists an optimal energy of oxygen binding to the compound surface, ensuring the maximum selectivity by nitrogen(II) oxide [11–14]. The deviation of the binding energy from the optimal value impairs the NO selectivity and improves the selectivity by N_2. The binding energies of the surface oxygen to the individual components of the catalytic system in the oxidized state were determined from the temperature dependence of the pressure of oxygen in thermodynamic equilibrium with the surface oxygen of the compounds [15] (kJ mol^{-1} O_2): α-Fe_2O_3 143.5, α-$Li_{0.5}Fe_{2.5}O_4$ 138.2, α-$LiFeO_2$ 179.8, Li_5FeO_4 224.3, and Li_2O 242.5.

For hematite and lithium ferrite, the energies of oxygen binding to the surface are close and the selectivities differ only slightly. The energy of oxygen binding to the surface of α-$LiFeO_2$, and especially to the Li_5FeO_4 and Li_2O surfaces, much exceeds that for α-Fe_2O_3 and lithium ferrite. The product of stronger ammonia oxidation (i.e., nitrogen(II) oxide) is formed with breaking of a greater number of oxygen–catalyst bonds, compared with molecular nitrogen. This means that the selectivity by NO decreases with increasing binding energy of adsorbed oxygen [11, 13, 14], and it is this phenomenon that is observed for α-$LiFeO_2$, Li_5FeO_4, and Li_2O.

The limiting ammonia load grows with increasing specific surface area of the catalyst: it is the highest for lithium ferrite [7.82×10^3 m^3 NH_3 h^{-1} m^{-2}] and the lowest for lithium oxide (0.44×10^3 m^3 NH_3 h^{-1} m^{-2}] (Table 2). The limiting load for iron(III) oxide (6.50×10^3 m^3 NH_3 h^{-1} m^{-2}] is slightly lower than that for lithium ferrite. This parameter depends on the rate of the chemical reaction on the surface, which is, in turn, determined by the chemical composition of the catalyst. Under the critical process conditions ($\tau = 1.2 \times 10^{-3}$ s), no decomposition of nitrogen(II) oxide by pathway (1) is observed, but part of unreacted ammonia is found after the catalyst (breakthrough) (Table 2). With increasing specific surface area of the catalysts, the ammonia breakthrough decreases, which is consistent with the higher activity of such catalysts. The ammonia breakthrough is the highest for lithium oxide (1.97%) and the lowest for lithium ferrite (0.21%). In this respect, α-Fe_2O_3 is close to lithium ferrite (0.30%), their specific surface areas differing insignificantly.

The kinetic characteristics of the reaction on lithium ferrite, which is the most active and selective component of the Fe_2O_3–Li_2O system, were determined using the “burning” and “dying” temperatures of a lithium ferrite pellet, i.e., the temperatures at the critical points. The reaction rate was calculated by the method in which the temperature limits of the external diffusion region were determined using the “dying” of a catalyst pellet on lowering the AAM temperature [16]. The temperature of the catalyst surface was measured with a TPP-2 thermocouple inserted into the pellet from the side of AAM flow. A layer of lithium ferrite granules $(2.0–3.0) \times 10^{-3}$ m in size was placed between the pellet and the reactor walls to eliminate the heat loss. The kinetic parameters of the process were calculated by the Buben equation [17] solved for two reaction rates at a constant oxygen concentration. The equation has the form

$$(1 + a)\left[1 + (m - 1)\frac{a}{b}\right] - \frac{a}{\varepsilon}\left(1 - \frac{a}{b}\right) = 0, \quad (4)$$

$$a = T/T_0 - 1, \quad b = Q\beta C_0/(\alpha T_0), \quad \varepsilon = RT_0/E,$$

where m is the reaction order by ammonia, T is the catalyst surface temperature at the critical point (K), T_0 is the AAM temperature, C_0 is the ammonia concentration in the flow, α and β are the mass- and heat-transfer coefficients, Q is the heat effect of the reaction, and E is its activation energy.

The coefficients α and β were calculated from the known equations [18].

The kinetic parameters of ammonia oxidation on lithium ferrite are as follows: temperature of catalyst “burning,” 527 K; ammonia concentration in AAM, 10 vol %; activation energy of the reaction, 9.54 kJ mol^{-1} NH_3; reaction order by ammonia, 0.19; and catalyst selectivity by NO (at 1053 K), 95.5%.

A study of the dependence of catalyst selectivity on operation time confirmed the high stability of lithium ferrite at 1073–1173 K (Fig. 2).

The selectivity of lithium ferrite at 1073 and 1173 K decreases by 0.4 and 0.7%, respectively, after 160 h of operation. The iron(III) oxide selectivity at

1073 K decreases by 3.5% after the same period of time [7]. With the process temperature raised to 1273 K, lithium ferrite undergoes deactivation under the influence of the elevated temperature and the reaction medium: the catalyst selectivity after 160 h of operation decreases by 3.5%. To elucidate the deactivation mechanism, the chemical and phase composition of the catalyst were studied along with its structure. X-ray diffraction patterns of the surface layer of a catalyst that operated at 1273 K contain lithium ferrite reflections and reflections with interplanar spacings of 0.485, 0.297, 0.253, 0.242, 0.2101, 0.1712, 0.1614, and 0.1485 nm, characteristic of magnetite Fe_3O_4 [19]. This conclusion is confirmed by IR spectral data. The IR spectra of the surface layer of a catalyst after operation contain the magnetite absorption peaks at 407, 427, 480, 557, 673, and 980 cm^{-1} [20]. Magnetite suppresses the catalyst selectivity, i.e., it is the low-active phase [7] (the magnetite selectivity at 1073 K is 7%). The intensity of the phase transformations occurring in the catalyst grows with increasing reaction temperature, as shown by X-ray diffraction analysis and IR spectroscopy. The increase in the concentration of the low-active phase with growing temperature results in a more abrupt decrease in the catalyst selectivity. In addition, the catalyst operated at 1273 K contains a new, relatively low-active phase—α-modification of lithium metaferrite α-$LiFeO_2$. The selectivity of α-$LiFeO_2$ at 1053 K is 51%. The appearance of the new, low-active phases of magnetite and α-$LiFeO_2$ at elevated temperatures is associated with the redox mechanism of ammonia oxidation [1, 5, 11] and is in good agreement with the results of thermodynamic calculations [21]. According to these data the high probability of lithium ferrite transformation at $T \geq 1273$ K ($P_{0_2} = 0.021$ MPa, air) by the reaction

$$6Li_{0.5}Fe_{2.5}O_4 = 3LiFeO_2 + 4Fe_3O_4 + O_2 \quad (5)$$

results in the formation of new phases, found in experimental studies. Similar transformations during heat treatment of lithium ferrite were observed in [22].

Under the influence of high temperature, the catalyst recrystallizes, with the specific surface area decreasing (Table 4). After 160 h of operation the size of lithium ferrite granules increases from 200 to 340 nm. The reaction conditions being far from critical, i.e., the reaction being limited by ammonia diffusion toward the catalyst surface, the specific surface area does not exert decisive influence on the selectivity of lithium ferrite [1, 3, 6]. This means that the drop in selectivity at 1273 K is mainly due to phase and chemical transformations of the catalyst. Under the critical conditions of the reaction (catalyst dying) the activity of lithium ferrite decreases and the limiting load falls from 7.49×10^3 to 2.97×10^3 m^3 NH_3 h^{-1} m^{-2}) as a result of recrystallization and a decrease in the specific surface area of the catalyst.

Table 4. Changes in selected structural and catalytic properties of lithium ferrite α-$Li_{0.5}Fe_{2.5}O_4$ during operation at 1273 K

t, h	S_{sp}, m^2 g^{-1}	Root-mean-square granule size, nm	Limiting load by ammonia, $A \times 10^{-3}$, m^3 h^{-1} m^{-2}
4	6.8	200	7.49
40	6.6	207	7.27
60	6.4	218	7.05
80	5.8	240	6.39
100	4.9	265	5.40
140	3.3	308	3.63
160	2.7	340	2.97

Thus, a set of chemical and phase transformations of the catalyst, yielding low-active and low-selective components (Fe_3O_4 and α-$LiFeO_2$) with rearranged structure is the reason for lithium ferrite deactivation. In the temperature range 1073–1173 K, lithium ferrite is a highly selective and stable catalyst for ammonia oxidation.

CONCLUSIONS

(1) The catalytic properties of the $Fe_2O_3\Lambda i_2O$ system in ammonia oxidation were studied in the component concentration range 0–100 wt %.

(2) The catalytic properties of the individual components (α-Fe_2O_3, Li_2O, α-$Li_{0.5}Fe_{2.5}O_4$, α-$LiFeO_2$, and Li_5FeO_4) of the system were determined.

(3) The influence of the phase composition of the system on the physicochemical and catalytic properties of the catalysts, including the activity and selectivity by nitrogen(II) oxide, was revealed. The activity and the selectivity of the system depends on composition and, in particular, on the ratio of the amount of α-Fe_2O_3 phase to that of the α-$Li_{0.5}Fe_{2.5}O_4$ phase of a two-component catalyst. The same is true for the $Li_{0.5}Fe_{2.5}O_4$ and α-$LiFeO_2$, α-$LiFeO_2$ and Li_5FeO_4, and Li_5FeO_4 and Li_2O phases.

(4) The process parameters were determined on the ferrite catalyst, which is the most active and selective component of the Fe_2O_3–Li_2O system.

(5) A set of chemical and phase transformations of the $Li_{0.5}Fe_{2.5}O_4$ catalyst, resulting in the formation of low-active and low-selective components (Fe_3O_4 and α-$LiFeO_2$) with rearranged structure, is responsible for the deactivation of lithium ferrite at 1273 K.

(6) The obtained data on the catalytic properties of the Fe_2O_3–Li_2O system can be used in developing highly efficient modified catalysts for ammonia oxidation.

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