

Towards real-time spectroscopic process control for the dehydrogenation of propane over supported chromium oxide catalysts

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Abstract

UV–Vis and Raman spectroscopy are applied under realistic reaction conditions to investigate the changes occurring to an industrial-like supported chromium oxide catalyst during the dehydrogenation of propane. Linking the catalytic activity to the simultaneously collected spectroscopic data has shown that coke is a key parameter to the activity of the catalyst. A small amount of coke improves its activity, most likely by an improved adsorption of propane on the catalyst, but the activity of the catalyst drops when the amount of coke exceeds a certain value. This point is visualized by a sharp increase in the overall absorbance of the sample as can be observed by UV–Vis spectroscopy and this information can be used as a signal for starting a regeneration cycle.

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1. Introduction

In chemical industry, catalytic processes are often controlled using an end-of-pipe approach, i.e. by analyzing the products leaving the reactor and using that as a feedback for controlling the reactor temperature and feed rates. However, using new fiber optic spectroscopic techniques, it is now possible to directly gather information on the active catalyst in the reactor. By using techniques, like UV–Vis and Raman spectroscopy, information can be collected on for example the oxidation state of the catalyst, the formation of coke, the amount of active sites available, and adsorbates (Nijhuis et al., 2003; Weckhuysen, 2003). All this information is gathered in real-time directly at the site where the reaction occurs. Therefore it can be used as the most direct method to control a chemical process. As a result the control system can intervene faster to maintain the desired conversion levels and selectivities in the reactor. In this paper, a

first step towards the development of such a process control system for the dehydrogenation of propane over supported chromium oxide catalysts is being presented. Both UV–Vis and Raman spectroscopy are used simultaneously under realistic reaction conditions to track changes to the catalyst, primarily the coke content.

Over the past decade the demand for propene has increased significantly, outgrowing the quantity that can be supplied by the conventional sources, ethane steam crackers and FCCs (fluidized catalytic crackers) (Tullo, 2003). Consequently, the dehydrogenation of propane is becoming more attractive. One of the propane dehydrogenation processes available is the Catofin process (ABB Lummus) (Bhasin et al., 2001). A Catofin plant usually contains 5 cyclically operated reactors containing a chromium oxide on alumina catalyst. The process is run at a temperature of around 850 K and a subatmospheric pressure of 0.2–0.5 bar. Each reactor undergoes a cycle of typically 12 min of propane dehydrogenation, 3 min purge/evacuation, 12 min of catalyst regeneration using air, 3 min of purge/evacuation optionally followed by a catalyst reduction. The 5 reactors are switched in such a manner that the overall plant operates in a

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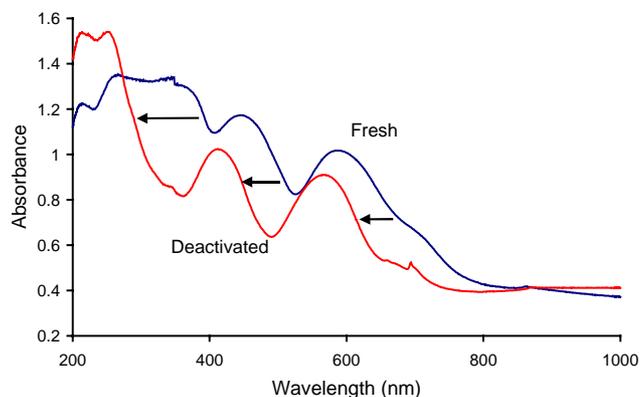


Fig. 1. Comparison between the UV-Vis spectra of a fresh 13 wt% chromium on alumina catalyst and a deactivated catalyst in which the chromium has moved into the alumina lattice by a high-temperature treatment (1473 K, 12 h).

continuous manner, with always 2 reactors dehydrogenating, 2 regenerating and 1 under purge.

During the dehydrogenation cycle the catalyst activity changes because of two main reasons: the formation of coke on the catalyst and the reduction of Cr(VI) to Cr(III). In the regeneration cycle the coke is combusted and the chromium is reoxidized. The catalyst is reheated by the heat of combustion of the coke and usually the combustion of a small amount of natural gas added to the regeneration air, in this way providing the heat required for the endothermic dehydrogenation reaction.

Currently the cycle times for the Catofin process are fixed and based on past experience. During the lifetime of the catalyst (typically 2 years), the reaction temperature is gradually increased to maintain the desired conversion level. Spectroscopy is an excellent manner to track the state of the catalyst during the process. A combination of UV-Vis and Raman spectroscopy to monitor the state of the catalyst during its lifetime would provide a much better insight in the catalyst health and allow making other choices based on this information to keep the process running most efficiently. Adjustments to the cycle times, pressure, temperature and feedrates can be made. UV-Vis spectroscopy is a good method to track the oxidation state of the catalyst and thereby see the chromium go through its redox cycle. It is assumed that the amount of the so called redox-chromium is linked directly to the activity of the catalyst (Puurunen and Weckhuysen, 2002). Chromium oxide is slowly 'lost' during the catalyst life as a result of migration of chromium into the alumina support, which can also be monitored excellently using UV-Vis spectroscopy as this results in the absorption bands shifting to shorter wavelengths (Fig. 1). Especially, if the catalyst reaches a high temperature during coke combustion, this migration occurs more rapidly. Raman spectroscopy is an excellent method to track the different types of coke as they are being deposited on the catalyst (Chua and Stair, 2003). The advantage of using both UV-Vis

and Raman spectroscopy simultaneously is that they provide complimentary information: electronic for UV-Vis and vibrational for Raman. Both techniques can be applied easily in Operando (under realistic reaction conditions), since they both are non-contact techniques and can be done using optical fibers with the measuring electronics a safe distance away from the reactor. In this study it will be shown how information gathered using UV-Vis and Raman spectroscopy can be linked to the observed catalytic activity for the propane dehydrogenation. This is done for a chromium on alumina catalyst similar to that being used commercially, the primary focus being on the role of coke as a function of the bed height. For this purpose, a new operando set-up has been constructed.

2. Experimental

A reactor system has been developed containing a square 5 mm inner diameter quartz reactor tube with optical grade quartz windows. Typically, 1 g of catalyst (total bed height 45 mm) is placed in the reactor as a packed bed supported on quartz wool. The reactor is placed vertically in the center of a 15-cm long tubular oven block; a thermocouple is inserted in the catalyst bed to monitor the catalyst temperature. The metal oven block has on one side a horizontal 8-mm hole directed at the center of the catalyst bed for Raman measurements, on the opposite side is a vertical slit of 50-mm high and 5-mm wide for UV-Vis analysis. The slit is used to focus 4 Ocean Optics Bi-FL600 optical fiber probes (each containing two 600 μm fibers, usable up to 973 K) at the catalyst bed at a vertical spacing of 10 mm to be able to determine spatial profiles over the bed. Of each probe, one fiber is connected to one of the four channels of an Avantes Avaspec-2048-4 spectrometer and another fiber is connected to an Ocean Optics DH-2000 BAL halogen-deuterium light source. A Halon disk was used for white reference measurements for the spectrophotometer. The UV-Vis spectrometers were used with an integration time of 40 ms and 30 spectra were averaged for signal noise reduction. The measuring range of the spectrophotometers is 200–1100 nm.

Raman spectra were obtained using a Kaiser RXN spectrometer equipped with a 532 nm laser (1064 nm frequency doubled Nb-YAG laser). The Raman laser was focused at the catalyst using a 5.5" non-contact objective. The same objective is also collecting the Raman scattered light. Twenty spectra were accumulated with a 2 s exposure time. The laser output power of 70 mW is unlikely to cause any changes to the catalyst, since this energy input is negligible compared to the heat input by the oven. In Fig. 2 the reactor system is shown. The gas leaving the reactor is analyzed by an Interscience Compact GC system equipped with Porabond-Q (analysis of organics) and Molsieve 5A (analysis of permanent gases) columns. This GC system is capable of performing analyses within less than 60 s.

The reactor system has been used to monitor the changes in a catalyst during a number of propane

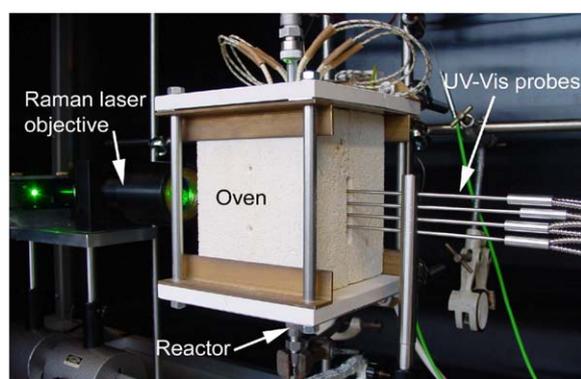
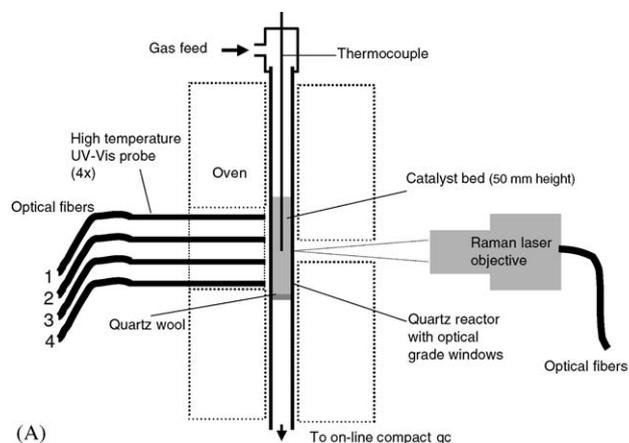


Fig. 2. Schematic presentation (A) and picture (B) of reactor system used for the Operando study of the propane dehydrogenation.

dehydrogenation–regeneration cycles using a 13 wt% Cr-on-alumina catalyst (150 μm particles). In these experiments the reactor was heated at 10 K/min to a catalyst temperature of 823 K in a gas stream of 10 ml/min of O_2 in 40 ml/min of He. After heating, the reactor was operated isothermally in cycles of alternating dehydrogenation for about 50 min with 10 ml/min of propane in 40 ml/min of He and regenerating for about 50 min with 10 ml/min of O_2 in 40 ml/min 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 60 s interval. Raman measurements were performed at 300 s intervals. During the entire experiment the product gas composition was monitored using the GC. The temperature of the catalyst was monitored by a small thermocouple in the middle of the bed. The heat capacity of the reactor/oven assembly and the heating power of the oven was sufficient to keep the whole reactor isothermal within 1 K during the endothermic dehydrogenation reaction, in the regeneration phase, typically short temperature increases of 10–20 K were observed due to the combustion of coke on the catalyst. After the experiments, the coke contents at different vertical positions in the catalyst bed were

determined using thermogravimetric analysis in artificial air using a PerkinElmer Pyris 1 TGA.

3. Results

The experiments with the chromium oxide on alumina catalyst could be performed reproducibly with no observable changes in activity, selectivity, and spectra (UV–Vis and Raman) in the regenerated state after up to 10 consecutive dehydrogenation–regeneration cycles. Therefore, only the behavior of the catalyst during a single cycle will be discussed. The length of this cycle was extended to 4 h to gain more insight in the changes occurring to the catalyst over time. In Fig. 3 the conversion and selectivity during this cycle are given. As can be seen, there is a clear trend in the conversion over time. During the first 2 h it increases and then goes down slowly. The initially high conversion at $t = 0$ is caused by the combustion of some propane as it reduced the catalyst. This also explains the initially lower selectivity. Except for water and carbon dioxide from the propane combustion, the only co-products that are observed in a significant amount (approximately 0.2 vol%) are ethene and methane. The remainder of the 20% non-selectively converted propane therefore must end up largely as coke on the catalyst. This coke formation is confirmed by the fact that the hydrogen produced exceeds the amount of propane by 15%.

Some of the typical UV–Vis and Raman spectra that are obtained during the dehydrogenation cycle are shown in Fig. 4. Using UV–Vis it can be seen that the catalyst is rapidly reduced at the start of the dehydrogenation cycle (decrease in Cr(VI) band at 460 nm and increase in Cr(III) band at 630 nm), after which the spectrum slowly becomes less distinct as a result of darkening of the sample by coke

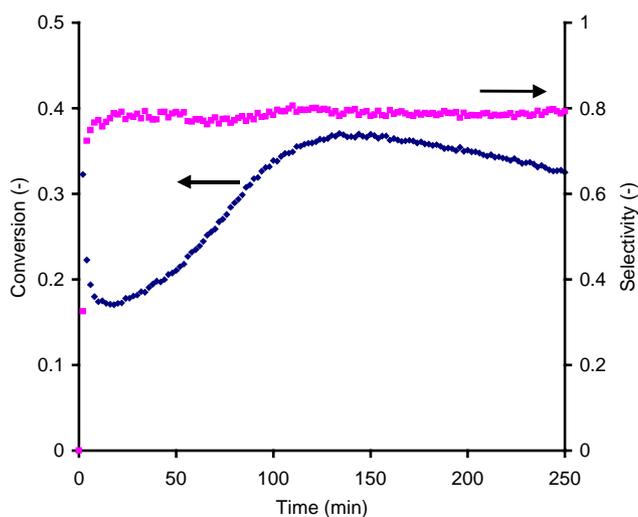


Fig. 3. Selectivity and conversion during a single dehydrogenation cycle (823 K, 20 kPa propane).

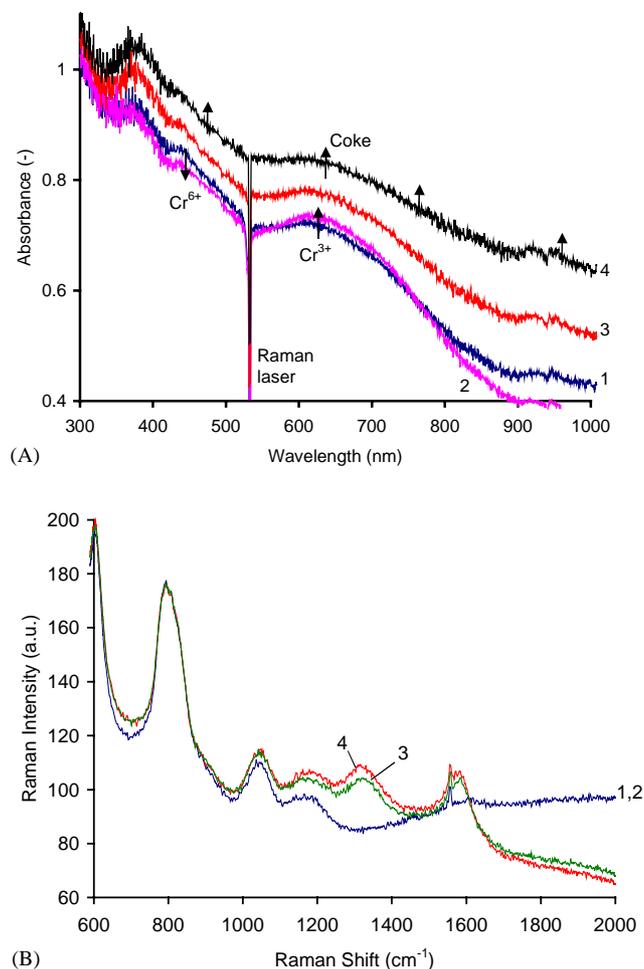


Fig. 4. UV-Vis (A) and Raman (B) spectra of chromium oxide catalyst during a dehydrogenation cycle. (1) immediately before and (2) immediately after switch to dehydrogenation, (3) and (4) during dehydrogenation after 2 and 4 h, respectively.

deposition. The Raman spectra show no changes to the catalyst as a result of the reduction during dehydrogenation, but do show bands characteristic of coke deposits appearing in the range $1200\text{--}1700\text{ cm}^{-1}$.

After cooling down the reactor in helium at the end of the dehydrogenation cycle, the reactor was removed from the oven. A clear coke gradient could be observed visually over the reactor. The top of the catalyst bed was light green colored, slowly changing into dark gray towards the bottom of the bed. In Fig. 5 Raman spectra are given recorded at the top, middle and bottom of the reactor, again showing that the top of the catalyst bed contains significantly less coke than the lower part. Thermogravimetric analysis (coke combustion in air) showed a coke content on the catalyst increasing from 0.1 wt% at the top of the catalyst bed to 1.0 wt% at the bottom of the bed.

4. Discussion

Comparison of the obtained conversion (30%) and selectivity (80%) values to those reported in industry for this

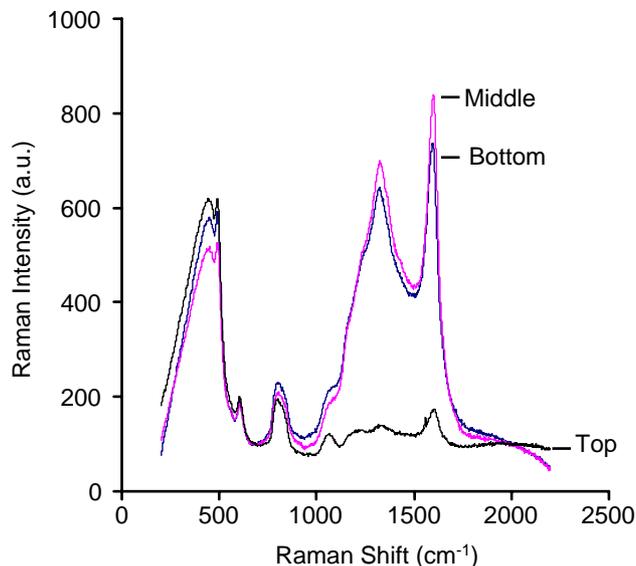


Fig. 5. Raman spectra recorded ex situ on 3 different heights of the catalyst bed after the end of a dehydrogenation cycle and cooling in helium to room temperature.

system (48–65% conversion, 82–87% selectivity at 860–920 K, 33–50 kPa, $0.4\text{--}2\text{ h}^{-1}$ LHSV, [Buonomo et al., 1997](#)) shows that the conversion obtained here is significantly different. This can be explained by the somewhat lower temperature and lower propane partial pressure used in this study (feed rate is similar). The most remarkable in the behavior of the catalyst is that the activity passes through a maximum. Since the catalyst performance is perfectly reproducible when consecutive cycles are measured, both the increase and decrease in activity must be caused by reversible/regenerable changes to the catalyst, i.e. the result of changes to either the oxidation state of the catalyst or the coverage of coke on the catalyst. The change in oxidation state, can be monitored excellently using UV-Vis. It is seen, however, that the catalyst reduction takes place instantaneously as propane is fed to the reactor. Within 10 s the intensity of the Cr(VI) charge transfer band at 450 nm has decreased and the 630 nm d–d transition band of Cr(III) has increased in intensity. After this short time no more changes in intensity of these bands can be observed. Furthermore, [De Rossi et al. \(1993\)](#) examined different reduction treatments and showed these had no effect on the catalytic performance.

For coke on the catalyst on the other hand, changes to both the type and quantity of coke are spectroscopically visible during the dehydrogenation cycle. This is visible in Fig. 6, showing the trends with respect to coke on the catalyst over time. Fig. 6A shows the UV-Vis absorbance at 1000 nm, where no specific absorption bands are present. The absorbance at this wavelength was used to characterize the darkening of the sample. For Raman the intensities of the bands of the two main coke species at $1577\text{ and }1320\text{ cm}^{-1}$ are shown in Fig. 6B.

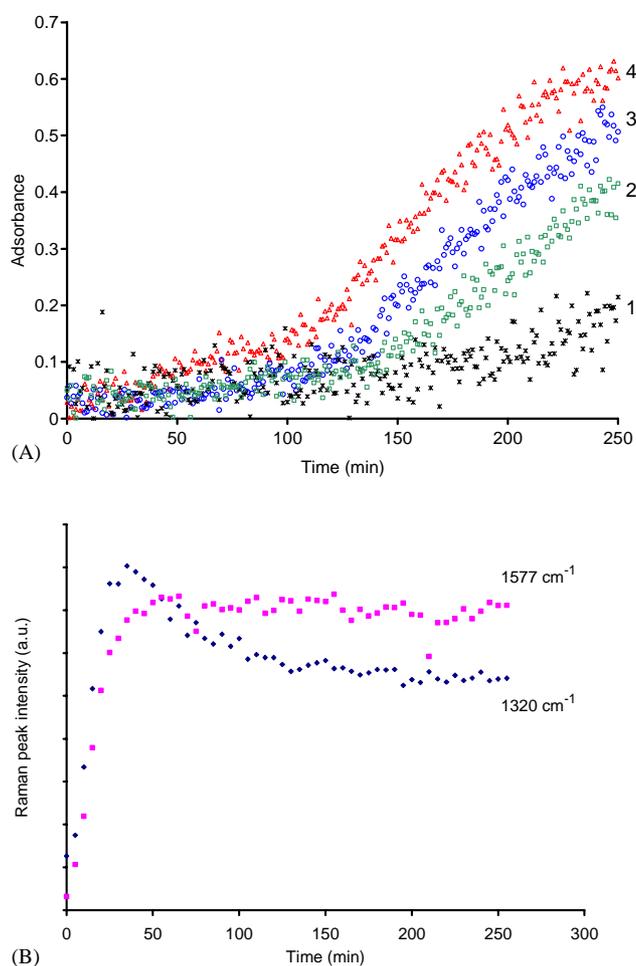


Fig. 6. Spectroscopic trends recorded during a dehydrogenation cycle. (A) UV-Vis trends of sample absorbance at 1000 nm over time showing the coke formation at different bed heights in the reactor (1 = top, 4 = bottom). (B) Raman intensities of bands of two predominant coke species.

The different coke formation rates at the different bed heights in Fig. 6A clearly shows that the coke on the catalyst is primarily produced at the end of the reactor bed, indicating that coke is formed primarily out of a secondary reaction from the product propene, agreeing with the visual observation after removing the reactor from the setup at the end of the experiment. This observation is in contradiction to the modeling work presented by Jackson and Stitt (2002), who calculated that for an isothermal propane dehydrogenation reactor the largest amount of coke deposits are present at the inlet. To verify our assumption of coke formation primarily out of propene, a separate experiment was carried out, in which a flow of propene in helium was fed over the reactor at the same conditions. In this case the four UV-Vis probes all showed a rapid increase in overall adsorbance of the catalyst in 10 min time.

When the coke profiles over time measured between Raman and UV-Vis are compared, it can be seen that they do

not show the same trend. While after 2 h the UV-Vis measurements indicate an increase in the rate at which coke is being built up on the catalyst, the Raman measurements show one coke band (1577 cm^{-1}) remaining at the same level, while the other main coke species (1320 cm^{-1}) decreases in intensity. This might seem contradicting. However, a complexing factor is that as the sample gets darker as a result of coke deposition, self-absorption increases, resulting in a reduction of Raman scattered light at the detector. Since the catalyst itself has no observable Raman bands (the bands at 800 , 1020 , and 1150 cm^{-1} are from the quartz reactor), it is not possible to scale the coke bands to correct for this effect and Raman should mostly be used to identify which types of coke are present. The assumption that darkening of the sample would be the cause of less intense coke bands was confirmed by the experiment in which propene was fed over the catalyst. Both UV-Vis and a carbon mass-balance showed a continuous coke formation, while the intensity of the coke bands observed by Raman decreases after 5 min. It should therefore be concluded that it is best to use the darkness of the sample as measured by UV-Vis spectroscopy as a means to quantify the amount of coke, while relative peak intensities measured using Raman provide only information on the type of coke present.

Based on Raman characteristics of different coke species reported by Chua and Stair (2003) assignments for the two most dominant types of coke observed can be made. Since the position and shape of bands shift as a function of temperature, it is most convenient to use the Raman spectra shown in Fig. 5 for identifying the different classes of coke species. The spectrum in this figure can roughly be described two broad bands at 1600 and 1320 cm^{-1} . These bands are generally assigned to the sum vibration of ring stretching of polyaromatic species. According to Chua and Stair for larger sheet like polyaromatics the intensity of the band near 1600 cm^{-1} is more intense than the intensity of the bands in the 1300 – 1450 region, when comparing these molecules to smaller chain like polyaromatics. In Fig. 6B it can be seen that initially the band at 1320 cm^{-1} is more intense. As the experiment proceeds, this band becomes less intense compared to the band at 1577 cm^{-1} . This relative shift is consistent with the gradual growth of a graphitic-type coke layer on the catalyst over time. Lespade et al. (1984) report a similar decrease in the relative ratio of Raman intensities of the bands at $1350/1581\text{ cm}^{-1}$ as the coke becomes increasingly graphitic in nature.

Combining the information from Figs. 3 and 6, one can see that during the first 2 h of dehydrogenation there is a slow formation of coke on the catalyst, while at the same time the catalytic activity increases. Considering that the catalyst was already reduced in a very short time and that the catalyst is not being reduced further than to Cr(III), the most probable explanation for the increase in activity is that coke in some way is beneficial for the catalytic activity. This is supported by the observation that for other low-loaded chromia and vanadia catalysts on different supports, an

increasing catalytic activity is only observed for catalysts producing coke (Tinnemans et al., 2004). The most likely explanation is that the coke layer facilitates the adsorption of propane on the catalyst. Propane adsorbs on the coke and migrates over the coke surface to the active chromium sites. In a paper on the effect of coke on catalysts by Menon (1990) such an adsorption effect is mentioned as one of the manners in which coke can be beneficial for the performance of a catalyst. For the ethylbenzene dehydrogenation it is actually seen as part of the active site, a possibility that cannot be completely ruled out for this case, but is less likely since also non-coking catalysts can have a similarly high activity.

After 2 h of reaction time the visible amount of coke on the catalyst increases, while at the same time also the conversion of the catalyst begins to drop. It should be noted that although after 2 h in Fig. 6A the rate at which the absorbance of the sample increases becomes higher, this does not mean that the actual coke formation rate also increases. Since the selectivity of the dehydrogenation reaction does not change, this implies that neither more propane nor more propene is converted into coke. The increase in absorbance can be best explained by the coke patches on the catalyst surface increasing in size and starting to connect and cover the entire surface of the catalyst, effectively blocking the scattering and reflection of light. At the same time as it starts covering the chromium oxide, this becomes less accessible and the activity of the catalysts drops. Since this front of complete coke coverage of the catalyst starts at the exit of the reactor and then moves forward only slowly towards the entrance, the overall conversion only drops slowly.

The possibility to track the coke content at the catalyst in a chemical reactor is highly attractive for the chemical industry. Using cheap and robust spectroscopic probes linked via optical fibers to a spectrometer, one can gain information on how changes or disturbances to a process affect the amount of coke produced. This is a more direct approach than by monitoring the reactor performance. Especially, in the case of the propane dehydrogenation, in which a small amount of coke is beneficial and only larger quantities are deactivating, this can help to make process control decisions to keep the catalyst in its most active state. Having knowledge on coke quantities on the catalyst can help to adjust cycle times for a process like Catofin. Cycle times can be extended if one observes that a larger amount of coke will utilize the catalyst longer in a more active state, or cycle times can be reduced if the amount of coke accumulating on the catalyst will be resulting in too much heat liberated during the regeneration phase.

5. Conclusions

Operando spectroscopic analysis is an effective method to study the dynamics of a chromium oxide catalyst in the dehydrogenation of propane. UV–Vis shows the oxidation

state of the catalyst and Raman and UV–Vis together provide information on the coke content on the catalyst. The coke profiles prove that coke is formed out of propene rather than propane. Raman shows that the coke is polyaromatic, becoming more graphitic over time. Coke is a crucial parameter for the activity of the catalyst. A small amount of coke increases the activity, while it becomes a deactivating agent as the coke content increases. Using UV–Vis measurements to determine the coke content by determining its ‘darkness’ shows that there is a link between the moment the catalyst loses activity and the moment the catalyst becomes fully covered by coke. These affordable and robust UV–Vis probes can give valuable insight in industrial processes where coke formation is an important parameter in the process.

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