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Catalysis Today 45 (1998) 109–115

CATALYSIS TODAY

Reversible sorption–desorption of NO_x by mixed oxides under various atmospheres

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Abstract

Characteristics of MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3 as reversible sorbents of NO_x were investigated under dynamic changes in atmosphere. These sorbents can be used reversibly with a change of C_3H_8 concentration in the reaction gases. Catalytic reduction of NO occurred in the presence of propane, which was more pronounced on Pt–ZrO_2–Al_2O_3 than on MnO_y-ZrO_2 due to high activity of Pt surface for this reaction on MnO_y in MnO_y–ZrO_2. The sorption was observed as soon as the atmosphere changed from a reducing to an oxidizing one. This implies that a high equilibrium partial pressure of O_2 is necessary for NO uptake since the sorbed NO_3^- species becomes stable. The beginning of NO_x desorption atmospheres was somewhat dependent on the amount of stored NO_x. The presence of propane in the gas phase strongly affected the characteristic sorption and desorption properties of MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3. The sorption and desorption properties are different for MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3, since the noble metal or metal oxide possesses unique activity for the NO reaction with C_3H_8 and the amount of oxygen available for oxidative sorption of NO. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Nitrate formation; NO_x sorption; Mn-Zr oxide; Pt-ZrO_2-Al_2O_3; Selective catalytic reduction

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1. Introduction

Nitrogen oxides (NO_x) are one of the major air pollutants in exhaust gases. Selective catalytic reduction (SCR) of NO_x with ammonia has been well accepted for large power stations. SCR with hydrocarbons has been actively investigated by many researchers. Cu-exchanged ZSM-5 [1,2], metallosilicates [3], alumina [4], and metal-exchanged zeolites [5–7] have been reported as candidates for this approach. Catalysts deactivation by coexisting gases, such as H_2O and SO_2, has been often pointed out for SCR with hydrocarbons. Three-way catalysts, which have high activity for removing NO_x and converting CO and hydrocarbons to CO_2, have been well known as established technology for treating automotive exhaust. However, excess oxygen in exhaust gases from lean-fuel engines, which have been developed recently in terms of fuel economy, makes the three-way catalysis ineffective for removal of NO_x.

Recently, a new de-NO_x concept to separate concentrated NO_x from exhaust gases has been proposed as an NO_x storage reduction catalyst by Toyota motors [8]. The sorbent used for this purpose should store

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PII: S0920-5861(98)00256-9

NO_x in the presence of O_2 at relatively low temperatures, and can be regenerated easily on heating or by exposing sorbent to a reducing atmosphere without deactivation by coexisting gases in the exhaust, such as H_2O or CO_2. The reversible sorption of NO_x in solids has been reported so far for the Y–Ba–Cu–O [9], Ba–Cu–O [10], and Y–Sr–Co–O [11] systems. Although these oxides have been reported to be active for removing NO_x in excess O_2 atmosphere, deactivation of sorbent is expected in the CO_2-containing atmospheres due to surface carbonate formation on rare-earth or alkaline-earth components. We have developed BaO-, Y_2O_3- and ZrO_2- based mixed oxides [12–14] as reversible sorbents of NO_x. The sorption capability of ZrO_2-based mixed oxides, which was promoted by Pt (Pt–ZrO_2–Al_2O_3) or MnO_y (MnO_y–ZrO_2), was not affected by the presence of CO_2 and H_2O, as we have already reported [15]. A series of NO_x storage materials mentioned above consist of at least two components having different roles: the first component is an oxidation catalyst for NO or NO_2 to nitrate ions, NO_3^-, and the second comprises metal ions that bind strongly to the NO_3^- ions. The stored NO_x species in the solids could be released either by heating at high temperatures or by exposing the solid in reducing atmospheres, since the stored species becomes unstable in these conditions. The desorbed gas from Pt–ZrO_2–Al_2O_3 or MnO_y–ZrO_2 was fairly affected by the noble-metal and metal-oxide components which were mixed with ZrO_2.

A series of these sorbents are operative in dynamic conditions consisting of NO_x storage and subsequent desorption operation or catalytic processing. The sorption–desorption response of the oxides under varying atmosphere is of significant importance. The NO_x storage reduction catalyst has been reported as undergoing pulse-like atmospheric change between oxidizing and reducing conditions [16]. However, it is not easy to evaluate the effect of oxygen potential in the atmosphere on the sorption–desorption behavior, if an abrupt change in concentration is employed. In the present study, we have not only investigated the characteristics of MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3 but also proposed a method to evaluate the quasi-equilibrium sorption–desorption property under dynamic change in atmosphere.

2. Experimental

2.1. Sample preparation

Mixed oxide samples were prepared by coprecipitation from the solution of corresponding nitrate mixtures [15]. For the preparation of Mn–Zr oxides (Mn/Zr=1), calculated amounts of $Mn(NO_3)_2 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ (Kishida Chemical) were dissolved in water. After adding ammonia water to the nitrate solution, the solution with precipitate was evaporated to dryness and then heated at 450°C for 6 h.

Samples of 1 wt%Pt–10 wt% ZrO_2, supported on Al_2O_3, were prepared by the impregnation method. $H_2PtCl_6 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ (Kishida Chemical) were dissolved in distilled water. Then, γ-alumina powder (Catalysis Society of Japan, ALO4) was immersed in the solution. The dispersion was stirred for 12 h and then evaporated to dryness. The obtained powder was then heated at 850°C for 6 h in H_2 atmosphere, and sieved to 10–20 mesh. [15]

2.2. NO removal experiment and analysis of sorption–desorption behavior

The experiments on NO_x sorption and desorption were carried out in a flow system at 300°C. The reaction gas, which consisted of NO, O_2 and C_3H_8, was diluted in He. One gram of the solid sample was fixed in a quartz tube reactor and pretreated in He at 300°C. Two kinds of experiments were carried out. Basic sorption characteristics were observed under steady supply of NO-containing gases. Total gas flow rate in this case was 60 ml min^{-1}, which corresponded to 1.0 g s cm^{-3}. On the other hand, dynamic sorption–desorption behavior was observed by the following procedure. A gas flow rate of diluted C_3H_8 in He was controlled continuously between 6 and 18 ml min^{-1} by a mass-flow controller in order to synthesize various atmospheres, whereas those of NO and O_2 were constant to set the total flow rate between 54 and 66 ml min^{-1}. Transient responses of the concentrations of NO and NO_2 in the outlet gas were observed with a chemical-luminescence-type NO_x meter (Shimadzu, NOA305). The effluent gas was generally passed through a carbon reactor to reduce NO_2 before supplying to the NO_x meter for analyzing the sum of NO and NO_2 concentrations. The concentration of

N_2O was monitored from a band intensity at a fixed wave number (2234 cm^{-1}) by an infrared spectrometer (JASCO, IR810) with a gas analysis chamber. The gaseous compositions of inlet and outlet mixtures were also analyzed by gas chromatography.

3. Results and discussion

3.1. *Removal of NO by MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3 under steady supply of feed gas*

Manganese zirconium oxide (MnO_y–ZrO_2) and Pt–ZrO_2–Al_2O_3 are effective in removing dilute NO_x and the presence of gaseous O_2 promotes the sorption reaction for NO, as we have reported previously [12]. The total amount of NO removed at 200°C was 4.06×10^{-4} mol-NO $(g\text{-}cat)^{-1}$ for MnO_y–ZrO_2 and 2.68×10^{-4} mol-NO $(g\text{-}cat)^{-1}$ for Pt–ZrO_2–Al_2O_3. The sorption is initiated by oxidation of NO on MnO_y or Pt, and then completed by nitrate formation on Zr oxide. The stored NO_x species in these samples could be released either by heating at high temperatures or by exposing the solid to a reducing atmosphere, since the stored species becomes unstable in such a condition.

The oxidizing atmosphere was produced by supplying NO (500 ppm), O_2 (5%) and C_3H_8 (0.5%) to MnO_y–ZrO_2 (Mn/Zr=1, abbreviated as MZO) at 300°C. The oxygen concentration was larger than the stoichiometric composition of propane combustion (C_3H_8/O_2=0.2). Temporal course of NO removal for MZO in the oxidizing atmosphere is shown in Fig. 1min in these conditions. Then the concentration of NO in the outlet gas gradually increased with a lapse of time. The NO removal was lowered as the amount of stored NO_x in the solid was saturated. Finally, a steady state of the reaction was attained at NO removal of ca. 30%, when the sum of NO and NO_2 concentrations in the outlet gases became constant. This behavior is in contrast with our previous research that the NO removal gradually decreased to zero percent, under similar conditions but without propane [11]. This implies that catalytic reduction of NO proceeded in the presence of propane in this experiment. The selectivity from NO to N_2 was 24% and to N_2O – 22% in these conditions. A reducing atmosphere was produced by supplying excess propane (1.5%) to the stoichiometry of combustion at 300°C, as is also shown in Fig. 1. The amount of stored NO_x in these conditions should be small, since the equilibrium O_2 concentration in the gas phase was

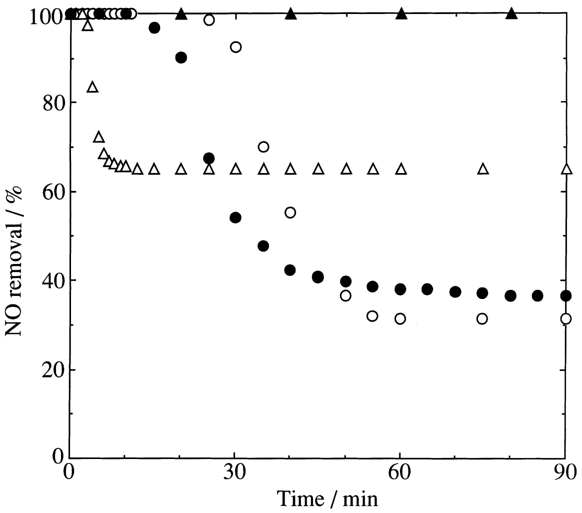

Fig. 1. Temporal course of NO removal for MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3 in oxidizing atmosphere (circles) or reducing atmosphere (triangles). T=300°C, and W/F=1 g s cm^{-3}. Open symbols for MnO_y–ZrO_2 (Mn/Zr=1); and closed symbols for 1wt% Pt–10 wt% ZrO_2–Al_2O_3.Oxidizing atmosphere: 500 ppm NO, 5% O_2, 0.5% C_3H_8, balance He. Reducing atmosphere: 500 ppm NO, 5% O_2, 1.5% C_3H_8, balance He.

quite low. The stored species, NO_3^- ions, becomes unstable in this atmosphere. Complete removal of NO was briefly observed even under this reducing atmosphere, whereas the period was much shorter than in the oxidizing atmosphere. Manganese oxide serves as a reservoir of lattice oxygen which is available for the oxidative sorption reaction. The steady state NO removal was higher than that in the oxidizing atmosphere owing to the presence of excess propane. The selectivity from NO to N_2 was 29% and to N_2O it was 36%, larger than in the oxidizing atmosphere.

The NO removal experiment for Pt–ZrO_2 supported on Al_2O_3 (1 wt% Pt and 10 wt% ZrO_2, abbreviated as PZA) was also carried out under the same conditions of oxidizing and reducing atmospheres (Fig. 1). The general behavior of the NO removal on PZA under oxidizing atmosphere was similar to that of MZO. The period for complete removal of NO under oxidizing atmosphere was ca. 15 min on PZA which was shorter than on MZO. The sorption capacity is obviously smaller for PZA, as we have reported previously [15]. The steady-state NO removal under an oxidizing atmosphere on PZA after 10 min, from the supply, was somewhat higher than on MZO, since the selective reduction of NO with propane easily proceeds on the Pt surface at 300°C [15], the selectivity from NO to N_2 was 6.6% and to N_2O it was 31% in the oxidizing atmosphere. This property of NO reduction with propane on PZA was further promoted in the reducing atmosphere containing excess propane, i.e. the selectivity from NO to N_2 was 94% and to N_2O it was 6%. Supplied NO was completely removed by PZA for the whole period of the feed supply in Fig. 1.

3.2. *Sorption–desorption response under dynamic change in concentration*

The stoichiometric composition of propane combustion is $C_3H_8/O_2=0.2$. The gas flow rate of dilute C_3H_8 in He was changed continuously in order to observe the dynamic NO sorption–desorption behavior in various atmospheres, as we have described in the experimental section. The concentrations of NO and O_2 also changed slightly with the gas flow rate of dilute C_3H_8, where their deviations between two extreme conditions are presented in Table 1. The fuel-to-oxygen ratio in the feed gas $\{[C_3H_8]/[O_2]\}/\{[C_3H_8]/[O_2]\}_{\mathrm{stoichiometric}}$, (abbreviated, hereafter, as F/O ratio), was defined as a measure of deviation from the stoichiometry. The concentration of C_3H_8 was continuously changed between the two conditions in Table 1. The F/O ratio and concentrations of the component gases were changed linearly between these conditions, whereas the equilibrium oxygen potential abruptly changes 40 orders of magnitude as the F/O ratio crosses unity (Fig. 2). Since a rather slow rate for concentration change was employed in the present study, the sorption–desorption behavior is expected to follow quasi-equilibrium conditions. The temporal course of $NO+NO_2$ concentration under repeated zigzag changes in the F/O ratio with a period of 60 min/cycle for MZO and PZA is shown in Fig. 3. In both samples, the sorption of NO and desorption of NO_x was reproducible with the repeated change in F/O ratio, whereas the shape of the response was different between the two samples. NO sorbed in the oxidizing atmosphere and NO_x desorbed in the reducing atmosphere are expressed as the plots, respectively, below and above the broken line in Fig. 3. Although the NO_x

Table 1
Experimental conditions

	F/O ratio	
	0.5	1.5
C_3H_8	0.556%	1.36%
O_2	5.56%	4.54%
NO	556 ppm	454 ppm
Atmosphere	oxidizing	reducing

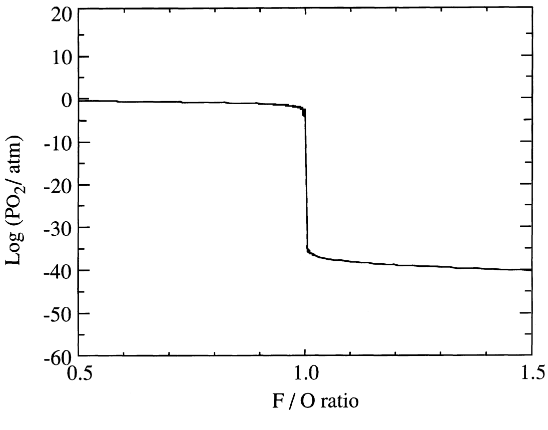

Fig. 2. Plot of log (PO_2) vs. F/O ratio, at 300°C; (———) equilibrium PO_2.

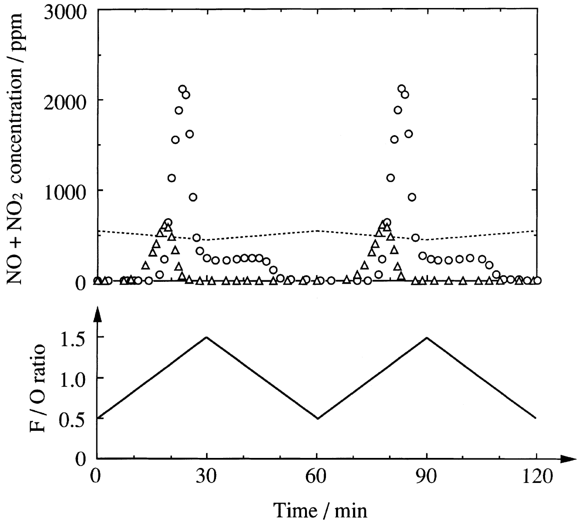

Fig. 3. Temporal course of $NO+NO_2$ concentration during a constant increase and decrease in C_3H_8 concentration. The cycle is 60 min. $T=300°C$; (○) MnO_y–ZrO_2 (Mn/Zr=1); (△) Pt–ZrO_2–Al_2O_3; and (- - -) initial concentration of NO.

desorption was also observed in case of PZA, the amount was much smaller than that of MZO. The outlet concentration of NO_x was almost zero, with the exception of these small peaks. The removal of NO in this case is due to the reduction and sorption of NO. Though this experiment was carried out for a long period of time, the same behavior was reproducible for both of them. This means that these sorbents can be used reversibly in the course of the repeated C_3H_8 concentration change.

3.3. *Sorption process with the change from a reducing to an oxidizing atmosphere*

The F/O ratio was changed from a reducing to an oxidizing atmosphere after complete desorption of NO_x in a reducing atmosphere (F/O ratio=1.5) as shown in Fig. 4. In case of MZO, the curves for three different d(F/O)/d*t* conditions agreed with each other. The curves could be explained by considering an initial removal by NO reduction followed by NO sorption. The amount of reduced NO at 1.5<F/O<1.0 was ca. 250 ppm. The beginning of NO sorption agreed with the point of the stoichiometry (F/O ratio=1), which resulted from the orders of jump of O_2 partial pressure in Fig. 2. The presence of O_2 in equilibrium mixture promotes the sorption of NO due to high stability of the sorbed NO_3^- species. It has been proven that the start of sorption or desorption is independent of d(F/O)/d*t* and the high equilibrium partial pressure of O_2 is necessary for the sorption of NO. It is expected that all the processes are under quasi-equilibrium conditions. In the case of PZA, however, the $NO+NO_2$ concentration was zero in the experimental conditions in Fig. 4. The complete removal at F/O ratio >1 is attributed to the high activity of Pt for NO reduction, while that at F/O ratio <1 owes to concurrent progress of SCR and sorption of NO. The concentration of NO in the outlet gas gradually increased with a lapse of time when the PZA sample was kept in the oxidizing atmosphere (F/O ratio=0.5) after saturation of sorption.

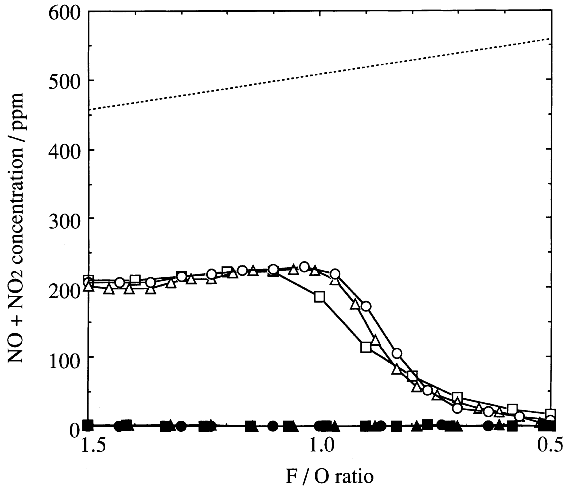

Fig. 4. Concentration change of $NO+NO_2$ for MnO_y–ZrO_2 (Mn/Zr=1) and Pt–ZrO_2–Al_2O_3 during the change in F/O ratio from a reducing to an oxidizing atmosphere. The F/O ratio was initially set at 1.5 for desorption; then it decreased at d(F/O)/d*t*= (○●) 1/30 min^{-1}, (△▲) 1/45 min^{-1}, and (□■) 1/60 min^{-1}. Open symbols for MnO_y–ZrO_2 (Mn/Zr=1), closed symbols for 1 wt% Pt–10 wt% ZrO_2–Al_2O_3. $T=300°C$, and (———) initial concentration of NO.

3.4. *Effects of the amount of presorbed NO*

The experiments in this section were carried out to examine the results in the previous section. The oxidizing atmosphere (F/O ratio=0.5) was maintained for several minutes before the dynamic change of the

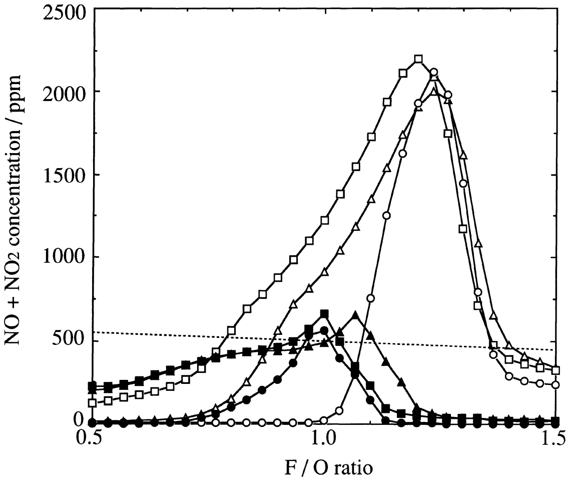

Fig. 5. The total concentration of NO+NO_2 during a constant increase (1/30 min^{-1}) in the F/O ratio after keeping the F/O ratio at 0.5 for (○●) 0, (△▲) 30 and (□■) 45 min. Open symbols for MnO_y–ZrO_2 (Mn/Zr=1) and closed symbols for 1 wt% Pt–10 wt% ZrO_2–Al_2O_3. T=300°C, and (———) initial concentration of NO.

F/O ratio from 0.5 to 1.5. The results for MZO and PZA are shown in Fig. 5. As the period at the constant F/O ratio (=0.5) was prolonged, the desorption of NO_x tended to start from the oxidizing atmosphere for both sorbents. The long exposure in the oxidizing atmosphere, promoting sorption of NO, results in a large amount of stored NO_x in the solid. In case of a small amount of sorbed NO, the desorption curve of NO_x was composed of only a sharp and high peak at the reducing atmosphere on MZO. A large amount of presorbed NO could be expected for the sample after prolonged sorption in an oxidizing atmosphere. The desorption curve, in this case, exhibited a small shoulder at F/O$\leq$1 in addition to the main peak at F/O>1 (the reducing atmosphere). Under such conditions, the desorption of NO_x is promoted by the hydrocarbons which come from incomplete combustion of propane in the gas phase present even in the oxidizing atmosphere. The general behavior of the NO desorption on PZA was similar to that of MZO, except for the size of NO_x desorption. The small desorption from PZA is due to the high activity for the reduction of NO_x on Pt. From these results, the beginnings of NO_x desorption atmospheres were largely dependent on the amount of stored NO_x. This means that the partial pressure of O_2 in the gas phase strongly affects the sorption and desorption properties of NO_x on MZO and PZA. The properties of NO_x sorption and desorption were affected in the presence of a reducing agent, the amount of stored NO_x, the partial pressure of O_2 and the noble-metal and metal-oxide components, especially those which are mixed with ZrO_2.

4. Conclusion

We examined the sorption–desorption characteristics of MnO_y–ZrO_2 and Pt–ZrO_2–Al_2O_3 with a dynamic change in atmosphere. The reaction on both sorbents is initiated by the oxidation of NO on the MnO_y or Pt surface, and the oxidized NO_x species are restored as nitrate ions in the solid. The stored NO_x species in manganese zirconium oxide could be released by exposing the solid in reducing atmospheres. These sorbents can be used reversibly with a change of C_3H_8 amount in the reaction gases. Catalytic reduction of NO proceeded in the presence of propane. The activity for NO reduction was higher on PZA than on MZO at 300°C. The beginning of sorption or desorption of NO is independent of the rate of change in the atmosphere, but the equilibrium partial pressure of O_2 plays a decisive role in the sorption–desorption behavior. The presence of propane in the gas phase strongly affects the sorption and desorption properties of NO_x on MZO and PZA. The sorbed NO_3^- species are stabilized only in an oxidizing atmosphere. The onset of NO_x desorption was fairly dependent on the amount of stored NO_x. The sorption and desorption properties of these sorbents are affected by the catalyst; that is, a noble-metal or metal-oxide catalyst exhibited contrasting behavior, depending on the partial pressure of O_2 and the presence of a reducing agent.

Acknowledgements

The present work was partially supported by a Grant-in-Aid for scientific research from the Ministry of Education, Science, and Culture, Japan.

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