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HYDROGEN ADSORPTION ON CLEAN AND OXYGEN COVERED Pt(111)

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The dissociative adsorption of hydrogen on oxygen covered Pt(111) has been investigated using molecular beam techniques. The D_2-sticking probability has been measured as a function of oxygen coverage ($0 < \Theta_O < 0.25$ ML) and angle of incidence for two incident energies, 14 and 63 meV. In addition, the order of the oxygen layer has been measured using thermal He-scattering. The measurements show clear evidence for the existence of two distinct adsorption processes both on the oxygen covered and on the clean Pt(111) surface, i.e. in the limit were Θ_O approaches zero: an activated process which depends on the total oxygen coverage and a non activated process which is sensitive only to the amount of locally ordered oxygen. The non activated process can be explained in terms of a mechanism involving a short living precursor state. The picture for the activated process is less clear. The dependence of this process on the incident energy seems strong evidence for a mechanism involving a barrier to dissociation directly upon impact, whereas the dependence on the oxygen coverage supports previously reported experiments which seem to be only compatible with a precursor mechanism.

Keywords: Hydrogen adsorption-on-platinum, hydrogen sticking probability, oxygen covered platinum, precursor state, energy dependent dissociation of D_2

1. Introduction

Adsorption of hydrogen on d-band transition metals such as Ni and Pt has been studied extensively, due to the central role played by these materials as catalysts in hydrogenation reactions. In addition, these studies serve also a more fundamental purpose. Since hydrogen is a relatively simple molecule, a detailed understanding based on theory seems easier to be reached than for adsorption systems involving more complex molecules. For the (111) faces of Ni and Pt, all studies reported in the literature [1–8] find that the adsorption process depends on the energy of the incident molecules, i.e. the sticking probability S increases with increasing energy E.

These results give evidence for the existence of an activation barrier which the H_2-molecules have to surmount to dissociate, a process which takes place directly upon impact [9–15]. However, for Pt other measurements [16–19] do not appear to be compatible with such a process: they indicate that adsorption takes place via a precursor molecule which dissociates when reaching an atomic step (see next section). The situation, therefore, is rather unsatisfactory. Some experimental results favor a barrier model and seem to contradict with a precursor mechanism, whereas other results favor a precursor model (in contrast to the recent remark in ref. [8]) and seem incompatible with a barrier model. It appears, therefore, that additional experiments, revealing more specific information about the H_2-Pt(111) interaction, are required to unravel this problem.

Adsorption of H_2 on oxygen covered Pt(111) has been studied less extensively than adsorption on clean Pt(111). The problem in this case was how to distinguish between effects related to the actual surface reaction between H and O atoms and effects which depend entirely on the adsorption characteristics [20–23]. Recently we were able to separate these two effects [19,24] and results of our experiments relating to adsorption are reported in this work (section 3). As a limiting case also zero oxygen coverage is included in these measurements. In fact, they allow to draw conclusions on some of the details of the hydrogen surface interaction at finite coverage Θ_O, which can be correlated to processes occurring on the clean surface. However, before describing the results, it is necessary to discuss previous results on the H_2-Pt(111) interaction reported in the literature in some more detail.

2. Discussion of previous work

All studies on H_2-adsorption on Pt(111) reported sofar agree that the adsorption is activated in the sense that the sticking probability S increases with increasing incident energy E of the H_2 molecules. At low incident energies ($E < 100$ meV) S was found to depend roughly on the square of the energy perpendicular to the surface, $E_\perp$, [3,5,6]. In an other study [7] which combined adsorption and desorption measurements, the energy dependence of S could be determined more precisely. It was found that in addition to the quadratic term also a more or less energy independent term was necessary to describe quantitatively the data:

$$S = S_0 + S_\perp E_\perp^2 . \tag{1}$$

The ratio $S_0/S_\perp$ was found to depend on temperature, increasing by a factor four in the considered surface temperature range ($670 < T_s < 1070$ K). This indicates that the two terms represent different adsorption channels. In addition a decrease of $S_\perp$ with increasing T_s was reported in ref. [7], though this effect was not really significant.

In an adsorption study by Luntz et al. [8] at $T_s = 295$ K, a different dependence of S on E was found. For glancing incidence, $\vartheta_i \gtrsim 45°$, the results can be described by eq.(1), i.e. they agree at least qualitatively with ref. [7]. However, for $\vartheta_i \lesssim 30°$, a linear or an even weaker dependence on E is observed. This is at variance with the observations reported in ref. [7], at least if the principle of detailed balance is not violated. The reason for this discrepancy is not clear, although we think that it is related to the characteristics of the H_2-Pt(111) adsorption system which make accurate measurements difficult. Because of the low sticking probability ($S \approx 0.0–0.1$ for $E_\perp < 70$ meV), the statistics in time of flight (TOF) desorption experiments [7] is usually poor, making an accurate measurement of the velocity destribution of desorbing molecules difficult. On the other hand, the dependence of S on hydrogen coverage, Θ_H, which is much stronger than for other adsorption systems (eq.(2), below), makes it very hard to accurately measure S in the limit of zero coverage. (In fact, the observed dependence on incidence rate, figs. 1 and 4 of ref. [8], indicates that Θ_H is not always negligible for the conditions used in ref. [8]1 to determine S.) In spite of the discrepancies between the experiments discussed above, one still has to conclude that all of them strongly favor a barrier model for the adsorption of H_2 on Pt(111).

However, other measurements seem to be not compatible with the barrier model. In a first experiment it was found that as little as 10^{-3} ML H_2O bound at step sites leads to a 20% increase of S (from 0.05 to 0.06) [17]. For a direct process, this would mean that a single H_2O molecule bound at a step effectively increases the H_2 sticking probability on an area of 70 Å^2 from 0.05 to 1. In addition, a rather intricate dependence of S on both the hydrogen coverage Θ_H and defect density Θ_d was found [5,18]:

$$S = S_{H_0}(\Theta_d) \cdot (1 - \Theta_H)^2 \exp(-5.6\Theta_H) + 0.25\Theta_d(1 - \Theta_H)^2. \qquad (2)$$

The decrease of S with increasing Θ_H is much faster than Langmuirian. In terms of a direct process, it would mean that a single H-adatom would block an area about 50 Å^2 for the dissociative adsorption of a H_2 molecule. Also the influence of atomic steps on the sticking probability seems hard to reconcile with a direct adsorption process. Only the second term in eq.(2) can be ascribed to such a process. However, at low coverage, the increase of S_{H_0} with Θ_d is a much more prominent effect which does not seems to be related to direct adsorption at step sites. To explain the measurements, a precursor model was proposed: Hydrogen incident on terraces are trapped in a weakly bound state and dissociate only upon encountering an atomic step.

To verify this model, experiments were performed in which the steps were decorated with CO molecules, in order to prevent precursor molecules to meet the step [25]. The results of these experiments seemed puzzling: On a well annealed surface ($\Theta_d \lesssim 10^{-3}$), S decreased only from about 0.05 to 0.04. However, on a randomly stepped surface ($\Theta_d \approx 0.15$) obtained by bombarding the surface with Ar-ions [18], S could be reduced from 0.15 to below 0.01 by decorating the steps with CO. This seems to indicate that steps on the annealed surface are of a different nature as those on a bombarded surface. Recently a similar difference between steps on an annealed and an Ar-bombarded surface was observed in a different experiment: The reactivity for the $O_2 + H_2$ reaction on a well annealed Pt(111) surface could be increased considerably by a mild oxygen treatment, which seems to be due to step roughening stabilized by a very small amount of strongly bound oxygen ($\Theta_O < 0.5\%$) [24]. However, this treatment had no effect on the reactivity of an Ar-bombarded surface. The reason for this could be that steps on an annealed surface are pinned by contamination or by crystal imperfections, and this may cause, possibly in combination with subsurface O [26], a change in the reactivity of the steps [27,28]. Further support for the precursor model came from an adsorption experiment performed at 25 K, showing a constant sticking probability up to a coverage $\Theta_H \approx 0.6$ [18,29]. Upon increasing the temperature, the coverage range in which S remains constant gradually decreases until around 100 K the high temperature behaviour described by eq.(2) is observed.

As already stated in the introduction, the situation is rather unsatisfactory: the energy dependent measurements favor a barrier model and seem to contradict a precursor model, whereas other results favor a precursor model and seem to be incompatible with a barrier model. Additional experiments revealing more specific information about the H_2-Pt(111) interaction, are required in order to settle this question. As will be discussed in this work, the study of H_2-adsorption on oxygen covered Pt(111) serves this purpose to some extent, although it still does not allow to draw a final conclusion on this matter. Of course, such a study is also of significance for understanding the catalytic water reaction on Pt(111), as will be discussed in a forthcoming paper.

3. Experiment

The sticking probability of D_2 on an oxygen covered Pt(111) surface has been deduced from titration measurements: The surface is exposed to O_2 until saturation ($(\Theta_O) = 0.25$ ML [19,20,23]) and the adsorbed oxygen is then reacted away by D_2 supplied by a mixed D_2/He or D_2/N_2 nozzle beam. The D_2-incidence rate is kept very low in order to ensure that the D_2-adsorption process is rate limiting for the formation of D_2O [19]. In that case the D_2O desorption rate is directly proportional to the D_2 sticking probability. By measuring the absolute intensity of the nozzle beam and using the known saturation coverage of oxygen, absolute values for S are obtained from the D_2O desorption rate. The incident energy of the D_2-molecules depends on the beam mixture: with the nozzle at room temperature, the energy of D_2 is 63 meV for the D_2/He beam and 14 meV for the D_2/N_2 beam. It is known that oxygen forms an ordered $p(2 \times 2)$ layer on Pt(111) at temperatures below about 400 K [20].

During titration of the layer with the D_2/He beam we measured also the half order He diffraction intensity. This signal is a measure for the amount of ordered oxygen in the adsorbed layer. Most of the measurements reported here were performed on a surface which underwent a mild oxygen treatment, which causes the reactivity of the surface to increase [24], but has no effect on the D_2 sticking probability [19]. Further details of the experiment and of the experimental set up can be found elsewhere [7,19,23,24].

Fig. 1 shows a typical measurement of the D_2-sticking probability as a function of Θ_O when using a low energy beam ($E_\perp = E \cdot \cos^2\vartheta_i = 7$ meV). At low oxygen coverage S is about 0.01 and independent of Θ_O until at a certain coverage Θ_s, the D_2-sticking probability starts to increase monotonically. In the same figure we also show the half order He diffraction intensity $I_{1/2}$ as a function of Θ_O. It exhibits a similar behaviour: at low coverage one observes a constant signal–the diffuse background–and only after the coverage increases beyond a critical coverage Θ_{He}, $I_{1/2}$ starts to increase indicating that ordered oxygen domains are present. From the figure it is clear that $\Theta_{He} > \Theta_s$. In order to quantify the results, we have defined Θ_s and Θ_{He} in a consistent (though arbitrary way): The data, for instance those in fig. 1, were fitted by two straight lines connected by a parabolic curve. Θ_{He} is defined as the coverage at which the fit of $I_{1/2}$ shows the transition from the low coverage horizontal line to the parabolic curve. Using the same definition for Θ_s resulted in less reproducible values for this quantity, due to the worse statistics of the sticking probability data. Therefore, we defined Θ_s as the coverage at which S has increased by 10% with respect to its zero coverage value. The Θ_s and Θ_{He} values determined for surface temperatures 325 K < T_s < 575 K are shown in fig. 2. The dependence of $I_{1/2}$ on Θ_O and T_s can be explained in

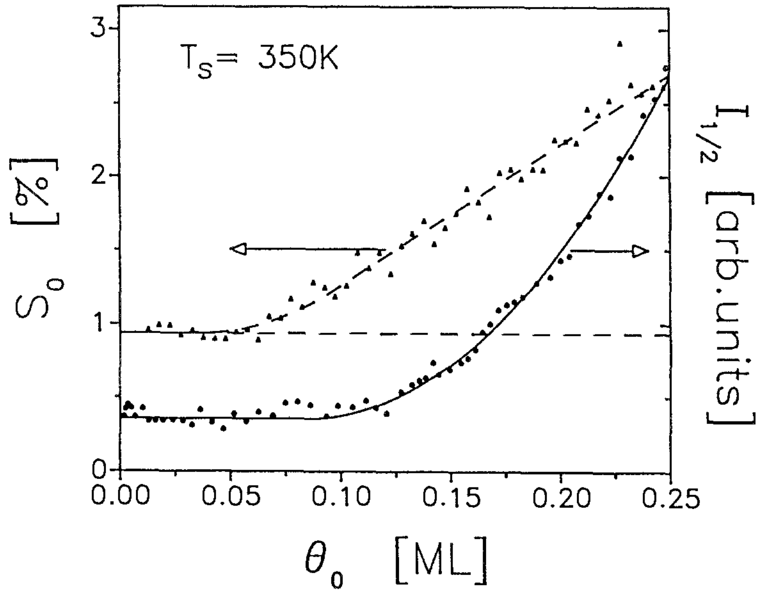

Fig. 1. The hydrogen sticking probability (▲), measured with the D_2/N_2 beam, and the half order He diffraction intensity (○) as a function of the oxygen coverage, $\vartheta_i = 46°$, $T_s = 350$ K.

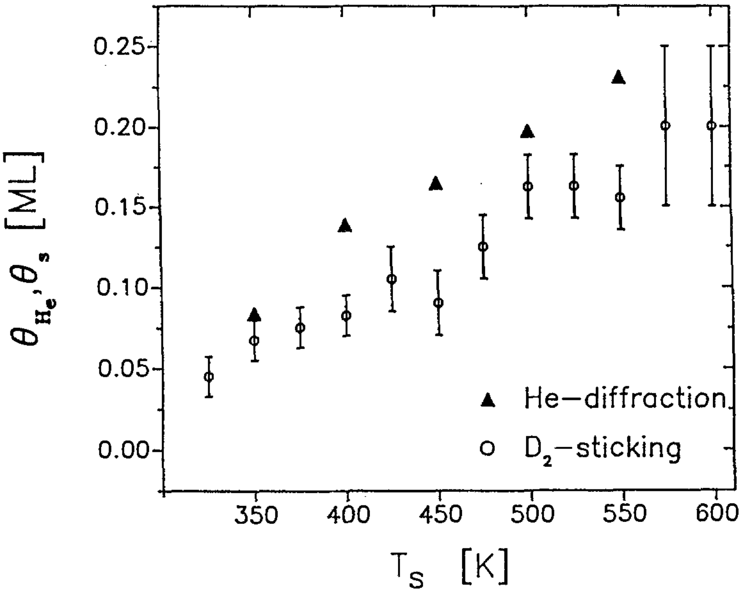

Fig. 2. The critical coverages Θ_{He} and Θ_s, characterizing the order/disorder phase transition of the oxygen layer as observed by He diffraction and low energy ($E_\perp = 7$ meV) hydrogen sticking measurements, as a function of the surface temperature (see text).

terms of an order/disorder phase transition of second order: Ordering starts in the form of small ordered domains which become larger upon increasing Θ_O or decreasing T_s (for more details see ref. [19]). We estimate that the smallest domains, which we can observe with He scattering are of the order of 10–15 Å.

Figs. 1 and 2 show that S and $I_{1/2}$ depend in a very similar way on both Θ_O and T_s indicating that the increase of the D_2-sticking probability with Θ_O (for $E_\perp = 7$ meV) is determined by the amount of locally ordered oxygen. Disordered oxygen appears to have no influence on the D_2-adsorption. Additional measurements with both the D_2/N_2 and the D_2/He beam in which the angle of incidence was varied were identical to those reported above, provided that the energy perpendicular to the surface $E_\perp \lesssim 10$ meV, i.e. they are independent of $E_\perp$ in this energy range. We conclude, therefore, that the adsorption process described above is not activated. Thus, it corrresponds to the adsorption channel found in ref. [7] which is described by the term S_O in eq.(1). The sticking probability for this channel appears to depend slightly on surface temperature: it increases by 30% when increasing T_s from 350 to 600 K. Finally, we want to stress that the adsorption channel discussed above is not due to the presence of steps but to adsorption on terrace sites. Indeed, when atomic steps are present a completely different behavior is observed: the D_2-sticking probability decreases with increasing oxygen coverage.

Let us now consider the activated adsorption (S_1 in eq.(1)) which becomes important for $E_\perp > 10$ meV. Increasing the perpendicular energy, $E_\perp$, above 10 meV leads to an increase of the sticking probability in the whole coverage range. However, the increase of S with $E_\perp$ at low coverages is larger than that at high coverages. Consequently, the shape of the $S(\Theta_O)$ curves changes completely. At intermediate energies the $S(\Theta_O)$ curves show a minimum, which lies, at $E_\perp \approx 20$ meV, at about the critical coverage $\Theta_O \approx \Theta_s$, but shifts to higher coverage upon further increasing $E_\perp$. Finally for $E_\perp > 50$ meV the minimum has disapperead and we observe that S decreases monotonically with Θ_O. The very different behavior observed for $E_\perp < 10$ meV and for $E_\perp > 50$ meV is clear evidence for the existence of two distinct adsorption processes, a non activated process which becomes more efficient with increasing order of the oxygen atoms and an activated process which is hindered by the adsorbed oxygen, whether ordered or not.

In order to investigate this latter process in more detail, we have decomposed the sticking probability, measured with the D_2/He beam ($E = 63$ meV) into two components. This was done by two different methods. Firstly, we have assumed that eq.(1) applies. This enabled us to deduce $S_1(\Theta_O)$ ($= S_\perp E_\perp^2$) from a series of $S(\Theta_O)$ curves measured at different angles of incidence ϑ_i. Secondly, we have assumed that the non activated adsorption process is independent of the beam energy. In that case S_1 is obtained by substracting the hydrogen sticking probability measured with the D_2/N_2 ($E_\perp = 7$ meV) beam from that measured with the D_2/He ($E_\perp = 63$ meV) beam.

The results of both procedures (○ and △ resp.) are shown in fig. 3 for $T_s = 400$ K. The fair agreement between the two data sets shows that the energy dependent

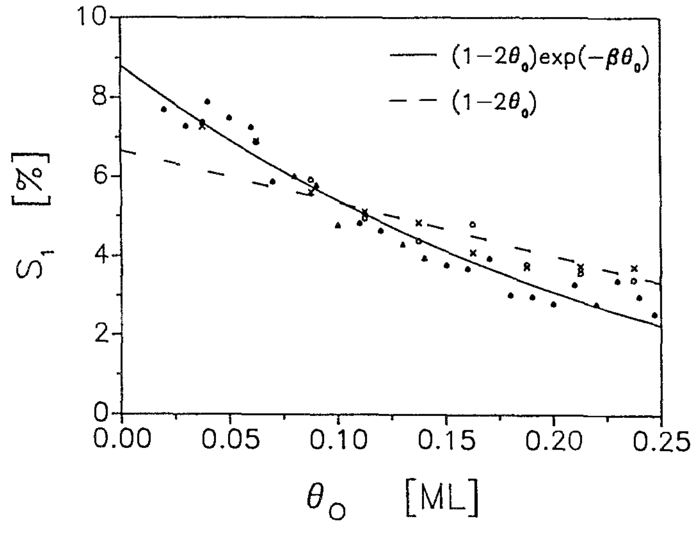

Fig. 3. The hydrogen sticking probability via the activated adsorption process, S_1 at an incident energy perpendicular to the surface of 63 meV, as a function of the oxygen coverage, △, ○: $T_s = 400$ K, ×: $T_s = 550$ K. Fits to the data (triangles): dashed line–Langmuir adsorption (linear [30]), solid curve–according to eq.(3) ($\beta = 2.4$.).

sticking process is well described by a quadratic term $S_1 = S_\perp E_\perp^2$, for $E_\perp \lesssim 70$ meV. Within the experimental accuracy S_1 is found to be independent of T_s in the range 350 K < T_s < 600 K, both with respect to the absolute value and with respect to the dependence on Θ_O. This is illustrated by the third data set (x) obtained at 550 K. The data in fig. 3 are clearly not linear with Θ_O. In analogy with eq.(2) one can describe them reasonably well by [30] (solid curve):

$$S_1 = (1 - 2\Theta_O)\exp(-2.4\Theta_O). \tag{3}$$

To explain this result in terms of adsorption via direct dissociation upon impact seems difficult. The area of the surface which is effectively blocked for D_2-adsorption by a single O atom is larger than the $p(2 \times 2)$ unit cell as can be deduced from the slope of S_1 at zero coverage. In terms of a simple blocking model, one would expect, therefore, the adsorption probability of hydrogen to be zero at the saturation coverage $\Theta_O = 0.25$. However, also with more sophisticated models it remains hard to explain these results in terms of a local adsorption process: The non linear dependence on Θ_O (fig. 3) has to be explained in such a model by the collective influence of at least two oxygen adatoms. Therefore, an effect of ordering of the adlayer and thus of the surface temperature on the sticking probability of hydrogen in the activated adsorption channel should be expected. Since no temperature dependence is observed, this seems to indicate that the adsorption process via channel S_1 is not local.

4. Discussion

In previous work [7] we have found evidence for adsorption of H_2 on Pt(111) terraces via two distinct channels. The present results confirm this conclusion. The different Θ_O and T_s dependence of the activated and non activated adsorption processes strongly indicate that the two processes are fundamentally different, i.e. a model assuming a distribution of barriers which vanish at some parts of the surface, cannot describe both processes.

Let us first discuss the non activated adsorption process described by S_0 (eq.(1)). This process was found to be very local, indicating that hydrogen dissociates directly upon impact or via a process involving a very shortly living precursor state. A possible mechanism could be that D_2 is trapped in a precursor state with a probability which does not depend on the oxygen coverage. From this state, the molecule may desorb almost immediately or dissociate via a transition state. Calculations on clean Pt(111) [10,11] indicate that bridge sites are very efficient for dissociating hydrogen molecules with their molecular axis perpendicular to the bridge. Ordered oxygen atoms may enhance the probability for this process if they are able to align the hydrogen molecules preferentially in this direction. Disordered oxygen atoms will also influence the orientation of the axis of the D_2 molecules, but randomly. Their effect is similar to the clean surface where no alignment is to be expected. Such a mechanism would explain both the sensitivity of S to ordered oxygen as well as the insensitivity of S to disordered oxygen. The temperature dependence of the non activated adsorption process may then be related to different properties of the transition state for desorption and the transition state for dissociation.

The adsorption process described above can explain the increase of the hydrogen sticking probability in the temperature range between 100 and 300 K reported in refs. [8] and [17]. Because of its dependence on T_s, S_0 will be negligible at 100 K and in fact it was not observed at this temperature [5]. At 300 K we observe that S_0 is about 0.01 and this is about equal to the increase of the total hydrogen sticking probability S according to refs. [8] and [17]. At high surface temperatures (670 K $< T_s <$ 1070 K) we have found [7] a much stronger dependence on T_s as found here for 350 K $< T_s <$ 600 K. Preliminary measurements indicate that this could be related to an irreversible change of the surface when heating it in a hydrogen environment to temperatures above 700 K. In fact, this could be an additional reason for the discrepancy between the results of refs. [7] and [8].

In contrast to the low energy data concerning S_0, which can be interpreted in a consistent way, the high energy data, concerning S_1 still seem to be contradictory. The observed energy dependence suggests a barrier model, i.e. a direct dissociation upon impact, whereas the dependence on oxygen coverage seems only compatible with a non local process, i.e. with a precursor mechanism. In addition, we found that S_1 does not depend on the surface temperature for $T_s >$ 300 K. This seems to be more in support of the barrier model. However, below 100 K a distinct T_s dependence has been observed [18,29] and this observation is more in support of the precursor mechanism. In fact, both the low and the high temperature behavior could be described by a revised precursor model in which the interaction between the trapped molecules and the clean surface is weak. In that case the precursor molecules are not thermalized. Desorption from this state may occur when the precursor encounters an adsorbate atom before a dissociation site (atomic step) is reached. The probability for desorption will depend on the vibrational excitation of the adsorbate atom. At a certain temperature, T_0 ($\approx$ 100 K), this probability will have increased to almost one, i.e. below T_0 this process depends on temperature, but above T_0 it is independent of T_s. In addition, some desorption from the precursor state may arise from scattering from the substrate surface, but provided that the interaction between precursor and surface is weak, this process will be almost independent of the surface temperature.

The conclusion which can be drawn from the present (and previous) results about the activated adsorption of hydrogen on Pt(111) remains, therefore, unsatisfactory: In terms of present theoretical knowledge, the experimental results are leading to contradictory conclusions. A conclusion in favor of a barrier model [8] or in favor of a precursor model [18] seems only possible if half of the evidence is ignored.

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