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Operando spectroscopic investigation of supported metal oxide catalysts by combined time-resolved UV-VIS/Raman/on-line mass spectrometry†

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A novel experimental set-up for characterizing supported metal oxide catalysts under working conditions has been developed. The set-up combines product analysis using on-line mass spectrometry (MS) with catalyst characterization by time-resolved operando UV-VIS and Raman spectroscopy. The potentials of this approach are illustrated by the propane dehydrogenation over a chromium oxide on alumina catalyst. It is demonstrated that these spectroscopic techniques give valuable complimentary information on the changing catalyst performance during successive propane dehydrogenation operating cycles.

Introduction

Probing events taking place on a supported metal oxide catalyst under reaction conditions has attracted considerable attention in recent years.[1–3] It requires the development of time-resolved characterization techniques and the construction of *in-situ* spectroscopic-reaction cells, which allow the identification of active sites, reaction intermediates and/or coke formation. A number of spectroscopic techniques—such as UV-VIS, NMR, EPR, IR, Raman and EXAFS—have already been adapted to study metal oxide catalysts in catalytic action, each giving information about the catalyst structure.[4] It is, however, very advantageous to combine two or more time-resolved spectroscopic techniques in one catalytic reactor set-up because complementary information can be obtained simultaneously for the same catalyst material under identical catalytic conditions.

In this work, we present a novel experimental set-up, which combines two operando time-resolved spectroscopic techniques, namely UV-VIS and Raman, directly coupled to a regular fixed-bed catalytic reactor *via* optical fiber technology. Fast product analysis is performed by on-line mass spectrometry. UV-VIS together with Raman spectroscopy is a very useful combination of *in-situ* techniques. The first technique provides electronic information on the catalyst system and the latter vibrational information. Both techniques can be conveniently applied to a catalytic reactor system, since they both are non-contact measurements.

The potential of this experimental set-up has been explored by studying the dehydrogenation of propane to propene over supported chromium oxide, vanadium oxide and molybdenum oxide catalysts. As an example, in this paper we will discuss the results obtained for a 13 wt% Cr/Al_2O_3 alkane dehydrogenation catalyst. This catalyst is similar to the one used in industrial processes. The dehydrogenation of propane is an industrially very important reaction with a relatively short catalyst lifetime.[5] Per year, close to 10 million metric tons of olefins are produced using catalytic dehydrogenation processes. In the propane dehydrogenation the catalyst deactivates fast. Commonly, a regenerative procedure in air is, therefore, used for the catalyst once every 20–30 min. After this regeneration, the catalyst can be re-used for the dehydrogenation. This study provides operando spectroscopic information on the short- and long-term deactivation process of the catalyst.

The aim of this study is to demonstrate the advantage of the multi-technique approach in catalytic testing and analysis. It will be shown that the information collected has good potential to be used as a tool to more efficiently operate a propane dehydrogenation process.

Experimental

The newly developed system (Fig. 1) consists of a 6 mm diameter quartz reactor tube with a special square section in which the tube wall is made of optical grade quartz windows. Typically, 300 mg of catalyst is placed in the reactor as a packed bed supported on a sintered glass grid just below the optical windows. Catalyst extrudates were milled to a typical particle size of 50 μm. The bed height is *ca.* 15 mm. The reactor is placed vertically in the center of a 10 cm long tubular oven block; a thermocouple is inserted in the catalyst bed to directly monitor the catalyst temperature. The metal oven block has on opposite sides two horizontal 8 mm holes directed at the catalyst bed. One of the holes is used to aim an Avantes FCD-UV400-G-01CHT UV-VIS reflection probe at the catalyst bed. This high-temperature probe contains three 400 μm optical fibers closely packed in a triangle. One fiber is connected to an Avantes AVS-SD2000 spectrometer and another fiber is connected to an Avantes halogen–deuterium light source. A Halon disk was used for white reference measurements for the spectrophotometer. The UV-VIS spectrometer was used with an integration time of 28 ms and 40 spectra were averaged for signal noise reduction. The resulting time resolution was, therefore, 1 s. The measuring range of the spectrophotometer is 200–870 nm. However, effectively the system only provided a usable signal to noise ratio above 250 nm, partly

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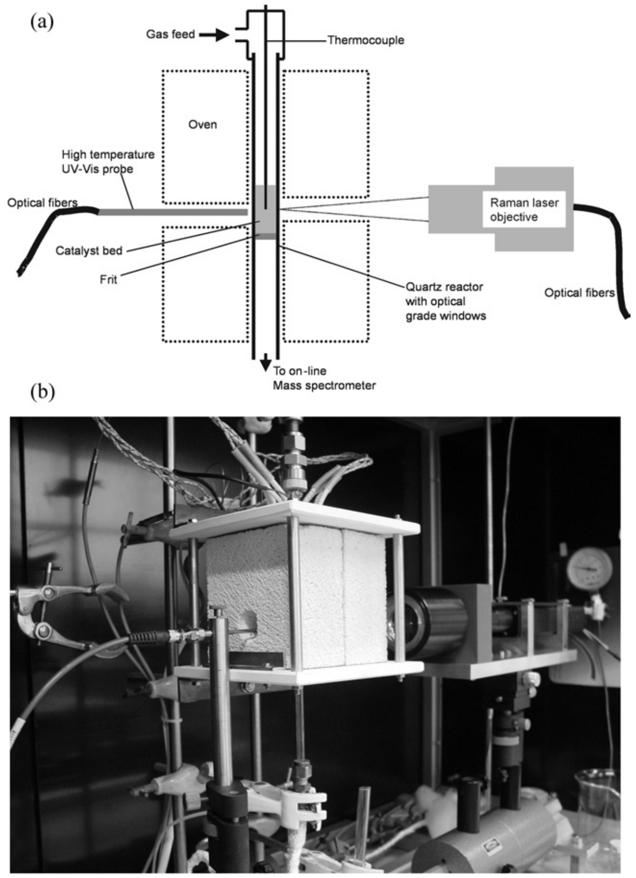

Fig. 1 Schematic presentation (A) and picture (B) of the reactor set-up with combined operando UV-VIS/Raman spectroscopy.

caused by the low transmittance of the optical fibers below this wavelength.

The second hole in the oven is used for focusing a Raman laser at the catalyst. Raman spectra were obtained by a Kaiser RXN spectrometer equipped with a 532 nm diode laser. A 5.5″ non-contact objective is used for beam focusing and collection of scattered radiation. 10 spectra were accumulated with a 3 s exposure time. The resulting total spectral recording time was 180 s. The laser output power of 70 mW did not cause any changes to the catalyst, since this energy input is negligible compared to the heat input by the oven to maintain the 550 °C reaction temperature. Furthermore, the high-loaded chromium on relatively low surface area alumina catalyst is very stable. Raman spectra measured during a period of over 1 h in which the catalyst was heated to the reaction temperature in oxygen/helium did not show any observable changes in the recorded spectra confirming this stability.

The gas leaving the reactor is analyzed using a Pfeiffer Omnistar quadrupole mass-spectrometer, to determine all mass components in the gas from 14 to 44 amu. The scanning time per mass was 50 ms, making the time resolution of the mass spectrometer 7.5 s. By performing a deconvolution procedure using the known fragmentation patterns of the reactants and all possible products, it is possible to convert the mass signals quantitatively to concentrations. For a more facile quantification of the product gas analyses, a Varian CP-4900 micro-GC system equipped with a Poraplot-Q and Molsieve 5A column was added to the reactor system. This GC system is capable of performing analyses at less than 60 s intervals.

The reactor system has been used to monitor the changes in a catalytic solid during a number of dehydrogenation–regeneration cycles of an industrial-like 13 wt% Cr-on-alumina catalyst for the dehydrogenation of propane. In these catalytic experiments, at start-up the reactor was heated at 10 K min^{-1} from room temperature to a catalyst temperature of 823 K in a gas stream of 3 ml min^{-1} of O_2 in 12 ml min^{-1} of He. After heating, the reactor was operated isothermally in cycles of alternating dehydrogenation for *ca.* 50 min with 2 ml propane in 20 ml min^{-1} of He and regenerating for *ca.* 50 min with 3 ml min^{-1} of O_2 in 12 ml min^{-1} of He. During the first 120 s of each cycle UV-VIS measurements were performed with a 1 s interval to track the rapid changes on the catalyst, after this time measurements were carried out at a 1 min interval. Raman measurements were performed at 5 min intervals. During the entire experiment the product gas composition was monitored using the MS. The temperature of the catalyst was monitored using a small thermocouple in the middle of the bed.

Results and discussion

Fig. 2 shows the measured catalytic and spectroscopic data of the 13 wt% Cr/Al_2O_3 catalyst. The catalytic activity data are presented in Fig. 2a for three dehydrogenation–regeneration cycles. It can be seen that catalyst performance does not change from one cycle to the next one, but changes significantly within one dehydrogenation cycle. The stable performance of the catalyst over the different cycles is in agreement with expectations, since a commercial catalyst is used in industry for *ca.* two years before it is replaced. In that case a catalyst will have undergone well over 10 000 cycles. Within one cycle, it can be seen that the conversion to propene increases gradually with increasing time-on-stream and reaches a maximum of 55% after 28 min. Longer reaction times result in a gradual decrease in propene formation.

Fig. 2b shows the fast changes taking place in the UV-VIS spectra in the first 6 s of the dehydrogenation reaction. The strong absorption in the 300–400 nm range is from the alumina support. There is an isobestic point present at 565 nm, indicative of the presence of at least two distinct chromium oxide species. It can be seen that the Cr^{6+} CT bands [6] located at 380 and 450 nm decrease in intensity with increasing reaction time. At the same time, the Cr^{3+} d–d transition at 630 nm increases in intensity.[6] This decrease in the absorption at 380 and 450 nm and the increase of the band at 630 nm are in agreement with the reduction of CrO_3 to Cr_2O_3 when the catalyst is switched from an oxidizing to a reducing environment. Furthermore, a shoulder at about 700–750 nm becomes visible. This band can be attributed to the interaction of Cr^{3+} with adsorbates.[7] The sharp peak in the UV-VIS spectrum at 532 nm is due to interference by light of the Raman laser scattered at the catalyst particles, while the spike at 656 nm is an artifact of the UV-VIS photometer system (most intense light emitted from the deuterium lamp).

Fig. 2c shows the UV-VIS spectrum changing over a longer time (50 min) in the propane dehydrogenation cycle. It is clear that no major peak intensity changes can be observed. On the other hand, the overall absorbance of the sample increases and this is related to the formation of coke. The Cr^{3+} d–d transition band at 630 nm becomes less pronounced over time. This can also be explained by the coverage of the chromium oxide by coke.

Coke formation is evident from the Raman spectra in Fig. 2d. The bands that appear in the region 1200–1650 cm^{-1} are attributed to (poly-)aromatic ring stretching C=C vibrations.[8] Fluorescence of the catalyst, causing the increasing baseline at high wavenumbers, decreases during the dehydrogenation cycle. It is likely that this phenomenon is also due to the coke formation on the catalyst. The bands at 200, 605, 810 and 1060 cm^{-1}, which can be observed in the Raman spectra, are originating from the quartz windows of the reactor.

Another interesting Raman band could be observed at 542 cm^{-1}. This Raman band is assigned to the presence of

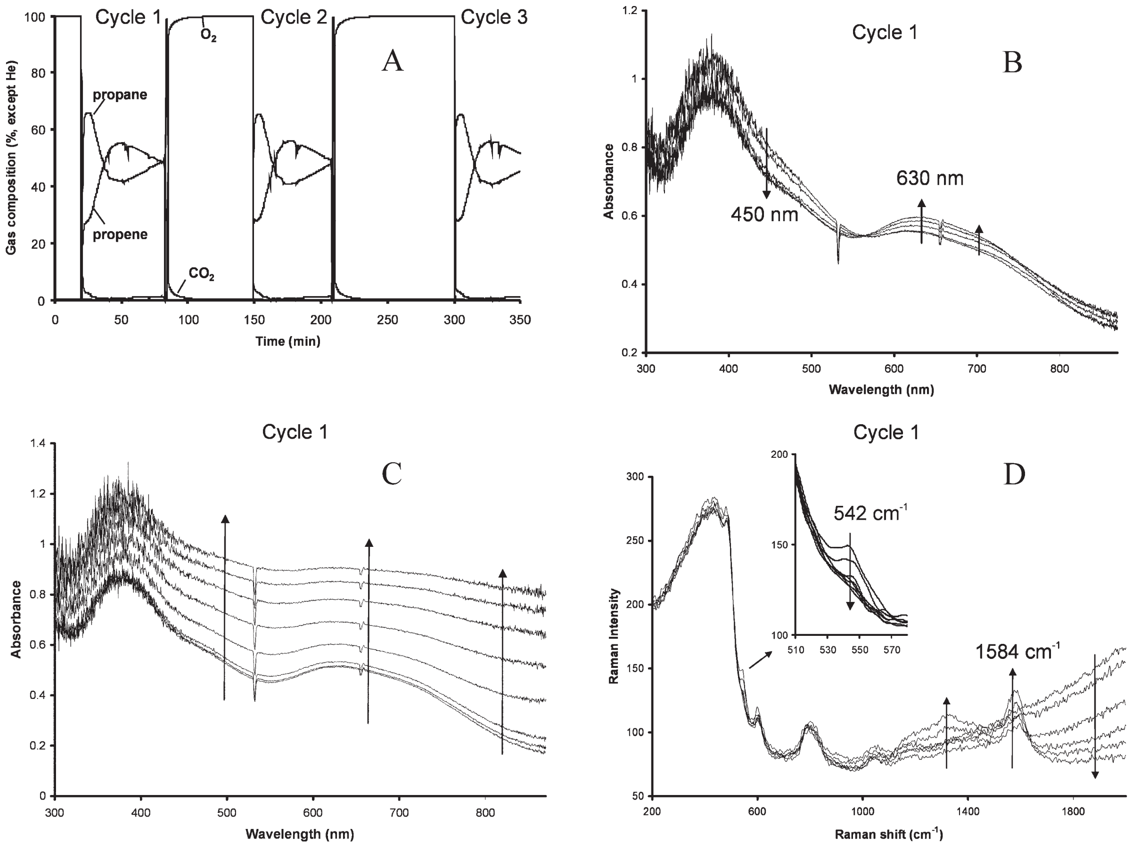

Fig. 2 Propane dehydrogenation using a 13 wt% Cr-on-alumina catalyst [1 bar(a), 823 K]. (A) Catalytic activity measurements for three dehydrogenation–regeneration cycles; (B) operando UV-VIS spectra showing the rapid changes during the first 6 s of the first dehydrogenation cycle; (C) operando UV-VIS spectra of the first dehydrogenation cycle as a function of time-on-stream after the first 6 s; and (D) operando Raman spectra of the first dehydrogenation cycle as a function of time-on-stream.

Cr_2O_3[6,9] and gradually decreases with increasing reaction time. Since Cr^{3+} is unlikely to be reduced further at the applied reaction conditions, this disappearance is most probably associated with the formation of coke covering the Cr_2O_3 surface as it limits Raman scattering of the underlying layer.

The coke formation, as observed by both Raman and UV-VIS, is the most likely cause of the decrease in catalyst activity over time. In our experiments we observe a maximum in the catalytic activity after *ca.* 28 min. Looking at the overall catalyst performance with an increasing activity for 28 min and then a slow decrease in activity, this might seem odd considering the typical industrial cycle time of 30 min. However, an industrial feed will contain undiluted alkanes, while in our experiments only a 9% alkane in helium stream was used. Having a pure alkane feed will drastically decrease the timescale in which changes on the catalyst are taking place (oxidation state and coke formation) compared to our observations. Furthermore, a more frequent regeneration is beneficial since the heat liberated by the coke combustion is used for heating up the catalyst for the next endothermal dehydrogenation cycle.

In the oxidation cycles this coke is combusted from the catalyst as can be concluded from the formation of CO_2 in the beginning of the regeneration cycle and from the increase in the catalyst bed temperature of about 10–15 K. During the catalyst regeneration the UV-VIS spectra return completely to the initial state of Fig. 2b in less than 15 s. Both coke combustion and (partial) chromium oxide reoxidation take place simultaneously. This rapid change in the observed catalyst state is in agreement with the fact that the mass spectrometer detects a short carbon dioxide production immediately after the start of the oxidation cycle. Also, the increased catalyst temperature resulting from the heat released by the coke combustion is observed only for a short time. The smaller CO_2 production peak observed by the mass spectrometer at the beginning of the propane dehydrogenation cycle is caused by the reduction of the Cr(VI) to Cr(III) by propane. In industry, this loss of propane is often circumvented by a short catalyst reduction using hydrogen immediately before switching to propane.

Both the UV-VIS and Raman spectra at the end of the regenerative cycle are identical to those at the beginning of the dehydrogenation cycle. This is in good agreement with the activity data, which shows an identical performance of the catalyst in subsequent cycles.

In Fig. 3, all relevant signals measured using the different methods are summarized in a single figure for one complete dehydrogenation–catalyst regeneration cycle. It can be seen that there is a good agreement for the observed coke formation between the UV-VIS and Raman measurements. The UV-VIS signal at 850 nm (indicative of the increasing overall absorbance of the sample due to coke formation) increases similarly fast as the Raman signal at 1584 cm^{-1} and at a similar rate as the Raman band at 542 cm^{-1} disappears due to coke coverage of Cr_2O_3. Furthermore, it can be seen that the decreasing catalyst activity observed using online mass spectrometry activity data agrees well with the spectroscopically observed coke build-up on the catalyst. For the combustion of coke in the catalyst regeneration steps the information obtained using MS, UV-VIS, Raman and reactor temperature is also in excellent agreement.

The fact that it is now possible to use fast and easily applicable operando spectroscopic techniques using fiber optics allows the use of it in the chemical industry as a means of advanced process control in the near future. Being able to monitor directly the amount of coke on the dehydrogenation catalyst allows for the use of process control system, which dynamically adjusts the cycle time for the dehydrogenation–regeneration phases to optimally run the process. Since the Raman measurements provide us with direct information on

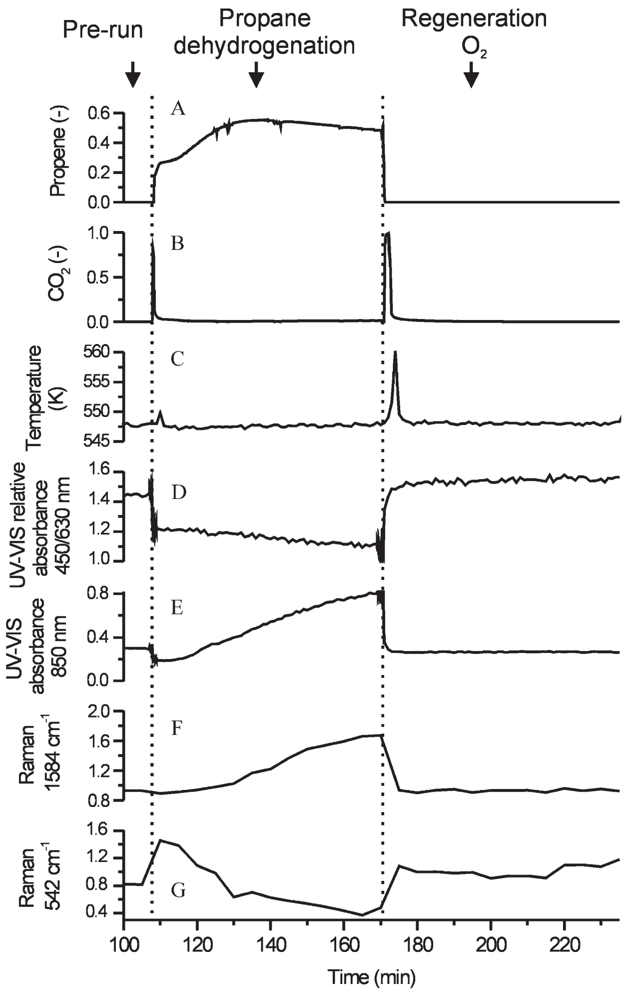

Fig. 3 Overview of the most relevant observed changes in measured signals during a complete dehydrogenation–regeneration cycle of propane over a 13 wt% Cr-on-alumina catalyst. (A) Observed propene fraction in the gas phase; (B) observed carbon dioxide fraction in the gas phase; (C) catalyst bed temperature; (D) ratio between the measured UV-VIS absorbances of the two oxidation states of chromium, Cr(III) at 630 nm and Cr(VI) at 450 nm; (E) UV-VIS absorbance at 850 nm, corresponding to the overall increase in absorbance due to coke formation on the catalyst; (F) Raman signal at 1584 cm^{-1} Raman shift corresponding to the major coke component formed; (G) Raman signal at 542 cm^{-1} corresponding to crystalline Cr_2O_3.

the amount of coke on the catalyst, this technique is most suitable for that. Operando UV-VIS measurements can be used to monitor the long-term deactivation of the catalyst. Puurunen and Weckhuysen[10] have reported that the active chromium oxide species in the dehydrogenation is most likely the chromium oxide, which undergoes a redox cycle in the dehydrogenation–regeneration cycles. Permanent deactivation of the catalyst is linked to a decrease in the amount of this redox type chromium oxide. Therefore, the change in the relative peak intensities of the 450 and 630 nm bands (Fig. 3) on switching from air to propane can be used to determine when the catalyst needs to be replaced.

The capability of operando UV-VIS measurements to determine long-term deactivation was verified by performing a propane dehydrogenation experiment in which the catalyst was purposefully deactivated. First propane was dehydrogenated for 100 hours at the usual reaction temperature of 823 K and a pressure of 1.5 bar(a). In Fig. 4 it can be seen that the UV-VIS spectrum of the catalyst in the oxidated state does not change significantly from the initial state compared to that after 100 hours of dehydrogenation–regeneration cycles. In each of these cycles the average propene yield was 63% confirming the catalyst stability observed with UV-VIS. After this the catalyst deactivation was accelerated by using it for a propane dehydrogenation at 933 K for 4 hours, followed by a normal regeneration at 823 K. In Fig. 4, it can clearly be seen that the absorbance of the active chromia species at 450 nm is significantly less, indicating catalyst deactivation by loss of active chromium sites. Also, the Cr^{3+} band at 630 nm has shifted a bit to the right, which is indicative of chromium moving into the alumina support. The average propene yield of this catalyst in a propane dehydrogenation cycle at 823 K indeed was only 31%. This change in the UV-VIS spectrum clearly shows this operando measurement can provide essential information on the catalyst activity. Since in industrial processes the alkane dehydrogenation is often carried out with some excess catalyst to obtain the equilibrium conversion of the reaction, this loss in catalyst activity cannot be determined immediately from the conversion of the reactor.

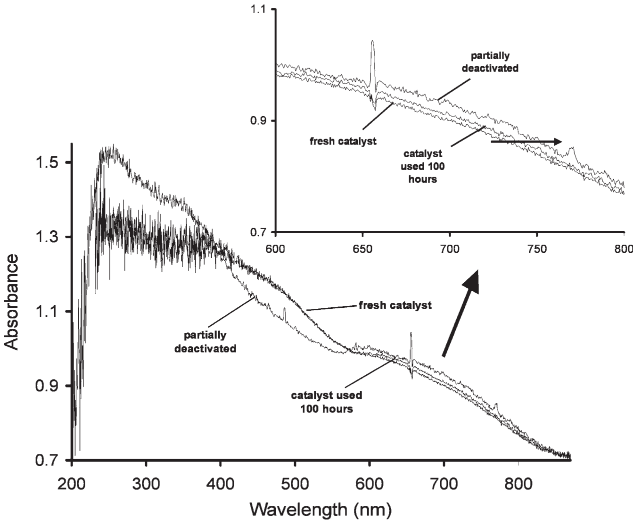

Fig. 4 UV-VIS spectra of 13 wt% Cr-on-alumina catalyst in its regenerated state (1.5 bar(a) 20% O_2 in He, 823 K). Spectra are compared of the fresh catalyst, the catalyst after 100 h of propane dehydrogenation cycles and after a deliberate deactivation procedure.

Conclusions

A novel operando spectroscopic reactor system has been developed. The results presented in this paper demonstrate the value of combining fast time-resolved operando spectroscopic measurements using UV-VIS and Raman with quantitative fast product analysis using mass spectrometry. Different states of the active metal oxide phase can be observed, as well as information on coke formation on the catalyst. It has been shown that the different techniques provide complimentary pieces of information, which are in excellent agreement with each other. We anticipate that this new set-up will become a very useful tool for operando catalyst characterization.

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