EXPERIMENTAL METHODS IN CATALYSIS
(CA5030)

Cell designing for the study of catalyst surfaces using UV- Vis and IR spectroscopy

Submitted by

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Vibrational spectroscopy provides the most definitive means of identifying the surface species arising from **molecular adsorption and the species generated by surface reaction,** and the two techniques that are routinely used for vibrational studies of molecules on surfaces are Infrared (IR) Spectroscopy and Electron Energy Loss Spectroscopy (HREELS).

IR spectroscopy is a highly versatile technique, being applicable to almost any **surface**, and capable of operating under both high and low pressure. It is of relatively low cost compared to a technique which **requires high vacuum for operation.** There are a number of ways in which **IR techniques may be employed in the study of adsorbates on surfaces.**

Let discuss the characterization of heterogeneous catalysts by UV-VIS-NIR spectroscopy and microscopy with special emphasis on **transition metal ion containing catalysts.**

Cell representation for UV-Visible :

Fig.1. Schematic representation of the apparatus for collecting UV-vis spectra from solid materials

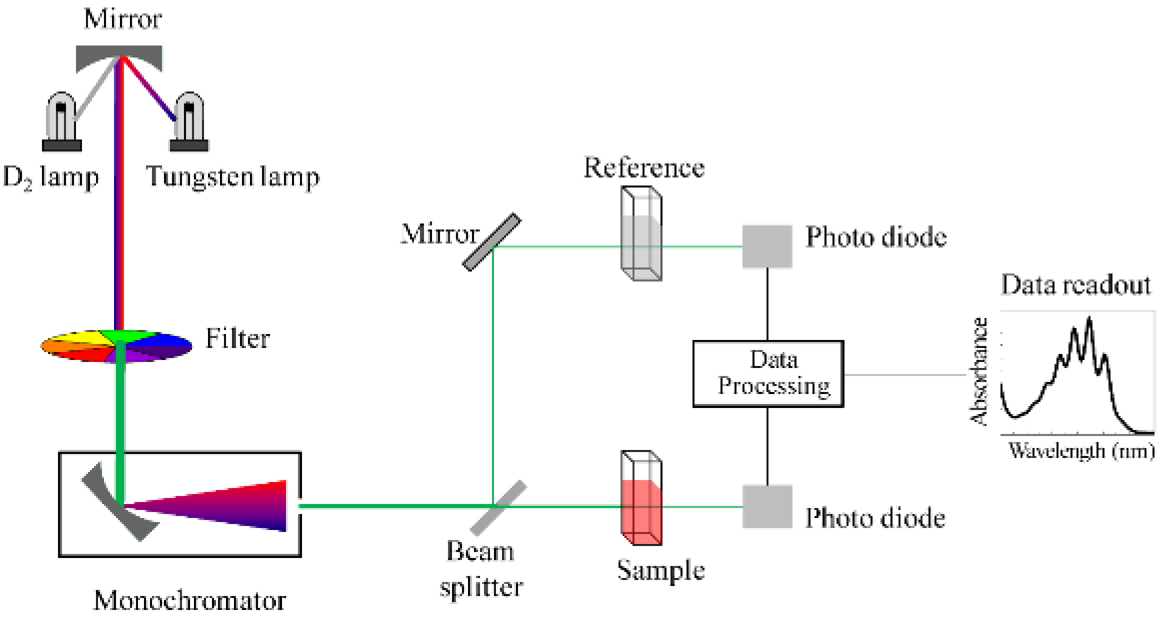


Fig.2. Block diagram representation of UV-Vis spectroscopy in the study of catalyst surface

UV-VIS-NIR spectroscopy and microscopy can be used in the study of heterogeneous catalysts and heterogeneous catalysis to tackle the following problems:

(1) understanding the coordination of TMI to surface oxygens.

(2) identification and quantification of specific oxidation states of TMI.

(3) study the changes in oxidation states and coordination geometries upon activation of catalysts and during catalytic reaction.

(4) identification of active TMI species etc.

In real **catalysts** TMI (transition metal ions) are often dispersed over the surface in a complex manner giving isolated ions, dimers, oligomers and clusters. Identification of the active sites in such a mixture by UV-VIS-NIR spectroscopy alone is very demanding. In many cases, one can identify the active oxidation state of the TMI, but whether these active TMI are mono-atomic, di-atomic or oligomeric species is often not known. Such is the **case for the dehydrogenation of alkanes over Cr/Al_2O_3. A correlation was found between the amount of**

Cr^{3+} and the catalytic activity, suggesting that Cr3+ was involved in the active site.

For zeolites the situation is more favourable. They are crystalline and they have ion-exchange properties. In **Cu-ZSM5**, for instance, the **Cu^{2+}** ions interact magnetically for loadings in the range 0.25 o Cu/Al2O3 0.5. As a consequence, the EPR lines of **Cu^{2+}** broaden and the intensity of the EPR spectrum does not increase anymore with increasing Cu loading. In the UV-VIS-NIR spectra, a broad unresolved band of d–d transitions is observed. This reasoning holds also for Cu^{2+} in ZSM-5 zeolites. However, Cu-ZSM5 samples with Cu/Al > 0.25 are peculiar, because of the UV-VIS-NIR spectrum of Fig.3, obtained upon activation in O2. It contains the typical broad and weak d–d band system of **Cu^{2+}** with maximum around 14400 cm^{-1} the broad LMCT band with maximum in the 40000–45 000 cm^{-1} and a band at 22 700 cm^{-1}, which was not observed before in any of the Cu zeolites studied.From mm-sized catalyst extrudates and pellets it is only a small step to mm-sized particles and crystals, typically zeolite crystals. UV-VIS microscopy is a versatile technique. A special sample holder has to be designed to allow in situ catalytic experiments (Fig. 15).84–88 It reveals the adsorption and alignment of organic molecules and reaction intermediates in the pores, thereby giving information on the intergrowth structure of the crystals under investigation. The band intensity of the reaction intermediates can be followed as a function of time, thus giving information on the kinetics of the reaction. These ideas have been worked out for the acid catalysed oligomerization of a series of styrenes, which produces dimeric and trimeric carbocations (Fig. 16) with typical UV-VIS bands at 590 nm and 635 nm respectively.86,89,90 The dimeric cation is dominant at the edges of the crystal, while the trimeric carbocation is the main species in the center of the crystal.(Fig.3) This is also revealed in the images of the crystals, wherein a different colour is observed at the edges and in the main body of the crystal. The carbocations are located and aligned in the 10-membered ring channels. Thus, polarized light UV-VIS microscopy is the method of choice to reveal this alignment.

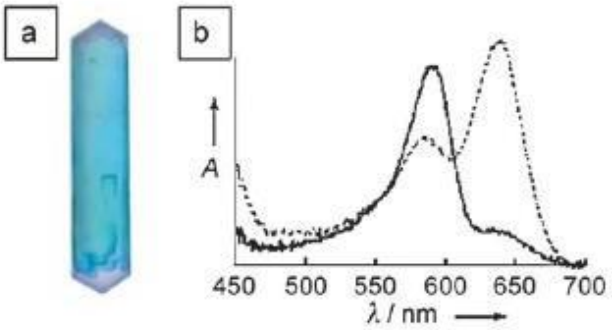
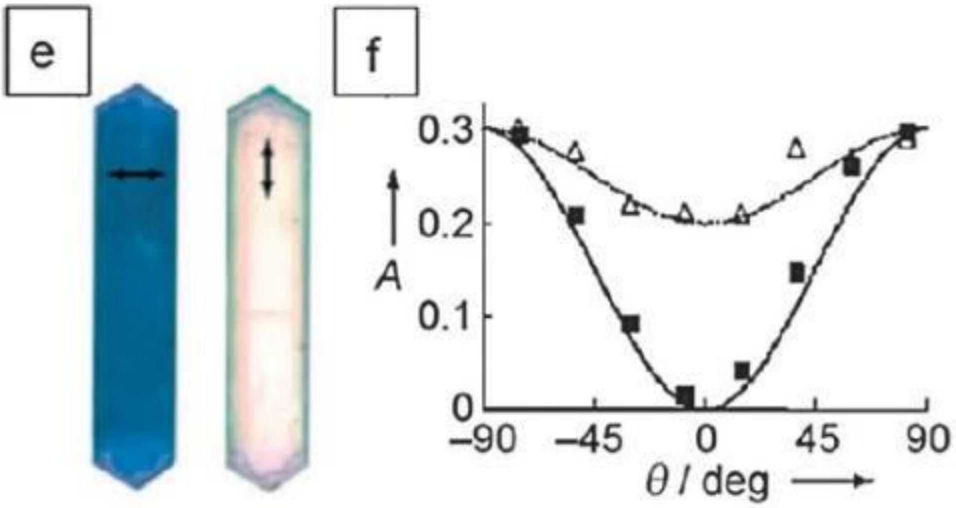


Fig.3 (a) Optical microphotograph of a H-ZSM-5 crystal after addition of 4-methoxystyrene, showing the different colours of the body (blue) and the edges (purple). (b) Spatially resolved optical absorption spectra measured along the long axis of the crystal after reaction at the edges (solid line) and the center (dotted line);



(e) Microphotographs of H-ZSM-5 exposed to 4-methoxystyrene and measured with polarized light (polarization is indicated by arrows). (f) Angular dependence of the optical absorption at 590 nm in the body (squares) and at the edges (triangles) of the crystal.

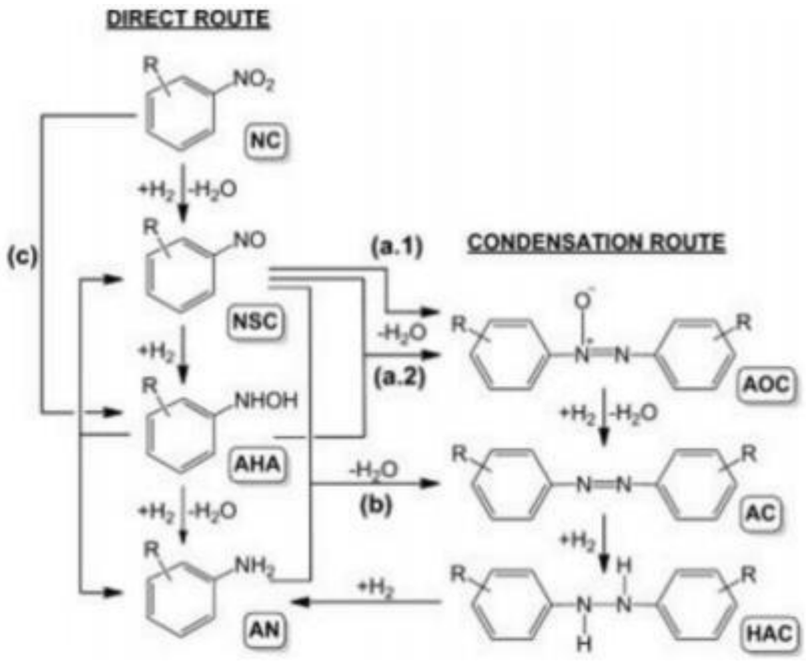
IR spectroscopy in catalyst to determination of the nature of catalyst surface sites:

IR spectroscopy provides detailed **molecular information of the nature of adsorbed species on a catalyst surface,** their interaction strength, and evolution **under controlled atmospheres and temperatures**. Using specific probe molecules, it allows to extract relevant information of the nature of surface sites on a catalyst, such as acid, base, and redox sites, surface defects, and the dynamic behaviour of those sites under reaction conditions.

Some examples related to relevant industrial processes like Fischer-Tropsch synthesis, ethylene oligomerization, dehydration of aldoxime compounds to their corresponding nitriles, and hydrogenation of nitrobenzene to aniline or azobenzene will be provided in order to illustrate the great potential of IR spectroscopy in the field of catalysis.

IR studies of the hydrogenation of nitrobenzene on Au/TiO2 catalysts:

The hydrogenation of nitrobenzene is followed by IR on the Au/TiO2 catalysts performing temperature-dependent studies. In the IR spectra (Figure 4A), simultaneous to the consumption of nitrobenzene (IR bands at 1523 cm1), nitroso benzene (1483, 1475 cm1), phenylhydroxylamine (1489 cm1), and aniline (1495 cm1) are formed [77, 78]. The micro-kinetic data IR displayed in Figure (4B) shows a low surface concentration of nitroso benzene and a high amount of phenylhydroxylamine. Being phenylhydroxylamine an intermediate compound (see scheme 1), its high surface concentration indicates a low hydrogenation rate to aniline and the coexistence of an additional parallel direct reaction path of phenylhydroxylamine formation starting from nitrobenzene in which nitroso benzene formation is circumvented (Figure 4C). These results and the absence of IR bands of azoxy and/or azo compounds help to propose a direct hydrogenation route. Moreover, it is shown that the low surface concentration of nitroso benzene during nitrobenzene hydrogenation is clue in this reaction path.



Scheme 1.

Reaction pathways in the hydrogenation of nitro compounds to anilines. NC = Nitro compound, NSC = Nitroso compound, AHA = Aromatic hydroxylamine, AN = aniline, AOC = azoxy compound, AC = Azo compound, HAC = Hydrazo compound

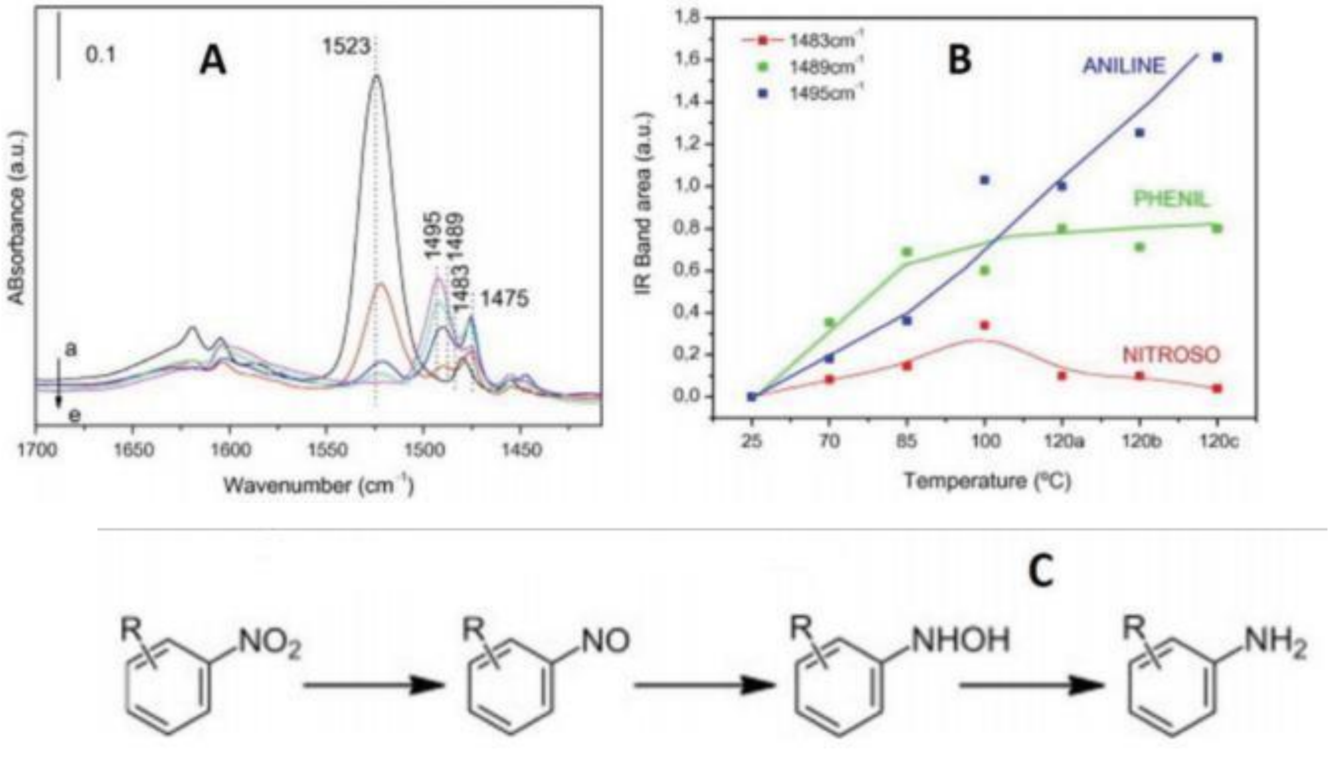


Figure 4.

IR spectra in the hydrogenation of nitrobenzene on Au/TiO2 catalyst at (a) 25°C, (b) 70°C, (c) 85°C, (d) 100°C, and (e) 120°C (0.5 mbar NB and 8 mbar H2). (B) Evolution of the IR surface reaction intermediates species with temperature. (C) Proposed reaction path.

This is confirmed by additional IR experiments where the surface coverage of nitroso benzene on the Au/TiO2 catalyst is modified and the evolution of surface species under hydrogenation conditions monitored. Thus, at low surface coverage, a fast hydrogenation of nitroso benzene to phenylhydroxylamine is observed, followed by further hydrogenation to aniline, whereas at high nitroso benzene coverage, azoxybenzene is mainly formed

Self-understanding by UV-Vis and IR Spectroscopy in the study of catalyst surface determination:

IR spectroscopy has been shown as a very powerful technique in the field of catalysis, enabling important information difficult to obtain with other techniques. Thus, surface sites and active species can be properly analysed, which combined with the analysis of the reaction mechanism and the rate-limiting step are key points to direct the synthesis of catalysts with improved selectivity. Moreover, the dynamism of catalyst surfaces under reaction conditions monitored by IR spectroscopy has been highlighted, a fact usually underestimated but with strong repercussion on the catalytic performance.

While **UV-VIS-NIR spectroscopy** is a mature but powerful technique for the study of heterogeneous catalysts, especially those containing transition metal ions. More recently, the use of fiber optical technology has expanded the application window of UV-VIS-NIR spectroscopy and heterogeneous catalysts can now be studied under almost real reaction conditions by coupling the UV-VIS-NIR spectrometer to the reactor. In recent years UV-VIS microscopy has been introduced for the study of respectively mm-sized catalytic bodies and mm-sized catalytic crystals and particles.

The analysis and the interpretation of the spectra can, however, be quite difficult, due to the complexity of the spectra and the catalysts. Three strategies can be followed to tackle these issues:

(1) chemo metrical analysis of the spectral dataset.

(2) combination of UV-VIS-NIR spectroscopy with other complementary spectroscopic techniques, such as fluorescence, Raman, EPR and FT-IR