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# Combining *operando* techniques in one spectroscopic-reaction cell: New opportunities for elucidating the active site and related reaction mechanism in catalysis

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## Abstract

*Operando* spectroscopic techniques are suitable for studying homogeneous and heterogeneous catalysts in real-time under working conditions at, e.g. elevated pressures and temperatures in the gas and liquid phase. These techniques are nowadays frequently used to obtain mechanistic insight into the active site and the related reaction mechanism. Over the past several years, new instrumental developments combining two or three *operando* spectroscopic techniques in one spectroscopic-reaction cell have emerged, giving ample opportunities for reaching a more detailed understanding of many relevant catalytic systems. In this paper, an overview of the different *operando* set-ups currently available for obtaining combined spectroscopic and catalytic information on catalytic systems is presented. The crucial advantage of such multiple couplings is the fact that in principle spectroscopic and catalytic data are obtained from the same catalyst system for which identical reaction conditions are guaranteed. Besides delivering complementary spectroscopic information on the catalyst system, it will be shown that there are additional advantages in combining spectroscopic techniques in one reaction set-up. This point will be illustrated with three examples. The first example focuses on the development of real-time quantitative *operando* Raman spectroscopy of supported metal oxide catalysts, making use of *operando* UV–vis spectroscopy. The second example deals with the problems of synchrotron radiation effects when measuring *operando* EXAFS spectra of homogeneous copper catalysts. The third example discusses the reduction process of supported metal oxide catalysts and the possible heating problems associated with the use of *operando* Raman spectroscopy.

*Keywords:* Operando technique; Catalyst system; Metal oxide; Spectroscopy; XAFS; Raman; UV–vis

## 1. Making "motion pictures" of catalytic systems

Ideally catalyst scientists would like to take "motion pictures" [1] inside a catalytic reactor when it is operating, giving him/her detailed insight in the working principles of the catalyst under study. On this basis, scientists can improve the existing catalyst formulations or design completely new ones, which are more effective and selective. Such rational catalyst design approach is in most cases still a dream since the experimental tools currently available for making "motion pictures" inside a catalytic reactor are very rudimentary [2,3]. In this review paper, we will start with some background on the motivation to perform real-time *operando* spectroscopy of a working catalyst. The paper continues with an overview of the different multiple technique *operando* set-ups currently available for obtaining combined spectroscopic and catalytic information on both homogeneous and heterogeneous catalytic systems. Also some difficulties, which can be encountered during the development of these set-ups, will be mentioned. In a third part, it will be shown that there are, besides obtaining complementary information on the same catalyst system under identical reaction conditions, additional advantages for combining spectroscopic techniques. This point will be illustrated with three examples. The first focuses on the development of real-time quantitative *operando* Raman spectroscopy based on a correction factor, which can be on-line obtained with *operando*

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UV–vis spectroscopy. The second example deals with the problems of synchrotron radiation effects when measuring *operando* EXAFS spectra of catalytic systems. UV–vis spectroscopy can be used to evaluate such irradiation effects. The third example involves the heating effects using a Raman laser, underlining the potential problems of accurate temperature determinations near the catalyst bed probed with *operando* spectroscopy. The paper will end with an outlook on the different opportunities for this exciting field of research.

Taking or making better ‘‘motion pictures’’ of an active catalyst means for a spectroscopist to be able to measure in a *time-resolved* and *spatially resolved* manner spectra of a *working* catalyst [3–5]. The three words in italics have to be better defined:

(1) Measuring *time-resolved* spectra implies that real-time spectroscopic techniques should be employed. This would allow monitoring in time the formation and disappearance of specific species inside the reactor vessel. Ideally, we would like to measure at timescales corresponding to the breaking and making of chemical bonds in molecules at the active site, but most of the *operando* techniques nowadays applied are only working in the second or subsecond regime. In other words, only differences in relative population of the active site can be assessed. Therefore, the time-resolved approach is ideally performed in combination with pulses or changing the gas or liquid feed concentration in an attempt to change the population of the active catalyst surface. While this time-resolved methodology can be performed in an attempt to change the population of the active catalyst surface, a recent investigation brought evidence that in the case of a Pt/$CeO_2$ catalyst for the reverse water–gas-shift reaction the reactivity of surface species and therefore the reaction mechanism can dramatically depend on the experimental procedure used during the investigation of the reaction [6,7].

(2) Measuring *spatially resolved* spectra means the combination of spectroscopy and microscopy at different length scales. First of all, on a macro-, meso- and microscopic scale it is important to have insight in the different species present in the reactor, e.g. in heterogeneous catalysis the catalyst extrudate and the pore structure of the support oxide. Secondly, we would like to have detailed insight in the phenomena, taking place at the nanometer scale; i.e., can we observe differences between different types of active sites and between active sites and spectator species.

(3) The word *working* implies that the experimental set-up in which spectra are measured can be regarded as a true catalytic reactor. Therefore, the spectra should be recorded at realistic temperatures and pressures at a conversion level comparable to industrial practice, preferably the catalytic performance is determined simultaneously by using e.g. on-line mass spectrometry or gas chromatography in the case of gas-phase reactions. Ideally, the spectrometer device is inserted in the normally used reactor vessel. In other words, the spectrometer is brought inside the catalytic device, unaltering the processing taking place in the reactor.

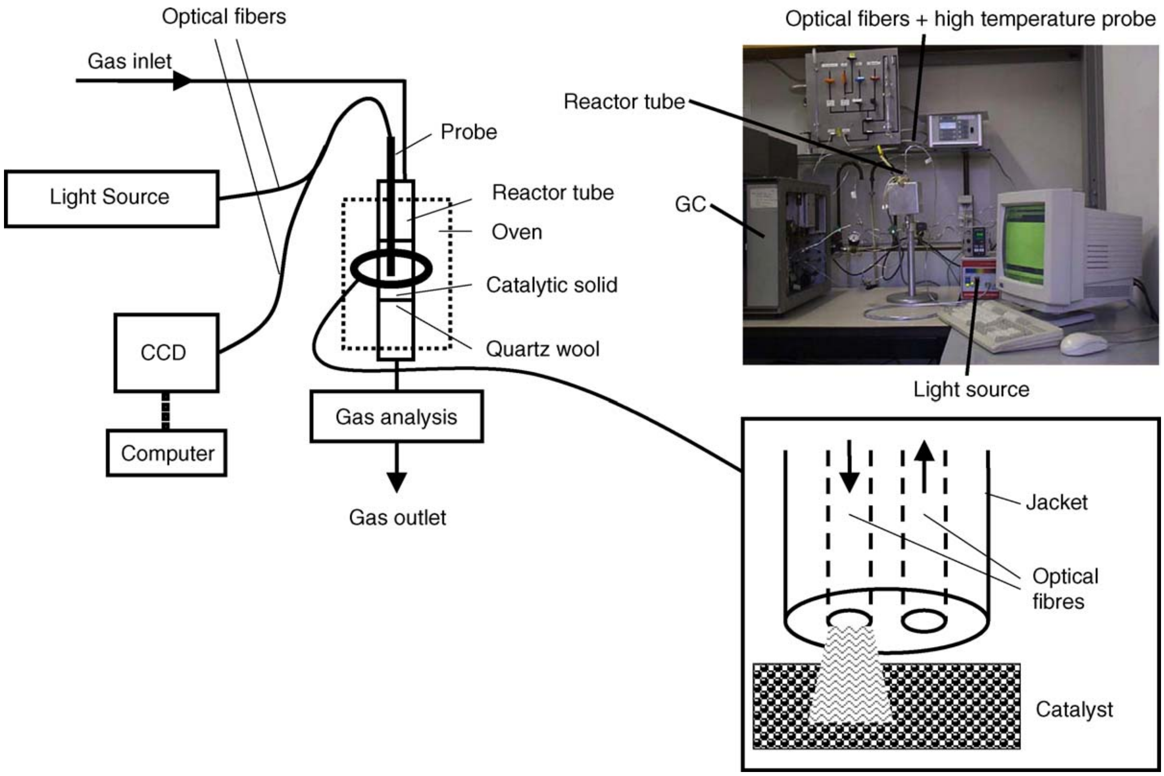

Fig. 1. Scheme and picture of an *operando* UV–vis set-up for measuring supported metal oxide catalysts operating in gas-phase reactions at elevated temperatures and ambient pressures.

In the last decade many *operando* set-ups have been built in various laboratories combining the application of a spectroscopic technique with on-line activity measurements. Fig. 1 shows as an example a set-up, which allows measuring *motion* UV–vis spectra of a catalytic solid performing a gas-phase catalytic reaction in a reactor. More specifically, this set-up has been used in our group to study the dehydrogenation of light alkanes over supported metal oxide catalysts as well as the decomposition of $NO_x$ over Cu-ZSM-5 zeolites [8–12]. Another example, shown in Fig. 2, is an *operando* ESR cell developed in the group of Brückner (Berlin, Germany) [13–18]. It has been used to study for instance the behavior of vanadium phosphate catalysts during the oxidation of *n*-butane, the dehydrogenation of alkanes over supported chromium oxide catalysts and the selective catalytic reduction of $NO_x$ over supported manganese oxide catalysts. Besides from a technical viewpoint these set-ups are not ideal. They suffer in that they only allow for the measurement of one spectroscopic technique. More specifically, the *operando* UV–vis set-up only allows to measure the d–d transitions and charge transfer transitions of supported transition metal oxides and the formation of organic molecules via their $n-\pi^*$ or $\pi-\pi^*$ transitions under working conditions, whereas the *operando* ESR set-up only probes paramagnetic transition metal ions or organic radicals present in the working catalytic solid.

The goal of this paper is not to give an exhaustive overview of the literature on the different spectroscopic techniques used in *single-mode* operation to study the working of catalysts. We refer the reader to many reviews and textbooks devoted to this important topic in the field of catalysis [19–30], as well as to the other papers included in this special issue on *operando* spectroscopy. It is fair to say that most studies make use of vibrational spectroscopy (more in particularly IR) and X-ray techniques [3].

It would be more advantageous to look on catalytic systems from different perspectives by making use of multiple characterization techniques [31]. One can compare a catalytic problem with a puzzle (Fig. 3) and each characterization technique allows obtaining additional information about the catalytic system positioned in the reactor tube. However, one has to keep in mind that adding additional spectroscopic techniques is most valuable if they provide complementary information. In regard to the puzzle of Fig. 3, identical pieces would not display the whole picture of the catalytic problem and would not enable us to discriminate between active species (cyclists) and spectator species (public gathered together to see the final rush of the cyclists). Bringing all the information together leads to a more detailed understanding of the catalytic system and therefore a better assessment on what is happening in the reactor. With these considerations taken into mind, it is fair to say that in the last years many attempts have been made by several research groups to combine multiple spectroscopic techniques into one *operando* set-up. The next section will give an overview of the available *operando* set-ups equipped with two or three spectroscopic techniques for catalyst characterization, which are nowadays available for catalyst scientists.

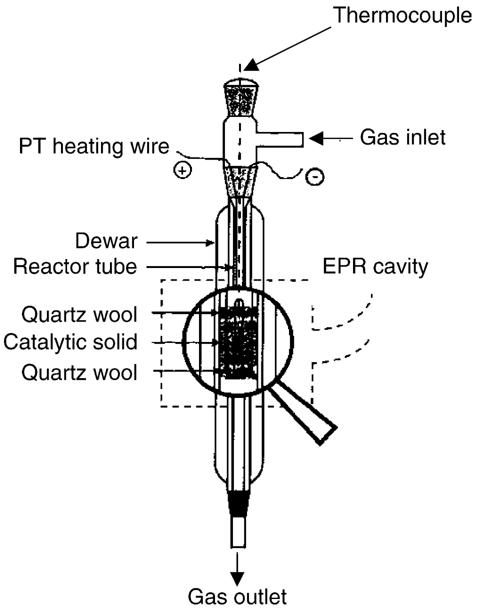

Fig. 2. Scheme of an *operando* EPR set-up for measuring supported metal oxide catalysts operating in gas-phase reactions at elevated temperatures and ambient pressures.

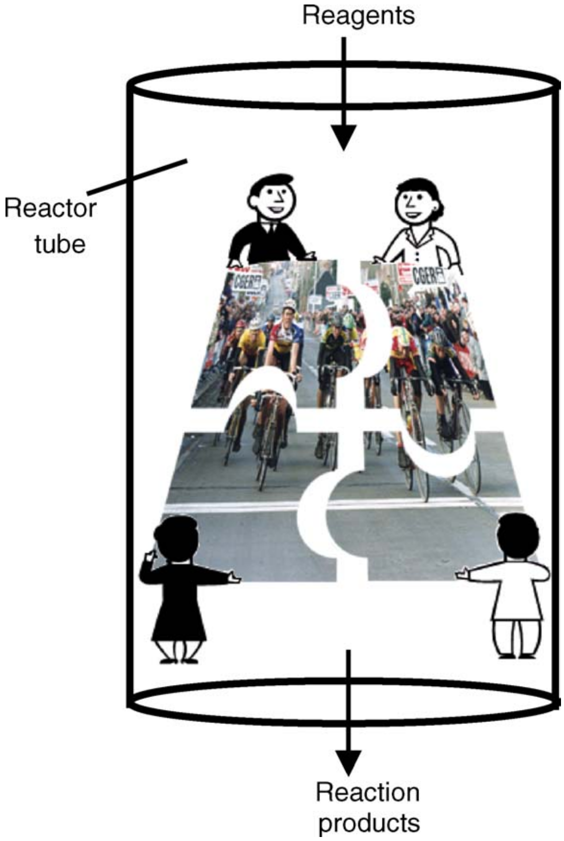

Fig. 3. Catalytic puzzle, in which active species (cyclists) should be discriminated from spectator species (public audience gathered together to see the final jump of the cyclists) in a catalytic solid placed in a reactor tube.

## 2. Overview of *operando* set-ups making use of multiple spectroscopic characterization techniques

Table 1 gives an overview of the currently available *operando* set-ups equipped with two or three spectroscopic techniques for catalyst characterization [32–49], together with the application domain (homogeneous and heterogeneous catalysis), the time resolution (in the second or sub-second regime) of the different techniques employed as well as the obtained information for each technique. To the best of our knowledge, the first techniques combined in one set-up and reported in the open literature were X-ray diffraction (XRD) and X-ray absorption spectroscopy (EXAFS). Such set-ups have been developed independently of each other by the groups of Thomas (Cambridge, UK) and Topsoe (Lyngby, Denmark) in the 1990s. The nice feature of this combination is the complementarity of the techniques combined; i.e., XRD provides long-range ordering information of the catalytic solid under investigation, whereas EXAFS is sensitive to the short-range ordering of the materials under study. Besides catalytic reactions, the set-up is also suitable to study crystallization processes of e.g. zeolite materials. Unfortunately, the time resolution was still relatively low and in the order of 30 seconds to minutes, although recent developments

Table 1
Existing combinations of characterization techniques for studying homogeneous and heterogeneous catalysts at work, together with the application domain, some technical details on time resolution and the obtained physicochemical information on the reaction system under investigation

| Techniques combined | Application domain | Time resolution (s) | Information to be obtained | References |
|---|---|---|---|---|
| XRD | Heterogeneous catalysis | XRD: 30 | XRD: long-range structural order | [32–35] |
| XAFS | | XAFS: 10–30 | XAFS: short-range structural order | |
| EPR | Heterogeneous catalysis | EPR: 60–300 | EPR: paramagnetic transition metal ions | [36,37] |
| UV–vis | | UV–vis: 0.01–1 | UV–vis: electronic d–d and charge transfer transitions of transition metal ions | |
| Raman | Heterogeneous catalysis | Raman: 2–120 | Raman: vibrational spectra of metal oxides and organic deposits, such as coke | [38,39] |
| UV–vis | | UV–vis: 0.01–1 | UV–vis: electronic d–d and charge transfer transitions of transition metal oxides | |
| ED-XAFS | Homogeneous catalysis | XAFS: 0.01–1 | XAFS: coordination environment and oxidation state of metals and metal ions | [40,41] |
| UV–vis | | UV–vis: 0.0008 | UV–vis: electronic d–d and charge transfer transitions of transition metal oxides | |
| Raman | Heterogeneous catalysis | Raman: 2–120 | Raman: vibrational spectra of metal oxides | [42] |
| FT-IR | | FT-IR: 0.01–1 | FT-IR: vibrational spectra of adsorbed species, such as NO | |
| NMR | Heterogeneous catalysis | NMR: 7200 | NMR: identification of organic molecules formed via chemical shift values | [43] |
| UV–vis | | UV–vis: 0.01–1 | UV–vis: electronic transitions ($n-\pi^*$ and $\pi-\pi^*$) of organic molecules | |
| ED-XAFS | Heterogeneous catalysis | XAFS: 6 | XAFS: coordination environment and oxidation state of metals and metal ions | [44] |
| FT-IR | | FT-IR: 0.01–1 | FT-IR: vibrational spectra of adsorbed species, such as CO and NO | |
| FT-IR | Homogeneous and heterogeneous catalysis | FT-IR: 0.01–1 | FT-IR: vibrational spectra of reaction mixtures and adsorbed molecules | [45,46] |
| Phase behavior monitoring | | | Video monitoring of phase behavior | |
| FT-IR | Heterogeneous catalysis | FT-IR: 0.01–1 | FT-IR: vibrational spectra of reaction mixtures and adsorbed molecules | [47] |
| UV–vis | | UV–vis: 0.01–1 | UV–vis: electronic transitions of the catalyst material | |
| EPR | Heterogeneous catalysis | EPR: 60–300 | EPR: paramagnetic transition metal ions | [48] |
| UV–vis | | UV–vis: 0.01–1 | UV–vis: electronic d–d and charge transfer transitions of transition metal ions | |
| Raman | | Raman: 2–120 | Raman: vibrational spectra of metal oxides and organic deposits, such as coke | |
| UV–vis | Heterogeneous catalysis | UV–vis: 0.05–1 | UV–vis: electronic d–d and charge transfer transitions of transition metal oxides | [49] |
| Raman | | Raman: 0.05–1 | Raman: vibrational spectra of metal oxides and organic deposits, such as coke | |
| ED-XAFS | | XAFS: 0.003–1 | XAFS: coordination environment and oxidation state of metals and metal ions | |

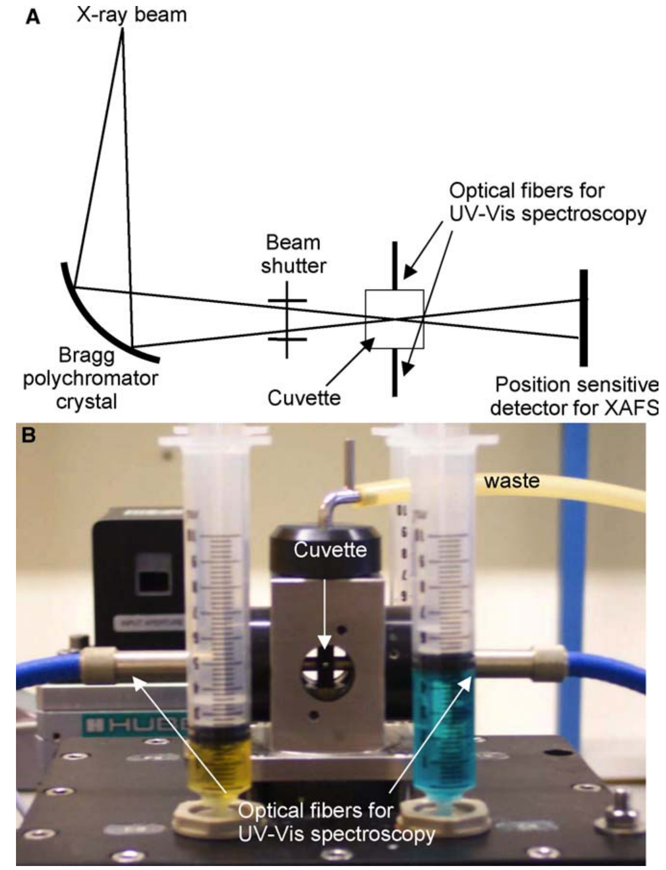

Fig. 4. Scheme and picture of an *operando* ED-XAFS/UV–vis set-up for measuring homogeneous catalysts, including a stopped-flow cell system.

in X-ray detection systems may lead to substantial improvements in time resolution.

Since this first coupling of techniques many other set-ups have been developed. Most combinations involve the use of vibrational (IR as well as Raman) and electronic (UV–vis) spectroscopies. Certainly, from a technical point of view these are the most simple to make, whereas in the case of magnetic resonance techniques (NMR and EPR) more technical hurdles have to be taken to make the combined *operando* set-up working. Two examples of a combination of two *operando* spectroscopies are shown in Figs. 4 and 5. Both set-ups have been developed in our group. The first system combines energy dispersive X-ray absorption spectroscopy (ED-XAFS) with time-resolved UV–vis spectroscopy (Fig. 4) and has been developed for homogeneous catalysts in Utrecht by Tromp [41]. It can be seen as a further development of the ED-XAFS equipment developed by the Evans group (Southampton, UK) for studying homogeneous catalytic systems [50]. The set-up allows measuring both type of spectra in the millisecond regime and is combined with a stopped-flow device. The second combination, shown in Fig. 5, combines time-resolved UV–vis and Raman spectroscopy to study heterogeneous catalysts in gas phase reactions, and is equipped with both online gas chromatography and mass spectrometry for product analysis. The time resolution of the two spectroscopic techniques is dependent on the catalytic system under investigation, but is close to the second regime for Raman spectroscopy and in the subsecond regime for UV–vis spectroscopy. Some applications of both set-ups will be discussed in more detail in Section 3.

Very recently, two experimental set-ups have been built making use of three *operando* spectroscopic techniques simultaneously applied to the same sample under identical reaction conditions. An *operando* UV–vis, Raman and EPR set-up has been constructed by the group of Brückner (Berlin, Germany), which allows studying supported vanadium oxide catalysts during oxidative dehydrogenation of propane [48]. Another *operando* set-up combines UV–vis, Raman and ED-XAFS in one spectroscopic-reaction cell. This design has been developed in our group [49]. A scheme, together with some illustrative pictures, of this set-up is given in Fig. 6. Beale et al. has studied with this three-in-one *operando* set-up the dehydrogenation of propane over 13 wt.% $Mo/Al_2O_3$ and

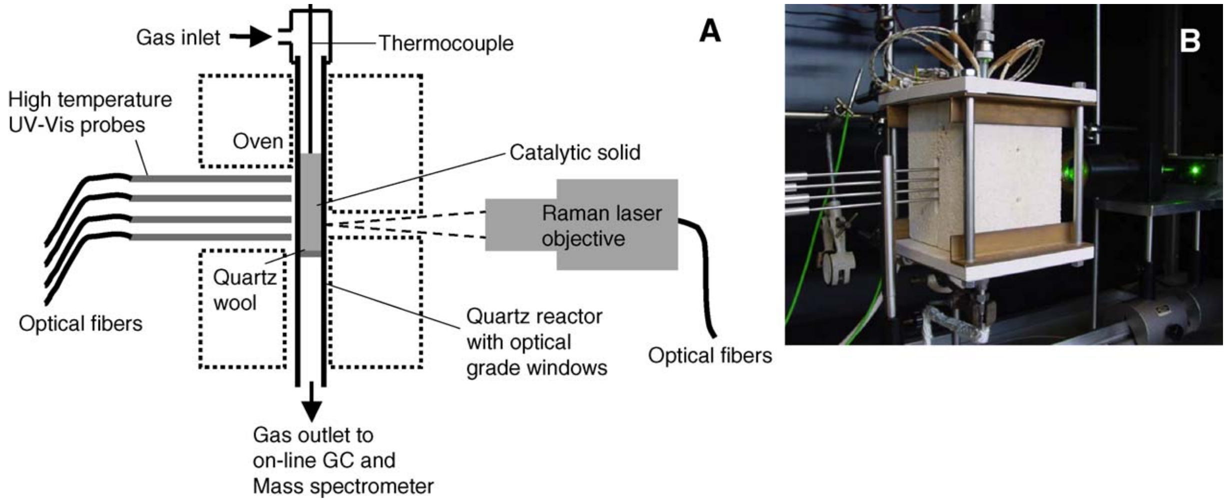

Fig. 5. Scheme and picture of an *operando* UV–vis/Raman set-up for measuring supported metal oxide catalysts operating in gas-phase reactions at elevated temperatures and ambient pressures.

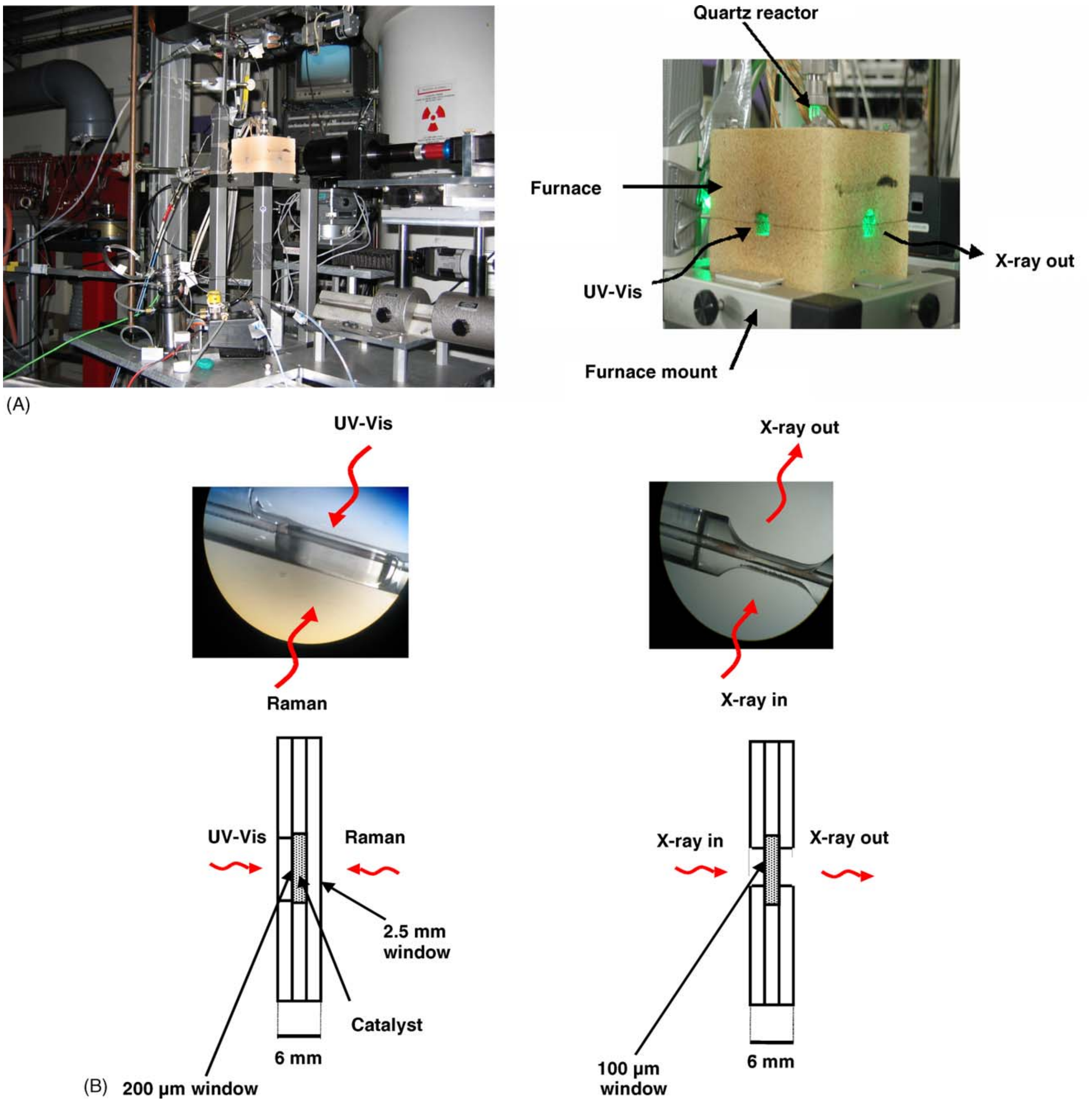

Fig. 6. (A) Picture and general scheme of an *operando* UV–vis/Raman/ED-XAFS set-up for measuring supported metal oxide catalysts operating in gas-phase reactions at elevated temperatures and ambient pressures. (B) Detailed outline of the capillary reaction-spectroscopy cell for simultaneously measuring Raman/UV–vis (reflectance mode) and energy dispersive XAFS (transition mode), together with illustrative pictures.

Mo/$SiO_2$ catalysts. A representative set of time-resolved ED-XAFS, UV–vis and Raman spectra of a typical dehydrogenation cycle is shown in Fig. 7. We concluded on the basis of a detailed comparison between the two different catalysts that (1) $Mo^{4+}$ is present under steady-state conditions in the presence of propane; (2) coke formation is responsible for catalyst deactivation, as well as in the case of Mo/$SiO_2$, the irreversible formation of $MoO_3$ crystals; (3) Mo/$Al_2O_3$ catalysts are more active and stable than Mo/$SiO_2$ catalysts during successive propane dehydrogenation–regeneration cycles.

Besides the *operando* set-ups described in Table 1 we are aware of several other combinations currently under construction. More specifically, it concerns the development of the following combinations: EPR-EXAFS (Che group, Paris, France) and EXAFS-SAXS/WAXS (Bras group, Grenoble, France). One would anticipate at first sight that making combinations of two or three *operando* spectroscopic techniques is rather straightforward since all techniques make use of electromagnetic radiation. As a consequence, in principle you could couple all the techniques mentioned in Table 1 in one catalytic reactor, creating a kind of *operando* dream machine. Unfortunately, this instrument will simply not work because each spectroscopic technique has its own sensitivity towards a specific catalytic system or towards the

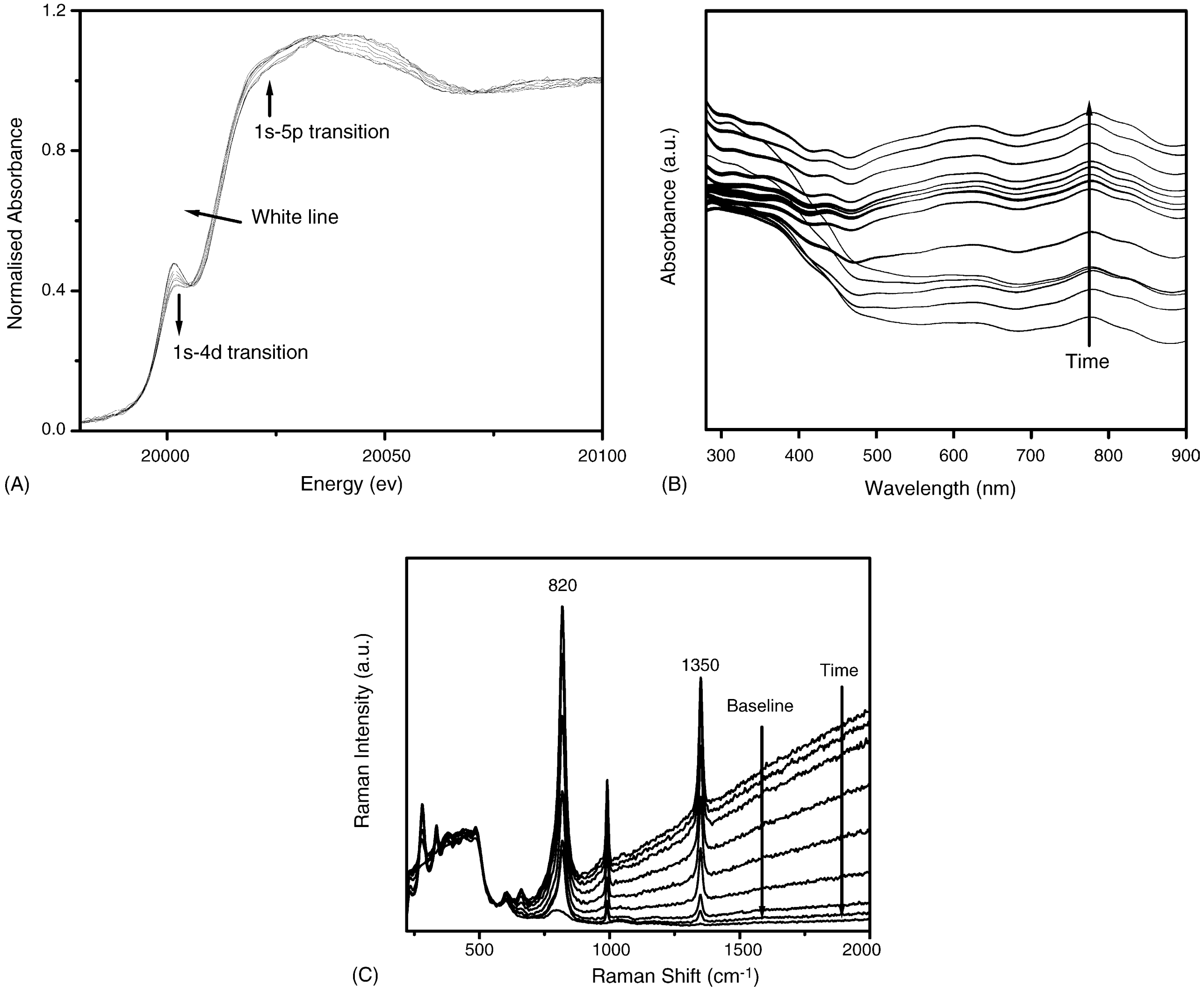

Fig. 7. Time-resolved (A) ED-XAFS, (B) UV–vis, and (C) Raman spectra of a working 13 wt.% Mo/$SiO_2$ catalyst during propane dehydrogenation.

reactants or solvents used. More specifically, we found that when combining e.g. *operando* Raman, UV–vis and ATR-IR in one experimental set-up for studying oxidation reactions with a homogeneous Co (salen) catalyst in aqueous solutions (Fig. 8), the concentrations of the Co solutions should be adapted for each particular technique, making the set-up impractical to work with [51]. In other words, one should first consider the catalytic application, the characteristics of the catalytic material as well as the reaction medium before starting to assemble the most appropriate *operando* techniques in one reactor system. One could even argue that a reaction mechanism proposed based on experimental data obtained for a catalytic system at low concentrations is different from that obtained at high concentrations. Another often given criticism to the coupling approach is that one could simply do the experiments in different *operando* set-ups and later on compare the results obtained. Although in principle this argument is correct, people should be aware that different *operando* cells could give different catalytic performances, making it not always trivial to compare the results obtained. Actually, there should be an effort in the scientific community to compare the performances of the different *operando* cells currently used by the research groups. This will allow appreciating the potential differences in conclusions made by different research groups on particular scientific issues. Finally, one should be aware that one technique might influence the other especially if they are probing the same catalyst volume. High intensity sources, such as UV lasers for Raman spectroscopy as well as X-rays used for EXAFS measurements, are most prone for such effects. Again, these effects are scarcely studied in the field of catalysis.

It should be clear from the above reasoning that the true *operando* machine is still a dream and further technical developments are needed to develop an instrument, which is able to monitor a catalytic transformation process on a particular active site *in real-time* and *in a spatially resolved way* under *true reaction* conditions. The main challenge to reach this goal will be to combine spectroscopy and microscopy at the atomic level under realistic reaction conditions. Further technical and instrumental developments will hopefully lead to such spectroscopic device in the years to come.

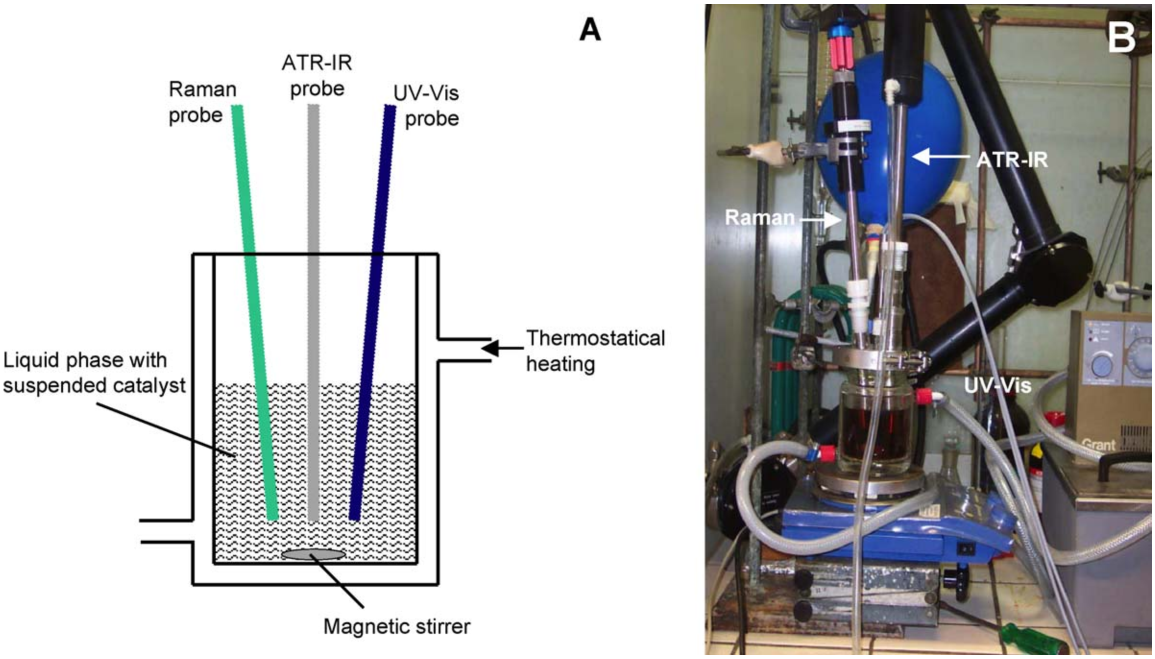

Fig. 8. *Operando* set-up for studying homogeneous catalytic systems, making use of Raman, UV–vis and ATR-IR spectroscopies. Although attractive, this set-up turned out not to work properly for studying the oxidation of veratryl alcohol by Co(salen) at high pH in aqueous solutions at 80 °C.

## 3. Additional advantages for coupling two spectroscopic techniques in one experimental set-up

In this section, we will describe three illustrative examples in which a combination of two *operando* spectroscopic techniques provides more information than the separate techniques.

### *3.1. Quantitative Raman spectroscopy of catalytic solids without the need of an internal standard*

Recently, we have shown that a combination of *operando* UV–vis–NIR and Raman spectroscopy is very advantageous, making it possible to quantify the Raman data using a correction factor obtained from UV–vis–NIR spectroscopy [52]. During reaction the catalytic surface composition can dramatically change. For instance, during propane dehydrogenation over a $Cr/Al_2O_3$ catalyst a reduction of $Cr^{6+}$ to $Cr^{3+}$ occurs, but besides this redox behavior, the catalyst is also gradually covered with coke. The build up of coke during reaction is measured with the set-up depicted in Fig. 5 and the obtained *operando* Raman spectra, given in Fig. 9, show the course of the coke bands, located at 1580 and 1330 $cm^{-1}$. An increase in intensity followed by a small decrease indicates that the amount of coke goes through a maximum. Simultaneously, the band of boron nitride (BN) located around 1350 $cm^{-1}$, an added internal standard decreases in intensity. It is not likely that the amount of coke decreases after ca. 20 min on stream, and independent TEOM measurements show a sudden increase in the amount of coke before leveling off as a function of time. It is known that Raman intensities depend on the scattering and absorption properties of the catalytic solid. As a consequence, progressive darkening of the catalyst during reaction by e.g. coke formation may strongly affect the intensities of the Raman spectra resulting in a conspicuous behavior.

To overcome this problem and obtain ‘true’ Raman intensities, a correction factor has to be applied. The application of an internal standard, such as BN, is a known method to do this [53]. However, a second method is possible in which a correction factor based on the changing scattering and absorption properties is applied. For this method, a relation between the Raman intensity ($\Psi_\infty$) and the diffuse reflectance of the catalytic solid of infinite thickness ($R_\infty$) is required. Already in 1967 Schrader and Bergmann [54] derived an expression to correlate the Raman intensity $\Psi_\infty$ to the diffuse reflectance $R_\infty$ based on the Kubelka–Munk formalism, by using the correction factor $G(R_\infty)$. This theory has later been

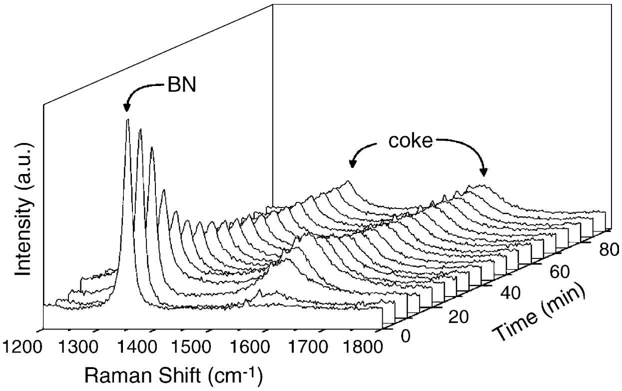

Fig. 9. *Operando* Raman spectra of a 13 wt.% chromium-on-alumina catalyst measured during 90 min of propane dehydrogenation at 550 °C.

improved by Waters [55] and Kuba and Knozinger [56] into the following expression:

$$\Psi_\infty = \frac{\rho I_0}{s} G(R_\infty) \qquad (1)$$

$$G(R_\infty) = \frac{R_\infty(1 + R_\infty)}{1 - R_\infty} \qquad (2)$$

In Eq. (1), $\Psi_\infty$ represents the observed Raman intensity for a powdered sample of infinite thickness, $I_0$ the exciting Raman laser intensity, $\rho$ the coefficient of Raman generation and $s$ is the scattering coefficient. The equation is valid based on the assumption that the scattering s of the solid does not change. This implies e.g. that the catalyst particles may not aggregate during reaction leaving the scattering coefficient $s$ unaltered. $G(R_\infty)$ can then be directly determined via Eq. (2) by measuring $R_\infty$ with diffuse reflectance spectroscopy in the UV–vis–NIR region. It is evident that when $R_\infty \rightarrow 100\%$ the function $G(R_\infty)$ goes to infinity. Furthermore, small changes of $R_\infty$ between 90 and 100% strongly affect the observed Raman intensity $\Psi_\infty$. Thus, Raman bands may undergo significant time-dependent intensity changes during reaction although the density of the corresponding Raman sensitive species remains unchanged. Fortunately, Eqs. (1) and (2) allow then to calculate the true Raman intensity ($\rho I_0$) of such species assuming $s$ to be constant.

Since the absorption/reflection of a sample is wavelength dependent, it is very advantageous to use UV–vis–NIR spectroscopy for determining the correction factor since Raman excitation lines fall within this region. Therefore, a selection of *operando* UV–vis–NIR spectra is presented in Fig. 10A. An increase and straightening in absorption is observed. This is a clear indication that the catalyst becomes darker as the reaction proceeds. As the absorption increases, the reflectance decreases. In Fig. 10B, the $G(R_\infty)$ values are plotted against time on stream. $G(R_\infty)$ was determined by the reflectance at 580 nm and a Halon white reference standard was used for calibration. This corresponds to the location of the coke band (580–532 nm (laser excitation wavelength) $\approx$17 200–18 800 $\approx -1580$ cm$^{-1}$). In Fig. 10B, $G(R_\infty)$ decreases as a function of time. This can be explained by the fact that as the reaction proceeds, the absorption increases and thus the reflection ($R_\infty$) decreases. As a result of a decreasing $R_\infty$, $G(R_\infty)$ will decrease as well, lowering the total observed intensity $\Psi_\infty$. As a result the effect on the 'true' Raman spectrum ($\rho I_0$) becomes larger as time proceeds.

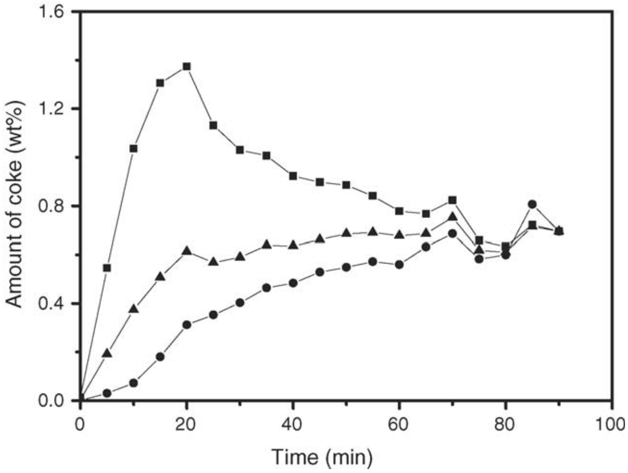

Fig. 11. Amount of coke obtained based on the Raman intensity band at 1580 cm$^{-1}$ during propane dehydrogenation without any correction (■), after $G(R_\infty)$ correction (▲) and after BN based correction (●).

After application of the correction factor $G(R_\infty)$ or making use of the internal standard BN to the spectra presented in Fig. 9, a totally different behavior emerges. To compare these two different Raman quantification methods, the integrated intensities of the 1580 cm$^{-1}$ coke band are plotted against time in Fig. 11. The amount of coke was measured after reaction, which allowed quantifying the amount of deposits formed [57]. The result showed that the amount of coke based on the raw data of Fig. 9 clearly does not reflect the true behavior of an increase before leveling off. This in contrast to both correction methods, which do show the expected trend.

The method using a $G(R_\infty)$ correction factor provides an elegant and more generally applicable procedure to determine the amount of surface species measured with Raman spectro-

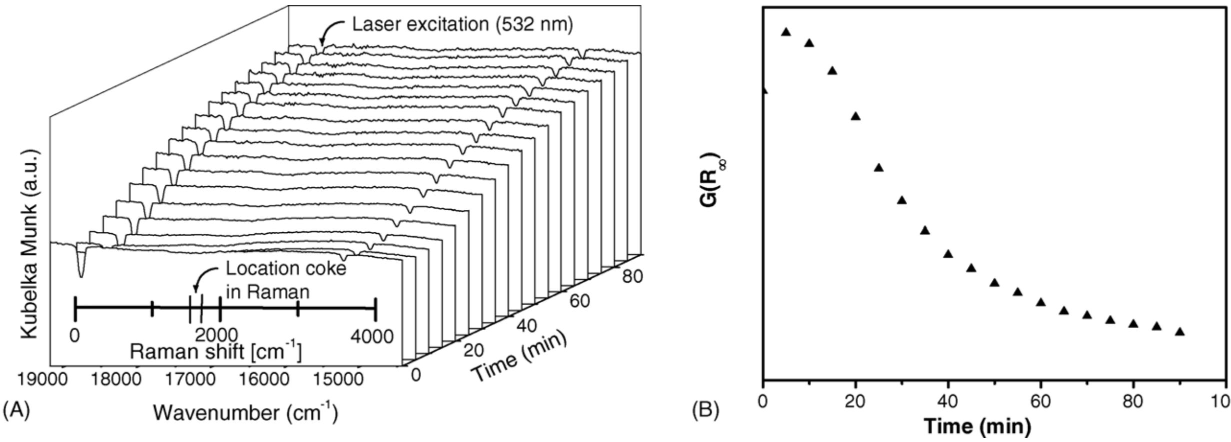

Fig. 10. (A) *Operando* UV–vis–NIR diffuse reflectance spectra simultaneously measured from the opposite site of the reactor on a 13 wt.% chromium-on-alumina catalyst during 90 min of propane dehydrogenation. (B) The change of $G(R_\infty)$ as function of the reaction time.

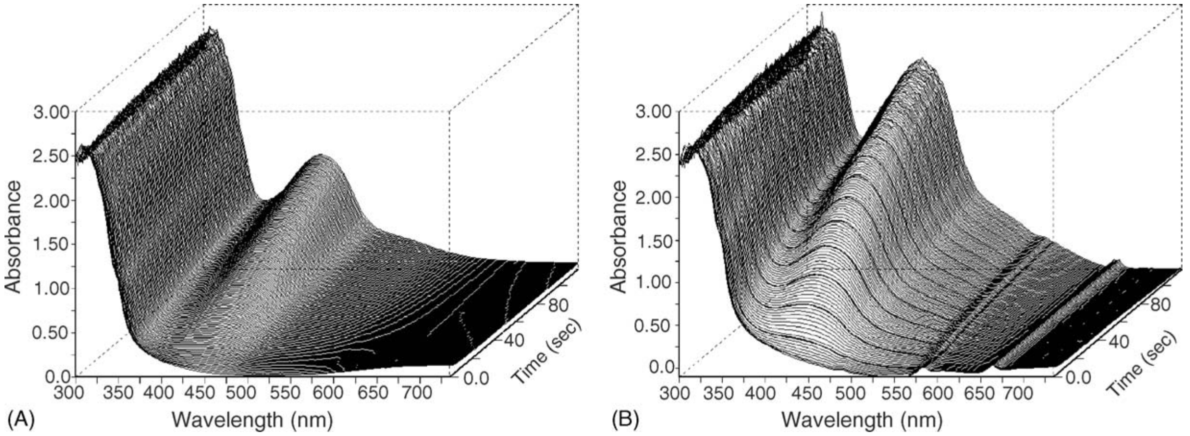

Fig. 12. The development of the UV–vis absorption spectra in time of the complete copper–phenanthroline reaction mixture: (A) without X-ray beam and (B) with X-ray beam exposed to the sample.

scopy. This first example shows the advantage of combining two *operando* spectroscopic techniques in one experimental set-up. Separately, the two applied techniques (UV–vis–NIR and Raman) reveal only qualitative information, whereas the combination makes it possible to use the obtained Raman spectra also in a quantitative manner.

### *3.2. Synchrotron radiation effects when measuring XAFS spectra*

The coupling of *operando* UV–vis and ED-XAFS in one set-up, as shown in Fig. 4, can be useful to study active sites and reaction mechanisms of catalytic processes in the homogeneous phase. However, this coupling also allows checking with one technique what the influence is on the sample by applying a second technique. In this specific case, it allows the probing of the effect of synchrotron radiation used for measuring XAFS spectra of homogeneous oxidation catalysts by UV–vis spectroscopy. Such effects have been recently studied in detail in our group for $CuBr_2$/bipyridine (1:1 molar ratio) [58,59] and $CuBr_2$/phenanthroline (1:2 molar ratio) [59] catalysts. The reaction under study was the oxidation of benzyl alcohol in a *N*-methylpyrrolidone/$H_2O$ solvent mixture (1:1 molar ratio) at room temperature. To start the reaction four different solutions were mixed: a solution with the copper complex as catalyst; a solution of benzyl alcohol as reagent, a 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) solution as co-catalyst and a tetraethyl ammonium hydroxide (TEAOH) solution as co-catalyst. The four solutions were mixed in a 1:1:1:1 ratio, resulting in a final copper concentration of 0.01125 M. Until now the exact mechanism of the oxidation reaction is still under discussion [60,61], making it a challenge to use combined *operando* techniques to shed more fundamental insight.

Fig. 12 shows a set of *operando* UV–vis spectra of a $CuBr_2$/phenanthroline reaction mixture measured with the set-up in Fig. 4 in the presence and absence of the X-ray beam, used to measure *operando* ED-XAFS spectra. It is evident that both sets of spectra show with reaction time a sudden increase of an absorption band around 433 nm, as well as a decrease of a broad absorption band at 735 nm. However, there are remarkable differences for the spectra obtained in the presence and absence of the X-ray beam. In order to substantiate this point the intensities of the absorption bands at 433 and 735 nm are

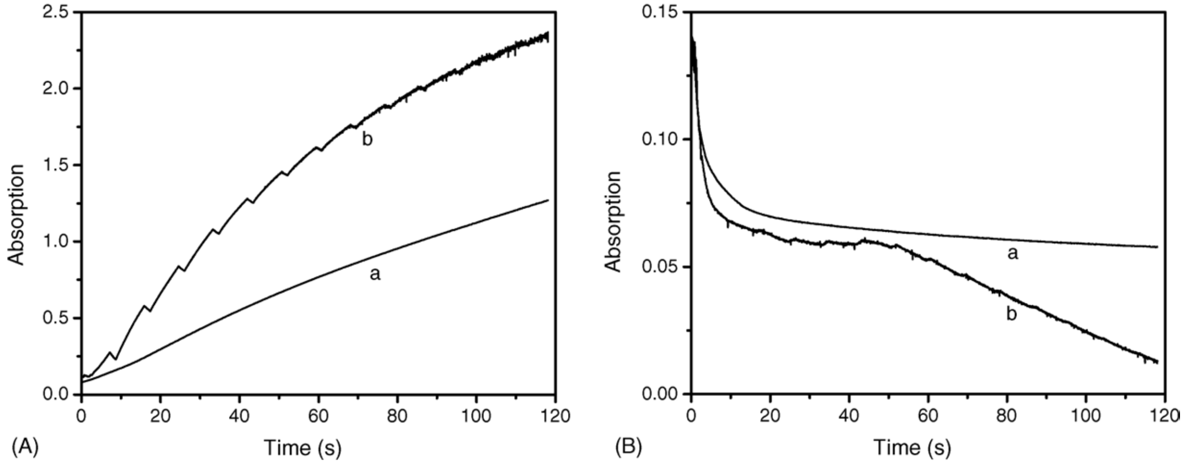

Fig. 13. Development in the intensity of the absorption at 430 nm (A) and 735 nm (B) of the complete copper–phenanthroline reaction mixture: (a) without X-ray beam and (b) with the X-ray beam on the sample.

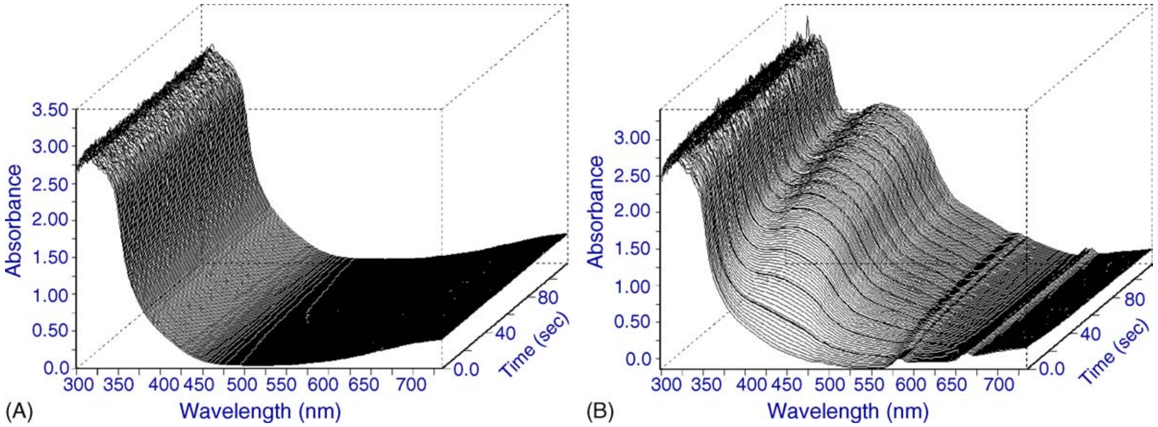

Fig. 14. UV–vis absorption spectra of the copper–phenanthroline solution mixed with benzyl alcohol as a function of time: (A) without X-ray beam exposure and (B) with X-ray beam exposure.

plotted versus reaction time in Fig. 13. In the presence of the X-ray beam the 433 nm band increases in intensity much faster than in the absence of the X-ray beam. In addition, in the presence of an intense light source, a saw tooth behavior can be noticed in the intensity plot. The saw tooth pattern is caused by the closing and opening of the X-ray beam shutter, which is closed for 1.5 s between two successive X-ray absorption measurements for data read-out. In other words, the X-ray beam has clearly had an effect on the reaction system as indicated by the UV–vis spectra measured in the *operando* set-up. The decrease in the intensity of the d–d transition at 735 nm can be attributed to the reduction of the $Cu^{2+}$ phenanthroline complex to the $Cu^{+}$ phenanthroline complex, which is characterized by a CT transition at 433 nm [62].

Figs. 12 and 13 showed the development of the spectroscopic features for the complete reaction mixture. The reaction mixture was also studied without the presence of the reductant and the obtained results are summarized in Figs. 14 and 15. It was found that without the X-ray beam the solution was stable and no spectral changes were occurring in time (Fig. 14A). This is certainly not the case when the same solution is exposed to the X-ray beam for XAFS analysis. Fig. 14B clearly shows strong changes in the corresponding UV–vis spectra as a charge transfer band starts to develop around 433 nm, while the d–d transition at around 735 nm starts to decrease in intensity for increasing reaction time. In other words, the X-ray beam has a reducing effect on the Cu solutions under study and the formation of $Cu^{+}$ during catalytic reaction (Fig. 12) cannot solely be assigned to a potential active site in the catalytic oxidation cycle under study. In order to further substantiate this point we have included the XANES spectra of the $CuBr_2$/phenanthroline system in the absence of reductant in Fig. 15. The trends in the development of the X-ray absorption spectra clearly indicate a reduction of $Cu^{2+}$ to $Cu^{+}$ when the Cu solution is exposed to the X-ray beam.

Summarizing, the use of the UV–vis-ED-XAFS set-up of Fig. 4 provides evidence for a reducing influence of the X-ray beam on homogeneous Cu catalyst. Other experiments, not shown in this paper, indicate that the extent of the reducing effect is influenced by the choice of the copper-precursor salt and that the speed of the reduction process is influenced by the flux of the X-rays on the sample and the counter-ion type and concentration [59]. It is important to realize that the observed phenomena not only occur under ‘‘severe’’ X-ray exposure (undulator source, white beam), but also are observed (although at different time scales) under ‘‘more mild’’ X-ray exposure (bending magnet, monochromatic X-rays). This study also illustrates the advantage of coupling a second technique, such as *operando* UV–vis, to a reaction vessel to evaluate the effect of synchrotron radiation used to measure XAFS on catalytic systems. Finally, we would like to stress that the data reported do not imply that all synchrotron measurements are prone to radiation damage. Merely, we would like to draw attention to an often-underestimated phenomenon in literature, which may lead to wrong interpretations of the obtained *operando* XAFS data and consequently incorrect conclusions on the catalytic reaction cycle. The same holds most probably also for other high intensity sources, such as Raman lasers, as will be shown by the next example.

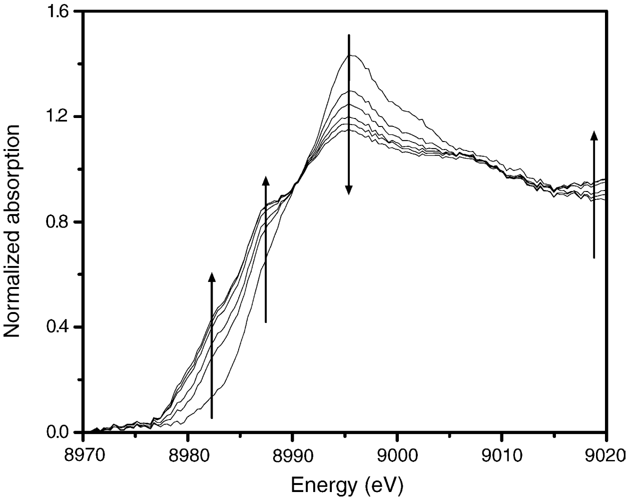

Fig. 15. The development of the XANES features for the complete copper–phenanthroline reaction mixture. Trends in the development of the X-ray absorption spectra are indicated with the arrows.

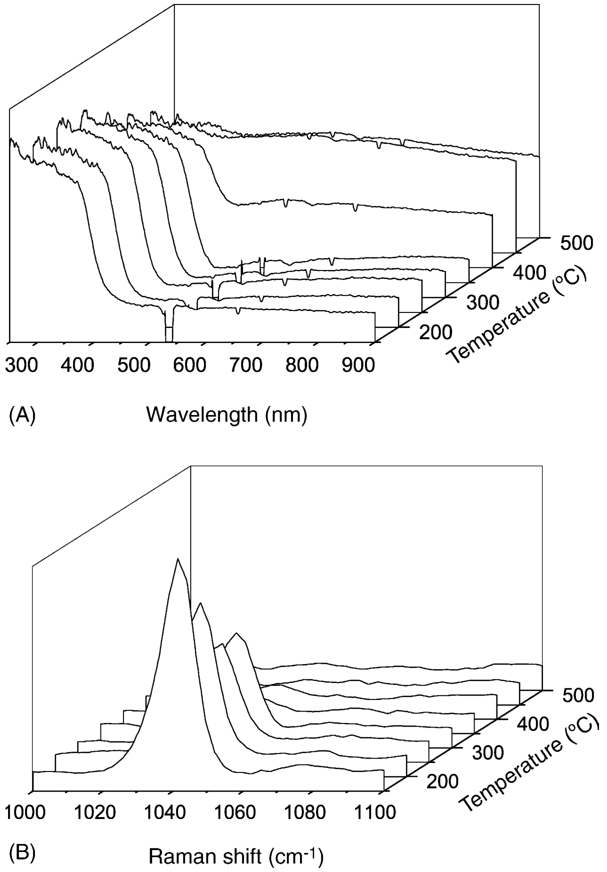

Fig. 16. Combined UV–vis/Raman spectroscopy during reduction with $H_2$ of a 4 wt.% $V_2O_5/SiO_2$ catalyst: (A) UV–vis data and (B) Raman data.

### 3.3. Heating effects induced by the light source

Raman laser light can also result in changes in the local temperature of the catalytic solid under investigation [63]. An example of such effect is given in Fig. 16. In this experiment a supported vanadium oxide catalysts has been subjected to a flow of hydrogen during heating. Continuously, both UV–vis and Raman spectra have been measured making use of the set-up of Fig. 5. At the start of the experiment the catalytic solid was in a fully oxidized state, which is evident from the charge transfer band of $V^{5+}$ at 350 nm (Fig. 16A). When the catalyst starts to reduce the intensity of this band decreases and a new broad band is formed around 625 nm. This absorption is typical for d–d transitions of $V^{3+/4+}$. The reduction of the supported vanadium oxide catalyst based on UV–vis spectroscopy started at 400 °C. When the temperature further increases, the charge transfer band almost completely vanishes at 500 °C. It was surprising to notice that a completely different behavior was observed in the corresponding Raman data, shown in Fig. 16B, obtained with a laser power of 70 mW. Here, the reduction process started at around 200 °C as evidenced by the decrease of the terminal V=O vibration located at 1040 $cm^{-1}$. This difference can only be explained by a local heating effect at the Raman laser spot. A possible solution for this problem is lowering the laser power, although this will be at the expense of the signal to noise ratio. Other groups have obtained on different materials similar heating effects by Raman spectroscopy as well [64–68].

## 4. Concluding remarks and outlook

The coupling approach in which two or more spectroscopic techniques are combined in one spectroscopic-reaction cell seems to be very powerful for elucidating the chemistry of catalyst materials, the mechanism of a catalytic reaction and the identification of active sites in homogeneous as well as heterogeneous catalysts. This approach looks at first sight simple, but a lot of experimental hurdles have to be taken before a successful set-up can be applied to a particular catalytic problem. Moreover, we have shown that in particular cases the coupling of *operando* techniques in one set-up results in more information than one would obtain from applying them separately. It is, in this respect, remarkable that people often seem to be unaware that high intensity radiation, such as synchrotron sources for measuring XAFS data, may affect the catalytic process under investigation. By using a second technique, it is possible to evaluate the effect of such intense light sources on the investigated system.

Evaluation of the still limited amount of literature reveals that there are – roughly speaking – two types of research groups working in the field of *operando* spectroscopy. On one hand, there are people focusing on the inorganic part of the catalyst material. More in particularly, these researchers make use of techniques, such as *operando* UV–vis and EPR spectroscopies, to unravel the oxidation state of a particular supported transition metal ion. On the other hand, there are scientists putting more emphasis on the organic part of a catalytic reaction. These research groups use e.g. *operando* NMR and IR spectroscopies. The combination of *operando* spectroscopic techniques opens new perspectives for studying at the same time the organic as well as the inorganic part of a catalytic reaction. In other words, an intelligent coupling of two or more techniques may lead to a better understanding of the catalytic problem.

Finally, other fields of catalysis are still hardly explored. An example of an under developed area of research is the study of heterogeneous catalysts operating in the liquid phase. Whereas a lot of spectroscopic research has been performed in homogeneous catalysis, only a limited number of studies report on the use of *operando* spectroscopy on catalytic solids in the liquid phase. Perhaps, that the coupling of IR-ATR, in combination with other *operando* techniques [47], opens new avenues to gather detailed insight in these important catalytic processes.

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[1] This term is borrowed from an instrumental development at the end of the 19th century in the field of cinematography. E.J. Muybridge (1830–1904) developed the first moving picture projector. This projector is often coined the Zoopraxiscope, since the first objects of which he made moving pictures were animals, such as horses. Projecting images drawn from photographs, rapidly and in succession on a screen, operates the Zoopraxiscope. The photographs were painted onto a glass disc, which rotated, thereby producing the illusion of motion. From this point forward in time, Muybridge's work began to clearly show that the possibility of actual moving pictures or cine-photography was a reality and even not so far from perfection.

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