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# Deactivation of Iron–Gallium Oxide Catalyst for Ammonia Oxidation

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**Abstract**—An iron–gallium oxide catalyst (97.0 wt %  $Fe_2O_3$ , 3.0 wt %  $Ga_2O_3$ ) was studied in high-temperature oxidation of ammonia. Reasons for the deactivation of the catalyst at elevated temperature were analyzed.

Catalytic oxidation of ammonia to nitrogen(II) oxide is the basis of the industrial method for manufacture of nitric acid [1]. In view of the high cost, shortage, and unrecoverable loss of commercial catalysts in industrial processes (platinum, rhodium, and palladium alloys), a search for effective nonplatinum catalysts is a topical problem. Iron(III) oxide is a promising base for catalysts of this kind; it is used industrially as a component of the second stage of a combined system for ammonia oxidation [1]. Commonly, high activity and selectivity with respect to nitrogen(II) oxide are preserved and the thermal and chemical stability of iron(III) oxide is improved using various modifying additives and, in particular, metal oxides [1–8].

Gallium(III) oxide (Ga<sub>2</sub>O<sub>3</sub>) is used as a modifying additive for iron-containing catalysts with varied content of modifying agent [1, 7, 8], but these catalysts are deactivated at elevated temperatures, with their selectivity with respect to nitrogen(II) oxide decreasing [1, 7]. Reasons for the deactivation of iron-gallium oxide catalysts are virtually unknown [1, 7]. The present study is concerned with deactivation of a highly selective iron-gallium catalyst (97.0 wt %  $Fe_2O_3$ , 3.0 wt %  $Ga_2O_3$ ) in high-temperature oxidation of ammonia.

The catalyst was prepared by thermal decomposition in air of a mixture of hydrated iron nitrate  $[Fe(NO_3)_3 \cdot 9H_2O]$  and gallium nitrate  $[Ga(NO_3)_3 \cdot 9H_2O]$  of chemically pure grade, taken in calculated amounts, using a procedure described in [9]. The temperature of finishing thermal treatment of the catalyst grains was 1143 K.

An X-ray phase analysis was made on a Siemens D-500 powder diffractometer ( $CuK_{\alpha}$  radiation, graphite monochromator) in the path of the diffracted beam. The phases manifested in the diffraction patterns were

identified using a JCPDS file shipped with the diffractometer.

IR absorption spectra were measured on a Perkin-Elmer 577 spectrophotometer at 200–2000 cm<sup>-1</sup> using KBr technique. The selectivity of the catalysts with respect to NO ( $S_{NO}$ ) was determined on a flow-through installation with a quartz reactor  $2 \times 10^{-2}$  m in diameter, using the procedure described in [1]. The height of the bed of catalyst grains of size  $(2 \times 3) \times$  $10^{-3}$  m was  $(4-12) \times 10^{-2}$  m; content of ammonia in the ammonia-air mixture (AAM), ~10.0 vol %; time of contact,  $6.89 \times 10^{-2}$  s (normal conditions, n.c.), the optimal value according to previously obtained data; pressure, 0.101 MPa. The testing temperature was close to the optimal value for a single-component iron oxide catalyst (1103 K): in separate tests, it was varied within the range 1103–1173 K. The composition of the products of ammonia oxidation on the catalysts was determined using the known technique [10], by analyzing the gas mixture for the content of NH<sub>3</sub>, O<sub>2</sub>, N<sub>2</sub>, NO, and N<sub>2</sub>O before and after the catalysts. The sensitivity limit of this analytical procedure was (vol %)  $3.0 \times 10^{-3}$  for NH<sub>3</sub>,  $3.5 \times 10^{-3}$  for NO, and  $5.0 \times 10^{-3}$  for O<sub>2</sub>, N<sub>2</sub>, and N<sub>2</sub>O.

The specific surface area of the catalysts was measured by the method of low-temperature adsorption of nitrogen and calculated by the BET equation, using a standard procedure [11].

The binding energies of the surface oxygen to the catalysts were found from the temperature dependence of the equilibrium oxygen pressure over the surface of the compounds, using the procedure described in [12].

The basic characteristics of the iron–gallium catalyst are listed in Table 1.

According to the results of an X-ray diffraction analysis, the unused catalyst is a solid solution of

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Table 1. Basic parameters of a catalyst for ammonia oxidation containing (wt %) 97.0  $Fe_2O_3$  and 3.0  $Ga_2O_3$ 

Run no.	Parameter (designation)	Numerical value
1	Maximum selectivity with respect to NO ( $S_{NO}$ ) at optimal temperature, %	95.5
2	Optimal temperature T, K	1103
3	Specific surface area S, $m^2 g^{-1}$	9.0
4	Limiting ammonia load X, $m^3 h^{-1} m^{-2}$	$9.92  imes 10^3$
5	Breakthrough of ammonia under critical process conditions, Y, rel. %	0.04
6	Optimal time of contact, $\tau_{opt}$ , at linear flow velocity of reagents of 0.19 m s <sup>-1</sup> and $T = 1103$ K, s	$6.89 \times 10^{-2}$ (n.c.) or $2.25 \times 10^{-2}$ (work. cond.)
7	Optimal linear flow velocity of AAM, w, at $\tau = 6.89 \times 10^{-2}$ and $T = 1103$ K, m s <sup>-1</sup>	0.19 (n.c.) or 0.77 (work. cond.)
8	Ignition temperature, $T_{ign}$ , K	531



**Fig. 1.** IR absorption spectra of (1)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (2)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, (3) unused iron-gallium catalyst, (4) surface (ferromagnetic) layer of iron-gallium catalyst upon operation, and (5) iron-gallium catalyst (nonmagnetic fractions) upon operation. (v) Wave number.

gallium(III) oxide in hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), with the structure of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) type, i.e.,  $(Fe_xGa_{1-x})_2O_3$ . The X-ray diffraction patterns of the fresh catalyst are characterized by main lines with interplanar spacings of 0.3682, 0.2693, 0.2511, 0.2214, 0.1846, 0.1695, 0.1484, and 0.1454 nm. These values are typical of the rhombohedral structure of  $\alpha$ -Fe<sub>2</sub>O<sub>2</sub> [3], but are shifted to greater reflection angles, which corresponds to a decrease in the lattice constant a of iron oxide from 0.5434 to 0.5423 nm. No gallium oxide lines were found in the catalyst, which points to the formation of a solid solution of gallium(III) oxide in hematite. IR spectra of unused catalyst contain absorption bands at 479 and 550  $cm^{-1}$ . These values are typical of iron(III) oxide (485, 555  $\text{cm}^{-1}$ ) (Fig. 1), but are shifted to lower frequencies, which is accounted for by replacement, in solid formation, of a part of Fe<sup>3+</sup> ions in the structure of hematite by havier  $Ga^{3+}$  ions. No  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> bands were found in the IR spectra of the catalyst, probably because of the fact that the absorption bands characteristic of gallium(III) oxide are close to those of hematite (Fig. 1), but the content of gallium oxide is insufficient for clear manifestation of the absorption bands of Ga<sub>2</sub>O<sub>3</sub>.

Studies of how the catalyst selectivity depends on the working time (Fig. 2) indicate that the iron–gallium catalyst exhibits higher stability than  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The catalyst selectivity at 1103 and 1173 K decreased by 1.7 and 4.5%, respectively, after 90 h of operation. At the same time, the selectivity of iron(III) oxide decreased under the same conditions by 2.3 and 6.4%, respectively (Fig. 2). Raising the process temperature leads to stronger deactivation of both iron–gallium and iron oxide catalysts (Fig. 2). X-ray diffraction patterns of the surface layers of an iron–gallium catalyst that

Run no.	Catalyst	Working time of catalyst, h	$q_{\mathrm{S}}$ ,* kJ mol <sup>-1</sup> O <sub>2</sub>	S <sub>NO</sub> , %, at 1173 K
1	Iron-gallium (Fe <sub>2</sub> O <sub>3</sub> 97.0 wt %, Ga <sub>2</sub> O <sub>3</sub> 3.0 wt %)	3	134.3	93.0
2	Iron–gallium	90	148.2	88.5
3	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	3	144.6	91.2
4	$\beta$ -Ga <sub>2</sub> O <sub>3</sub>	3	231.5	1.9
5	Fe <sub>3</sub> O <sub>4</sub>	3	226.5	4.1

**Table 2.** Binding energy of the surface oxygen of catalysts,  $q_s$ , and their selectivity with respect to nitrogen(II) oxide,  $S_{NO}$ 

\*  $q_{\rm S}$  in the oxidized state of the catalyst surface.

worked at 1173 K contain lines of a rhombohedral solid solution of gallium(III) oxide in hematite, together with weak lines with interplanar spacings of 0.4850, 0.2970, 0.2430, 0.2102, 0.1713, 0.1615, and 0.1487 nm, typical of magnetite ( $Fe_3O_4$ ) [3]. In this case, magnetite and the iron–gallium catalyst do not form solid solutions, being present as a mixture of separate phases.

The formation of magnetite is confirmed by IR data. The IR spectra of the surface layers of a catalyst after operation (magnetic fractions) contain absorption bands at 407, 427, 481, 558, and 673 cm<sup>-1</sup> (Fig. 1), characteristic of magnetite [13]. According to [9, 14], magnetite suppresses the catalyst selectivity, being a low-active phase: the selectivity of magnetite is 7.0% at 1073 K.

Only two nitrogen compounds were found in the products formed in ammonia oxidation on the catalyst under study:  $N_2$  and NO; no breakthrough of ammonia was detected. Thus, the overall conversion of the starting substance is 100.0%.

High-temperature catalytic oxidation of ammonia proceeds by two concurrent pathways [1, 15]:

$$4NH_3 + 5O_2 = 4NO + 6H_2O, \tag{1}$$

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

The redox mechanism of the reactions [15] predetermines the relationship between the selectivity and the binding strength of chemisorbed oxygen to the catalyst surface [12, 15]. As measure of strength of oxygen binding to the catalyst can serve the heat of chemisorption [12, 15]. For catalysts of certain nature and, in particular, metal oxides, there exists the optimal energy of oxygen binding to the catalyst surface, at which the selectivity with respect to nitrogen(II) oxide is the highest [12, 15, 16]. Deviation from the optimal oxygen binding energies leads to lower catalyst selectivity with respect to NO, and to higher selectivity with respect to  $N_2$ .

The experimental binding energies of surface oxygen of the iron–gallium catalyst and its constituents are listed in Table 2.

The energies of oxygen binding to the surface of the forming magnetite and of the catalyst after its operation surpass the corresponding characteristics of the iron–gallium catalyst before operation.

In the formation of a product of deeper oxidation of ammonia, i.e., nitrogen(II) oxide, a greater number of oxygen–catalyst bonds is ruptured than that in the formation of molecular nitrogen. This means that the selectivity of the catalyst with respect to NO must decrease with increasing binding energy of adsorbed oxygen, which is, indeed, observed for magnetite and used catalyst, in which  $Fe_3O_4$  was found.

Gallium(III) oxide is characterized, as a constituent of the iron–gallium catalyst, by high binding energy of oxygen to the surface (231.5 kJ mol<sup>-1</sup>  $O_2$ ), which is comparable with a similar characteristic for magnetite (226.5 kJ mol<sup>-1</sup>  $O_2$ ): the selectivities of these two phases with respect to NO are close (1.9 and 4.1%, respectively) and rather low.



Fig. 2. Catalyst selectivity with respect to nitrogen(II) oxide,  $S_{\text{NO}}$ , vs. working time t: (1)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 1173 K; (2) Fe<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> (3.0 wt % Ga<sub>2</sub>O<sub>3</sub>), 1173 K; (3)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 1103 K; and (4) Fe<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> (3.0 wt % Ga<sub>2</sub>O<sub>3</sub>), 1103 K.

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Run no.	Catalyst	Chemical composition, wt %			Content of $Ga_2O_3$ in (Fa Ga ) O solid	Mass loss
		Fe <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>	solution, wt %	%
1	Unused iron-gallium	97.00	3.00	_	3.00	_
2	Iron-gallium after 90 h of operation	94.52	2.56	2.92	2.64	0.5
3	Unused $\beta$ -Ga <sub>2</sub> O <sub>3</sub>	_	100.00	_	_	_
4	$\beta$ -Ga <sub>2</sub> O <sub>3</sub> after 20 h of operation		100.00			7.1

Table 3. Changes in chemical composition and mass of catalysts for ammonia oxidation in their operation at 1173 K

The product of phase transformations of the catalyst (magnetite) may be formed both in the redox reaction of ammonia oxidation [1–3, 5, 6, 15, 17] and in direct interaction of the parts of the catalyst surface that are characterized by low catalyst–oxygen binding energies with a strong reducing agent in the reaction medium, in accordance with the equation

$$9(\text{Fe}_{x}\text{Ga}_{1-x})_{2}\text{O}_{3} + 2x\text{NH}_{3} = 6x\text{Fe}_{3}\text{O}_{4} + 9(1-x)\text{Ga}_{2}\text{O}_{3} + x\text{N}_{2} + 3x\text{H}_{2}\text{O}.$$
 (3)

The deficiency of  $\text{Fe}^{3+}$  ions in the surface layers of the catalyst (magnetite formation) leads to a local increase in the content of gallium(III) oxide in a hematite-based solid solution and a decrease in the selectivity of the catalyst with respect to NO (Table 2). According to X-ray phase analysis, no gallium(III) oxide was found as a separate phase, i.e., there was no decomposition of the solid solution. Gallium(III) oxide, as a component of a solid solution, may undergo, under the action of a strong reducing agent (ammonia) at high temperature (1073–1173 K), phase transformations in accordance with the reaction equation

$$3Ga_2O_3 + 4NH_3 = 3Ga_2O + 2N_2 + 6H_2O.$$
 (4)

The transformation product,  $Ga_2O$ , readily sublimes at 1073–1173 [18] and thereby enters the gas flow of reagents. With account of the transformations of gallium(III) oxide, the equation describing reaction (3) can be written as follows:

$$9(\text{Fe}_x\text{Ga}_{1-x})_2\text{O}_3 + 2(6 - 5x)\text{NH}_3 = 6x\text{Fe}_3\text{O}_4 + 9(1 - x)\text{Ga}_2\text{O} + (6 - 5x)\text{N}_2 + 3(6 - 5x)\text{H}_2\text{O}, (5)$$

where  $0 \leq x \leq 1$ .

The thermodynamic probability of reduction by ammonia of iron(III) oxide [19] as a component of the  $(Fe_xGa_{1-x})_2O_3$  solid solution by the equation

$$9Fe_2O_3 + 2NH_3 = 6Fe_3O_4 + N_2 + 3H_2O$$
 (6)

is higher than that of gallium(III) oxide reduction [18] and grows with increasing temperature. After 90 h of operation of an iron–gallium catalyst at 1173 K, magnetite was found in amount of 2.92 wt % (Table 3). For the iron oxide catalyst, the content of Fe<sub>3</sub>O<sub>4</sub> in the surface layers was 4.80 wt % under the same testing conditions [9]. The intensity of phase transformations of the catalyst, (Fe<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution, to give magnetite is somewhat lower than that of individual iron(III) oxide.

Processes (4) and (5) may lead to mass loss by catalyst because of Ga<sub>2</sub>O sublimation. Indeed, its mass decreased by 0.5% after 90 h of catalyst operation at 1173 K. Hematite, magnetite, and gallium(III) oxide are nonvolatile thermally stable compounds in air at the testing temperatures [20]. To confirm the transformation of gallium(III) oxide, a component of the iron-gallium catalyst, in the course of high-temperature oxidation of ammonia, a mixture of substances after the catalyst was passed through columns cooled by a mixture of solid carbon dioxide and acetone (temperature of cooling mixture 213-203 K). The dramatic decrease in the temperature of the reaction products made it possible to minimize the interaction in the gas phase between gallium(I) oxide and oxidizing agents contained in the reaction mixture, nitrogen(II) oxide and oxygen, by the equations [18]

$$Ga_2O + 2NO = Ga_2O_3 + N_2,$$
 (7)

$$Ga_2O + O_2 = Ga_2O_3.$$
 (8)

In particular, process (7) may lead to nitrogen defixation, as in the side reaction of ammonia oxidation at short time of contact, in accordance with the equation

$$4NH_3 + 6NO = 5N_2 + 6H_2O, \qquad (9)$$

i.e., to a decrease in the catalyst selectivity with respect to NO. Under the experimental conditions,  $Ga_2O$  vapor condensed on column walls, and water was frozen to ice (other substances contained in the reaction mixture were carried away by the gas flow). After shutting down the reactor, the columns were purged with inert gas (Ar) and heated to T = 473 K to remove water. A film was found on the column walls. The substance of this film was identified by X-ray diffraction analysis as gallium(I) oxide. The IR spectra of this compound contain absorption bands at 472 and 809 cm<sup>-1</sup>, characteristic of Ga<sub>2</sub>O [21].

A low content of gallium(III) oxide in the solid solution leads to relatively small loss of mass by the iron-gallium catalyst at 1173 K. Chemical analyses performed using the procedure described in [22] demonstrated that the content of  $Ga_2O_3$  in the (Fe<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution decreased in the course of catalyst operation from 3.00 to 2.64 wt % (Table 3).

In tests of individual gallium oxide ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub>) as a catalyst for ammonia oxidation, a pronounced decrease in its mass, by 7.1% after 20 h of operation at 1173 K, was observed (Table 3). X-ray phase and IR spectral analyses demonstrated that, under the action of the reaction medium,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> undergoes, similarly to the iron-gallium catalyst, phase and chemical transformations to give volatile gallium(I) oxide. Thermal treatment of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> at the same temperature in air did not lead to any decrease in the oxide mass, i.e., the catalyst is nonvolatile and thermally stable under these conditions. Consequently, the mass deficiency of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> catalyst under the conditions of hightemperature oxidation of ammonia is associated with the influence of the redox reaction medium, redox mechanism of the reaction [1-3, 5, 6, 15, 17], and processes (4) and (5).

The thermodynamic probability of oxidation of the forming low-active compound  $Fe_3O_4$  by oxygen from AAM by the equation

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \tag{10}$$

is lower than that of processes (3) and (6) and decreases with increasing reaction temperature [19, 23]. It becomes possible that Fe<sub>3</sub>O<sub>4</sub> is accumulated in the surface layers of the catalyst at elevated temperature. Being a volatile product of phase transformations of the catalyst, gallium(I) oxide sublimes from its surface, which makes lower the content of Ga<sub>2</sub>O<sub>3</sub> in the iron–gallium catalyst (Table 3). High-temperature redox processes in which new phases (Fe<sub>3</sub>O<sub>4</sub>, Ga<sub>2</sub>O) are formed and the catalyst surface is regenerated are unbalanced and result in accumulation of the lowselectivity compound (magnetite) and changes in the composition of the (Fe<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution. With increasing temperature, the unbalance of the

**Table 4.** Changes in structural and catalytic properties of iron–gallium catalyst (3.0 wt %  $Ga_2O_3$ ) in the course of its operation at 1173 K\*

<i>t</i> , h	S <sub>NO</sub> , %	$s, m^2 g^{-1}$	<i>n</i> , nm	$\begin{array}{c} X \times 10^{-3}, \\ m^3 \ h^{-1} \ m^{-2} \end{array}$
3	93.0	8.7	120	9.58
11	92.8	7.4	134	8.15
20	92.5	6.1	150	6.72
30	92.1	4.8	170	5.29
43	91.3	3.7	200	4.08
51	90.9	3.1	220	3.42
60	90.3	2.7	237	2.97
70	89.7	2.3	253	2.53
82	89.0	1.9	270	2.09
90	88.5	1.7	280	1.87

\* t is the time of operation, and n, the rms particle size.

phase transformations of the catalyst becomes more pronounced.

In addition, the catalyst undergoes, under the action of elevated temperature, recrystallization with a decrease in the specific surface area (Table 4) from 8.7 to  $1.7 \text{ m}^2 \text{ g}^{-1}$  (90 h of operation at 1173 K) and, consequently, in the number of active centers on the surface [1]. The size of catalyst particles grows from 120 to 280 nm.

A study of an iron-gallium catalyst subjected to thermal treatment in air at 1173 K (90 h) demonstrated that the specific surface area of the catalyst decreases by 7.5  $m^2 g^{-1}$ , i.e., within the same limits as in the case of a catalyst operating in an ammoniaair medium (Table 4), but the selectivity of this catalyst decreases by only 0.6%. No phase transformations were observed in the catalyst treated in air. The energy of oxygen binding to the surface of a catalyst treated in air increases only slightly (from 134.3 to 136.0 kJ mol<sup>-1</sup> O<sub>2</sub>), which leads to an insignificant decrease in its selectivity. In the IR spectra of the deactivated catalyst (Fig. 1), the absorption bands at 492 and 567 cm<sup>-1</sup>, characteristic of "metal-oxygen" vibrations, are shifted to higher frequencies, compared to the similar absorption bands (479 and 550  $\text{cm}^{-1}$ ) of unused catalyst. Changes of this kind are also observed for a catalyst subjected to thermal treatment in air. Such a shift of absorption bands is accounted for by a decrease in the metal-oxygen bond length (an increase in the force constant of the bond), which is observed in recrystallization of solids [24], and leads to an increase in the energy of binding of adsorbed oxygen to the catalyst surface. The reaction occurs under conditions that are far from being critical, i.e.,

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is limited by diffusion of ammonia toward the outer surface of the catalyst. Therefore, the specific surface area has no significant influence on the selectivity of the iron–gallium catalyst with respect to nitrogen(II) oxide [1–3, 5, 6, 17], i.e., the decrease in selectivity at 1173 K is mainly due to phase and chemical transformations of the catalyst. Under critical conditions of the reaction (catalyst "decay"), recrystallization processes and decrease in the specific surface area of the catalyst diminish its limiting load, i.e., activity, from  $9.58 \times 10^3$  to  $1.87 \times 10^3$  m<sup>3</sup> NH<sub>3</sub> (h m<sup>2</sup>)<sup>-1</sup> (90 h of operation).

# CONCLUSIONS

(1) A study of factors responsible for deactivation of an iron–gallium oxide catalyst (97.0 wt %  $Fe_2O_3$ , 3.0 wt %  $Ga_2O_3$ ) in high-temperature oxidation of ammonia demonstrated that the catalyst undergoes phase and chemical transformations leading to formation of low-selective magnetite and volatile gallium(I) oxide. The deactivation process is accompanied by structural changes: recrystallization and decrease in the specific surface area of the system.

(2) Data on the deactivation of the catalyst can be used in developing theoretical and practical foundations for design of high-performance catalysts for ammonia oxidation.

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