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Stability of bimetallic Bi–Pd and Pb–Pd carbon-supported catalysts during their use in glyoxal oxidation

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Abstract

The incorporation of Bi or Pb as promoting elements in Pd-based carbon-supported catalysts drastically increases the catalytic activity in the selective oxidation of glyoxal into glyoxylic acid. Because partial dissolution of the promoter was clearly demonstrated by atomic absorption analysis of the reaction medium, experiments are performed to examine the stability of these catalysts. Dissolution tests in the presence of the individual constituents of the reaction medium (glyoxal, glyoxylate, glycolate, oxalate) were carried out in air or nitrogen to identify the factors responsible for Pb or Bi leaching. Pb- or Bi-promoted Pd/C catalysts were prepared by thermal degradation of acetate-type precursors and characterized by X-ray diffraction and X-ray photoelectron spectroscopy before and after their use in glyoxal oxidation. Promoter leaching increases with the reaction time. Monometallic Bi/C and Pb/C catalysts were found to lose smaller amounts of promoting agent than the bimetallic M–Pd/C (M=Bi, Pb) catalysts. Losses are more pronounced from Pb–Pd/C catalysts than from their Bi-based partners. Both glyoxal and glyoxylate seem to be among the main factors responsible for the promoter losses in relation to their complexing properties.

Keywords: Pd/C catalysts; Glyoxal oxidation; Bismuth; Lead

1. Introduction

Bismuth and lead are well known for displaying attractive properties as promoting elements in noble metal-based catalysts for the selective oxidation of alcohols or aldehydes by molecular oxygen in aqueous solution [1]. Carbon-supported bimetallic Bi–Pd/C catalysts were particularly studied for the selective oxidation of glucose into gluconic acid [2]. The incorporation of bismuth is assumed to increase drastically the catalytic activity of monometallic Pd/C catalysts by preventing deactivation of the catalyst in the presence of oxygen. However, the actual origin of the promoting role of these heavy post-transition elements on the catalytic activity of Pd- or Pt-based catalysts remains a debated matter. The interest of similar bimetallic Pb- or Bi-promoted Pd/C catalysts for the selective oxidation of glyoxal into glyoxylic acid has also been reported [3,4]. As illustrated in Scheme 1, this process remains a real challenge for two main reasons: (i) selectivity towards glyoxylic acid is essentially limited by the further oxidation to oxalic acid, and (ii) glycolic acid is a second by-product resulting from a competitive Cannizzaro reaction occurring in

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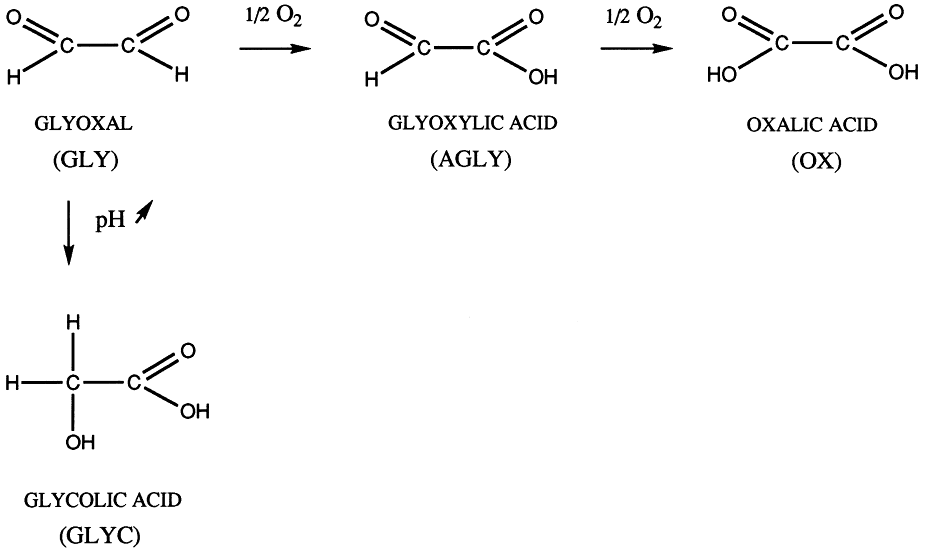

Scheme 1.

homogeneous phase. Its formation depends on the pH and is not influenced by the presence of the catalyst.

These heavy element-promoted catalysts suffer, however, from a severe drawback, related to the fact that partial dissolution of the promoting element occurs during the catalytic tests, as it was clearly demonstrated by atomic absorption analysis of the reaction medium. Previous experiments carried out on the glucose to gluconate oxidation using Bi–Pd/C catalysts suggested that the chelating properties of these species were responsible for the leaching process [2,5]. In contrast with bismuth or lead, dissolution of palladium was never detected under the usual experimental conditions. The fact that significant amounts of promoting elements are leached from these catalysts during their use remains a critical point which could restrict their industrial interest.

The present work examines the stability of such M–Pd/C (M=Pb, Bi) catalysts during their use for glyoxal oxidation. A detailed investigation of the time dependence of the promoter losses was carried out for the different catalysts, which were systematically characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) before and after their use. To improve the understanding of these phenomena, we looked more carefully at the individual effects of the various constituents of the reaction mixture (glyoxal, glyoxylate, oxalate, glycolate or none of them) on the dissolution process, with the objective of identifying the main relevant factors affecting this behaviour. Dissolution tests were performed under the same experimental conditions as the catalytic tests, under either air or nitrogen.

2. Experimental

2.1. Preparation of the catalysts

Activated carbon supplied by Norit (SXplus, $S_{BET}=1000\,m^2\,g^{-1}$; particle size=0.05–0.1 mm) is used as support of our catalysts. Monometallic carbon-supported M/C (M=Bi or Pb), Pd/C and bimetallic M–Pd/C catalysts (M+Pd=10 wt.%) were prepared from acetate-type precursors: $Pd_3(OAc)_6$, BiO(OAc) and $Pb(OAc)_2$.

For the preparation of the monometallic Pd(5 wt.%)/C, Bi(5 wt.%)/C and Pb(5 wt.%)/C catalysts, the selected carboxylate precursor of palladium, bismuth or lead was first dispersed in the presence of 4.5 g of activated carbon in 150 ml *n*-heptane under ultrasonic stirring for 30 min. The hydrocarbon was then evaporated at room temperature under vacuum and the precursor deposited on the support was subsequently decomposed upon heating under nitrogen at 500°C for 18 h.

To obtain the bimetallic Bi(5 wt.%)Pd(5 wt.%)/C and Pb(5 wt.%)Pd(5 wt.%)/C catalysts, the non-degraded monometallic Pd/C catalyst was dispersed in *n*-heptane under ultrasonic stirring for 30 min in the presence of the precursor containing the promoting agent. After evaporation of the hydrocarbon, the bimetallic catalyst was activated upon thermal heating under nitrogen at 500°C for 18 h.

2.2. Catalysts characterization techniques

Powder XRD patterns were obtained with a Siemens D-5000 diffractometer using the Cu Kα radiation (λ=154.18 pm). The samples were analysed after deposition on a quartz monocrystal sample-holder supplied by Siemens. The crystalline phases were identified by reference to the JCPDS data file.

XPS was performed on an SSI-X-probe (SSX-100/206) spectrometer from FISONS, using the Al Kα radiation (E=1486.6 eV). The energy scale was calibrated by taking the Au $4f_{7/2}$ binding energy at 84 eV. The C 1s binding energy of contamination carbon set at 284.8 eV was used as internal reference. The analyses of bismuth, lead and palladium were based on the Bi $4f_{7/2}$, Pb $4f_{7/2}$ and Pd $3d_{5/2}$ photopeaks, respectively.

2.3. Reaction conditions and analytics

2.3.1. Standard catalytic tests

Catalytic tests were performed in a double-walled glass reactor with water circulation. The glyoxal solution (0.1 mol/l) was heated in the reactor to 38°C. Reactions were carried out under constant stirring conditions (1000 rpm), ensured by a mechanical stirrer Heidolph RZR 2051. To limit the extent of glyoxal dismutation, the pH of the reaction mixture has to be kept at a constant value of 7.7. The produced carboxylic acids were therefore neutralized continuously by a 2 or 5 wt.% aqueous solution of sodium hydroxide which is added using Stat Titrino 718 from Metrohm. Air was bubbled through the solution at a constant flow rate of 0.4 l/min. Measurements were performed with 100 mg of catalyst during reaction times ranging between 0.5 and 24 h. The selected conditions correspond to a kinetic regime.

2.3.2. Dissolution tests

Dissolution tests were performed under the same general experimental conditions as described above, but by changing the composition of the reaction medium or the surrounding atmosphere. Experiments were carried out in the presence of glyoxal (0.1 mol/l), glyoxylate (0.012 mol/l), oxalate (0.019 mol/l) or glycolate (0.012 mol/l), or none of them, under air or nitrogen. The selected concentrations correspond to the highest values observed during the standard catalytic tests.

2.3.3. Analysis of the reaction medium

Reaction products were determined by high performance liquid chromatography (HPLC). Routine analysis was performed with a liquid chromatograph TSP Spectra SERIES P200 coupled with a TSP Spectra System UV6000LP diode array detector. The different carboxylic acids were separated on a BioRad Aminex HPX-87H column heated at 60°C. The mobile phase was a 0.005 mol/l sulphuric acid solution with a flow rate of 0.4 ml/min.

Bismuth, lead and palladium losses from the catalysts in the reaction medium were measured by atomic absorption spectrometry after removal of the catalyst from the reaction mixture, washing and subsequent concentration of the resulting filtrate. Analyses were performed on a Perkin-Elmer 3110 spectrometer equipped with an air–acetylene flame atomizer.

3. Results

3.1. Overall catalytic behaviour of Bi–Pd/C and Pb–Pd/C catalysts in glyoxal oxidation

3.1.1. Time dependence of the composition of the reaction medium

Because glyoxal contains two aldehydic functions, its oxidation easily leads to the formation of oxalic acid. Moreover, as mentioned before, a basic medium favours the Cannizzaro reaction resulting in glycolic acid. Experiments have shown that the production of the latter depends exclusively on the pH and is not related to the heterogeneous catalytic process. The yield of glycolic acid increases regularly with the reaction time and reaches 22% after 24 h of reaction.

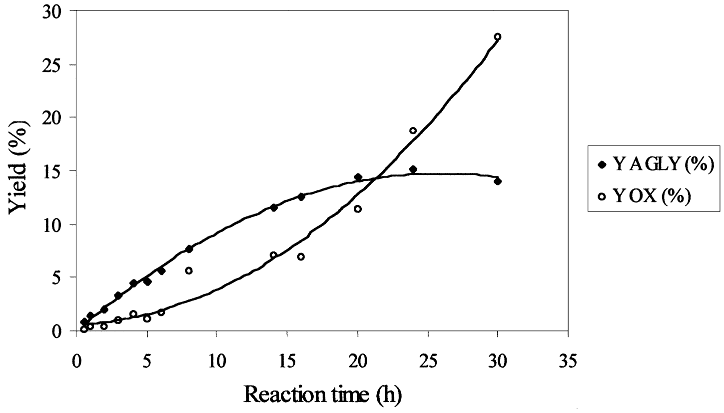

Fig. 1. Yields of glyoxylic (AGLY) and oxalic (OX) acids vs. time for a Bi(5 wt.%)–Pd(5 wt.%)/C catalyst.

Detailed investigations have been performed in order to determine the influence of the reaction time on the formation of the different oxidation products. Fig. 1 displays the overall evolution of the yields in glyoxylic (Y_{AGLY}) and oxalic (Y_{OX}) acids with the reaction time for a Bi–Pd/C catalyst. All the catalysts tested in the present work display a similar behaviour. Once air is admitted, glyoxal is oxidized essentially to glyoxylic acid. Then, after a certain time depending on the catalyst nature, overoxidation of this first reaction product into oxalic acid occurs. However, a kinetic study suggests that a small part of oxalic acid also results from direct oxidation of glyoxal [6]. For a catalyst composition corresponding to M/Pd=1/1 (wt.), the best performances are observed when Bi is used as promoter: the maximum yield and selectivity in glyoxylic acid amount to 15 and 31%, respectively, for a glyoxal conversion of 49%.

3.1.2. Promoting effects of Bi and Pb

The selective oxidation of glyoxal into glyoxylic acid is reported in the literature to proceed on various monometallic catalysts, but Pt/C catalysts were by far the most active ones [7]. The present work clearly demonstrates that, while the Bi/C or Pb/C catalysts are almost inactive, the incorporation of lead or bismuth in Pd-based catalysts increases the catalytic activity drastically (Fig. 2).

3.2. Time dependence of Bi or Pb losses under standard experimental conditions

Partial but significant dissolution of the promoting agent (up to ca. 20% Bi or Pb) during the standard catalytic operation was clearly demonstrated by performing atomic absorption analysis of the reaction mixtures after the catalytic tests. Palladium concentrations

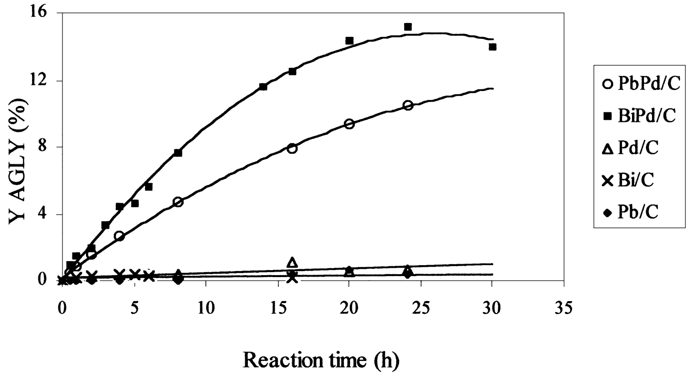

Fig. 2. Promoter effect on the yield of glyoxylic acid (Y_{AGLY}).

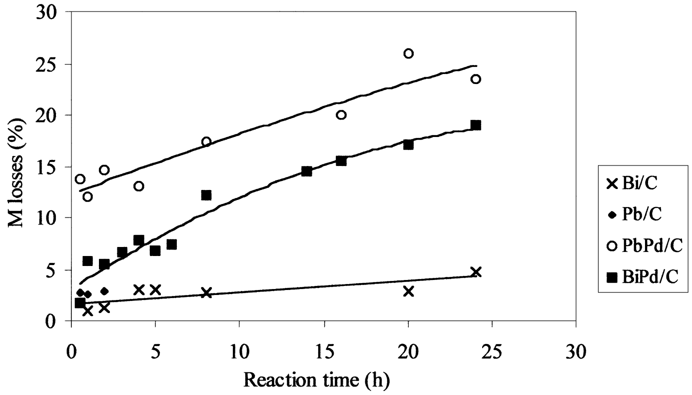

Fig. 3. Promoter losses from mono- and bimetallic catalysts vs. reaction time.

were always found to be lower than the analytical detection limit. This phenomenon is well-known in the literature and has been mentioned several times for Bi- or Pb-promoted catalysts [5,8–10]. Detailed investigations of the time dependence of the promoting element losses were carried out with Bi–Pd/C and Pb–Pd/C catalysts, and compared with that obtained with the monometallic Bi/C and Pb/C catalysts (Fig. 3). Promoter leaching increases with the reaction time. Under standard reaction conditions, monometallic catalysts were found to lose smaller amounts of promoting agent (<5%) than the corresponding bimetallic catalysts. When comparing the leaching behaviour of Pb- or Bi-promoted catalysts displaying the same overall composition, losses are found to be more pronounced from Pb–Pd/C than from their Bi-based partners. On the other hand, this leaching is much lower in the glyoxal/glyoxylic acid process than when the same catalysts are involved in the glucose to gluconic acid reaction, where Bi losses reach 65% [2].

3.3. Dissolution tests: influence of the medium composition

Investigations were undertaken to understand the individual effects of the various constituents of the reaction medium on the dissolution process. The results of these experiments are summarized in Table 1.

Table 1
Influence of the composition of the reaction medium and the experimental conditions on Bi or Pb leaching

No.	Catalyst	Reaction medium[a]	Atmosphere	M losses (M=Bi) (%)	M losses (M=Pb) (%)
1	M–Pd/C	Water	N_2	–	–
2	M–Pd/C	Water	Air	–	–
3	M–Pd/C	Glyoxal	N_2	3.2	30
4	M–Pd/C	Glyoxal	Air	1.7–19	12–26
5	M–Pd/C	Glyoxylate	N_2	7.1	16.5
6	M–Pd/C	Glyoxylate	Air	11.5–1.95	20
7	M–Pd/C	Oxalate	N_2	–	–
8	M–Pd/C	Oxalate	Air	–	14
9	M–Pd/C	Glycolate	N_2	–	–
10	M–Pd/C	Glycolate	Air	–	1–9
11	Bi/C	Glyoxal	N_2	2.4	–
12	Bi/C	Glyoxal	Air	3.7	–
13	Pb/C	Glyoxal	N_2	–	3–5
14	Pb/C	Glyoxal	Air	–	2

[a] Initial concentrations (mol/l): glyoxal=0.1, glyoxylate or glycolate=0.012, oxalate=0.019.

Measurements were carried out on Bi- and Pb-based catalysts in different experimental conditions described above. When the losses are dependent on the reaction time, the table gives two values corresponding to the losses observed at t=1 and 24 h, respectively. The absence of any value means that the result falls below the analytical detection limit (<2% loss).

In the presence of water (lines 1, 2), Bi and Pb losses from the bimetallic M–Pd/C catalysts are negligible, confirming that neither the standard pH value of 7.7 nor the presence of air alone are responsible for the dissolution. Bi losses from the Bi–Pd/C catalyst are already observed under a nitrogen atmosphere in the presence of glyoxal (line 3) and, slightly more, in the presence of glyoxylate (line 5). Since no Bi dissolution occurs in the absence of these products, even under a continuous air flow (line 2), or in the presence of oxalate or glycolate (lines 7–10), the two former constituents seem to be among the main factors responsible for catalyst leaching.

Measurements carried out on bimetallic Pb–Pd/C catalysts give more complex results. While glyoxal and glyoxylate solutions are also found to promote Pb leaching (lines 3, 5), Pb losses are also noted in oxalate and glycolate solutions under air (lines 8, 10), but not under nitrogen (lines 7, 9). Oxalate and glycolate ions themselves can therefore not be considered as directly responsible for lead dissolution. The behaviour in air suggests the formation of a soluble Pb complex which has not been identified so far. When referring to the literature which mentions that oxalic acid can be converted into CO_2 under similar conditions using noble metal-based catalysts [11], the mediation of hydrogenocarbonate ions in these processes could be possibly invoked. Although the solubility of neutral Bi and Pb oxalato complexes is known to be very limited in aqueous phase, the oxalate and promoting element concentrations involved in the present case are sufficiently small to prevent precipitation of these species.

3.4. Characterization of supported catalysts

3.4.1. XRD

Fresh and used catalysts exhibit very similar XRD spectra. The diffraction patterns of monometallic catalysts indicated the presence of metallic Pd, Bi or Pb, respectively, together with minor phases such as Bi_2O_3 or PbO. Bimetallic Bi–Pd/C catalysts are characterized by poorly resolved XRD spectra, suggesting an amorphous or microcrystalline structure, in which the occurrence of one or several binary Bi_xPd_y alloys is, however, suspected [12]. Bimetallic Pb–Pd/C catalysts are characterized mainly by the presence of the intermetallic compound Pd_3Pb. This interpretation was confirmed by the XRD investigations of the corresponding unsupported catalyst, prepared from the same Pb and Pd precursors, according to the same experimental procedure. $PbPd_3$ was indeed detected in the XRD pattern of the decomposition products of a mixture of $Pd_3(OAc)_6$ and $Pb(OAc)_2$ heated at 500°C for 18 h.

3.4.2. XPS

The 4f XPS spectra of Pb and Bi display two doublets which can be, respectively, assigned to Bi(0) (E_b=158.4 eV) and Bi(III) (E_b=160.1 eV), and to Pb(0) (E_b=138.1 eV) and Pb(II) (E_b=139.5 eV). The 3d XPS spectra of Pd also display two doublets which correspond to Pd(0) (E_b=335.8 eV) and Pd(II) (E_b=337.4 eV).

Tables 2 and 3 compare the experimental atomic intensity ratios with the theoretical values, i.e. those

Table 2
XPS atomic intensity ratios in fresh and used (t=24 h) catalysts for Bi-promoted catalysts

Bi-promoted catalysts		Bi/Pd		Pd/C (×100)		Bi/C (×100)	
		Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
Ac.Pd/C	Fresh	–	–	0.59	1.24	–	–
	Used	–	–	0.59	1.13	–	–
Ac.Bi/C	Fresh	–	–	–	–	0.30	0.46
	Used	–	–	–	–	0.29	0.39
Ac.BiPd/C	Fresh	0.51	0.77	0.62	1.24	0.32	0.95
	Used	0.41	0.49	0.62	1.27	0.26	0.62

Table 3
XPS atomic intensity ratios in fresh and used (t=24 h) catalysts for Pb-promoted catalysts

Pb-promoted catalysts		Pb/Pd		Pd/C (×100)		Pb/C (×100)	
		Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
Ac.Pb/C	Fresh	–	–	–	–	0.30	0.33
	Used	–	–	–	–	0.30	0.24
Ac.PbPd/C	Fresh	0.51	0.79	0.63	0.67	0.32	0.53
	Used	0.39	0.54	0.63	0.90	0.25	0.49

calculated from the overall catalyst composition. When Bi or Pb is concerned, these theoretical values take into account the partial loss of promoting element during the catalytic test. The atomic intensity ratios M/Pd observed in fresh bimetallic catalysts are systematically higher than the theoretical values. These results clearly indicate partial coverage of palladium by the promoting agent, a segregation effect which is in agreement with the lower surface energy of the latter. In most cases, the high experimental Pd/C, Bi/C and Pb/C ratios in these catalysts suggest an adequate dispersion of these elements on the surface. The fact that the M/Pd and M/C ratios decrease in the used catalysts is in line with the leaching behaviour.

4. Discussion and conclusions

It is important to point out that the Bi losses measured with the bimetallic Bi–Pd/C catalysts in the presence of glyoxal (Table 1, line 4) are in agreement with their catalytic behaviour: under oxidation conditions, the increase in Bi losses with the reaction time is in line with the formation of glyoxylate ions which have been recognized as responsible for such losses under nitrogen. Similarly, the decrease of the Bi losses when starting with glyoxylate as reagent (Table 1, line 6), in the presence of air, reflects the progressive conversion of this reagent to oxalate, which was previously shown not to take part in the leaching process under nitrogen. Furthermore, the behaviour of these bimetallic catalysts also agrees with that of the monometallic Bi/C catalyst, which is inactive and does not display any difference in stability in the presence of glyoxal, neither in function of time nor in function of the surrounding atmosphere (Table 1, lines 11, 12).

In comparison, the stability of the bimetallic Pb–Pd/C catalyst in the presence of glyoxylate and air (Table 1, line 6) is constant with time and this can be related to the fact that the reaction generates oxalate whose further oxidation was shown to induce a significant Pb leaching. An overall comparison between the leaching behaviour of Bi- and Pb-promoted catalysts is, however, not straightforward because the active phases present at the surface and involved in these processes are not the same. In particular, the changes in the XPS intensity ratios Pb(II)/Pb(0) and Bi(III)/Bi(0) as a function of the reaction times are quite different: while the relative amount of oxidized Pb progressively decreases in the used catalysts, the reverse situation is observed for Bi. Moreover, the presence of the $PbPd_3$ intermetallic in the Pb-promoted catalysts cannot explain by itself their overall behaviour with respect to leaching. This phase is known to be very stable, which results in a very low catalytic activity for the concerned reaction ($Y_{AGLY}(t=24\,h)=1.5\%$), and loses only minor amounts of Pb during the tests (3–6%).

The fact that the Bi losses observed in the glyoxal/glyoxylic acid process are significantly lower than those in the glucose/gluconic acid reaction can be rationalized by considering that the complexation properties of the various species present in the reaction medium are important to understand the stability of such bimetallic catalysts under the standard experimental conditions. The complexing properties of glucose and gluconic acid have been described and, in particular, their interaction with Bi(III) ions in solution has been investigated recently in relationship with the present work [13]. Lower complexing ability from the glyoxal and glyoxylate species can be expected and is presently under investigation.

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