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Representative examples of infrared spectroscopy uses in semiconductor photocatalysis

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ABSTRACT

In the domain of semiconductor photocatalysis, infrared spectroscopy is a technique able to provide information inter alia upon: the generation, accumulation, scavenging and/or trapping of electronic charges under band-gap irradiation; the surface radicals existing during or after irradiation; the irradiation effects on the interactions of the surface with water; surface species not observed in the fluid phase; the texture, structure and surface properties of photocatalysts and photocatalytic coatings. In practice, the challenges are to achieve conditions as close as possible to those of the photocatalytic reactions, especially satisfactory irradiation of the photocatalyst by both the exciting photons and the infrared beam. As usual in infrared spectroscopy, labeled molecules can be employed to ascertain the attributions of the vibrational bands. Obviously, time-resolved infrared spectroscopy is extremely useful regarding the basic photocatalytic mechanisms.

1. Introduction

The use of infrared (IR) spectroscopy to study solid catalysts and adsorbates started in the 1950s and the information provided became still more reliable and increasingly prolific with the advent of PC-driven Fourier transform infrared (FTIR) spectrometers. This information comprises: the nature of the chemical bonds within the catalysts, particularly composites; the types of surface groups, e.g. OH groups on oxides, and the interactions of these groups with various molecules; the acidic or basic character of the surface sites by use of probe molecules; the nature of the adsorbed species and the changes of these species (nature and relative amount) according to the pretreatments of the catalysts, etc. This list clearly shows the interest of IR spectroscopy for catalysts used in thermally activated reactions. In the case of heterogeneous photocatalysis, these kinds of information – which does not require irradiation with activating photons – can also be very useful to examine the structure and texture of photocatalysts and photocatalytic coatings, and to elucidate processes occurring in the dark; more investigations of this type should be encouraged in the author's view.

However, in both thermal catalysis and photocatalysis, an important objective is to obtain IR spectra under the conditions of the reactions (for which the terms "in-situ" and "operando" are commonly used) to extend the information. For thermal catalysis, conceiving and building IR cells enabling to heat uniformly the solid sample is not really easy and results obtained with such cells have not been very numerous. For photocatalysis, achieving complete irradiation of the sample by the exciting photons is also difficult and only homemade devices have been utilized so far.

This article presents illustrative examples of the information IR spectroscopy can provide about photocatalytic reactions and photocatalytic materials. These selected examples are simply meant to show the various typical kinds of information that can be drawn from IR spectra as is listed in the abstract. Other examples could have been chosen and the author apologizes in advance to the scientists whose papers are not cited because of space limitation. After a brief presentation of the IR methods, the examples are described, beginning with spectra recorded under irradiation or after irradiation, and ending with spectra obtained without irradiation.

2. IR methods

Spectra can be recorded by use of methods where the IR beam is either transmitted or reflected by the photocatalytic material (Fig. 1). Transmission is possible whenever the photocatalytic material is a thin film transparent in the IR spectral region. Powders can be pressed into thin wafers; however, it is often difficult to obtain wafers which are both sufficiently transparent and solid. Moreover, the pressure can have an effect on the photocatalyst morphology, particularly the porosity, so that the relevance to the powder employed in the photocatalytic reaction studied could be biased. Mixing with KBr to increase the transparency must be avoided because KBr can interact chemically with the photocatalyst. Attenuated Total Reflectance (ATR) is applicable to both thin

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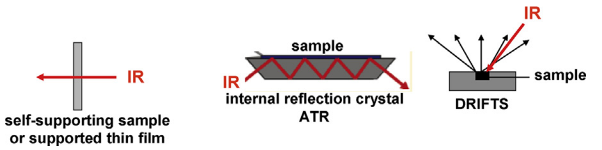

Fig. 1. Basic schemes of the three IR techniques used in thermal catalysis and photocatalysis.

films which are not necessarily transparent in the IR spectral region and powders provided they are uniformly deposited or pressed to yield a thin layer on the ATR crystal maintaining good optical contact. The information is from the upper few microns of the sample. The ATR crystals must be insoluble in water and of high refractive index. ZnSe crystals, sometimes combined with diamond crystals, are very often employed. The use of diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) is very common in thermal catalysis because it is applicable to powders which are simply poured into the sample-holder. In the case of photocatalysis, complete irradiation by the exciting photons cannot be achieved when a DRIFTS device is employed. This is obviously a drawback because the IR spectra relate to both irradiated and non-irradiated particles. Therefore it is more difficult to conclude about the effect of the exciting photons. In the case of photocatalysis in liquid water, ATR, compared with transmission and DRIFTS, offers the advantage of greatly decreasing interference from water because the evanescent wave created penetrates the water film to a shallow depth relative to a direct IR beam. For the three techniques, repeatability of the measurements may be difficult to achieve because of the sample preparation.

Describing IR cells corresponding to these methods is out of the scope of the present overview. Examples of cells can be found in the papers cited here and/or in other papers from the same research groups. Additionally, the types of cells employed for gas-phase photocatalysis have been very recently reviewed [1]. A modern bench-top FTIR with appropriate accessories (for solid-state investigations) is relatively inexpensive, as compared to other surface or bulk spectroscopic techniques, and offers excellent value for such studies.

3. Representative examples

3.1. Time-resolved IR spectroscopy

It involves the use of laser pulses to excite the photocatalyst and an appropriate IR detector coupled to an amplifier. It can provide valuable information about the short-lived photogenerated charges and radicals. For instance, the quasi-continuum absorption, intensifying toward higher frequencies induced by photo-excitation of a variety of semiconductor oxides has been assigned to electrons [2–4]. Therefore its decay after the end-of-pulse allows one to determine the effects of adsorbates, such as O_2, H_2O, CH_3OH, etc., upon the fate of electrons and associated holes, and thereby to distinguish photocatalysts as is mentioned hereafter for Bi_2WO_6 samples [5]. Also, this absorption was reported to be lower for Pt/TiO_2 than for the same TiO_2 specimen without Pt, which was interpreted as due to Pt acting as an electron sink [4].

Fig. 2 relating to Pt/TiO_2 shows that, on a time scale of a few μs, the decay of the absorbance at 2000 cm^{-1} resulting from a 10 ns-pulse at 355 nm was slower in the presence of water vapor but did not depend on the water pressure, at least in the 1–10 Torr range [6]. The 2000 cm^{-1}-wave number was selected because it corresponded to a satisfactory signal-to-noise ratio given the equipment used. By contrast, on a time scale of hundreds of μs, the decay at 2000 cm^{-1} was faster the higher the water pressure in the same range. The interpretation given by the authors was that the dominant phenomenon was initially the capture of holes by a species whose concentration was not affected by water above 1 Torr, whereas at longer times the dominant phenomenon was related to the reduction of water by the electrons produced by the laser pulse.

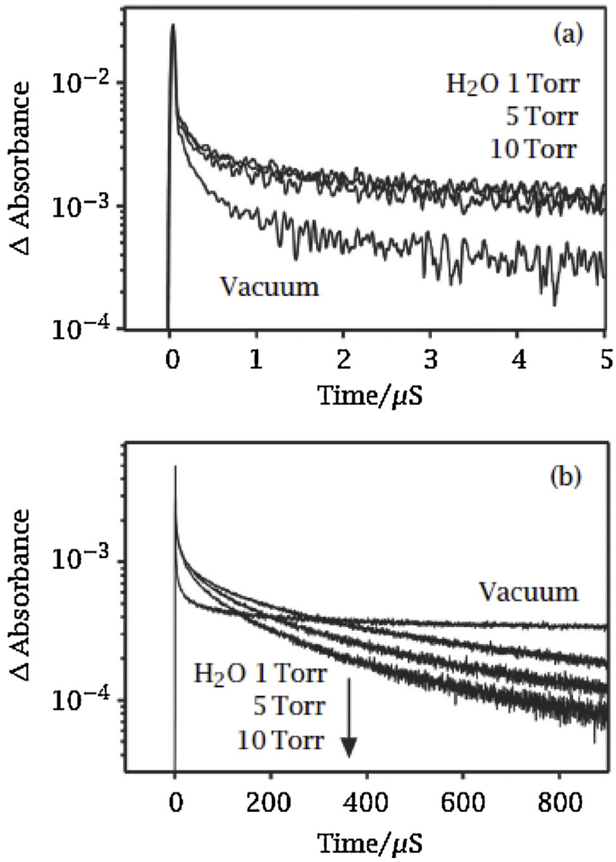

Fig. 2. Decays (shown on two time scales) of the absorbance at 2000 cm^{-1} following the laser-pulse under vacuum and in the presence of water at the pressures indicated.

Reproduced with permission from Ref. [5].

The example presented in Fig. 3 shows that the 2000 cm^{-1}-absorbance decay after excitation of Bi_2WO_6 by a 6 ns-pulse at 355 nm was slower in the presence of CH_3OH and faster in the presence of O_2 [5]. Moreover, the comparison of the decays on different time scales clearly indicated that the scavenging of electrons by O_2 was slower than that of holes by CH_3OH at least for the pressures used. The 2000 cm^{-1}-absorbance value and decay rate also enabled one to determine the effect of the crystallinity of Bi_2WO_6 upon the recombination rate of the photoproduced charges.

In fact, the information provided by these experiments is equivalent to that derived from time-resolved microwave conductivity. For instance, in the presence of CH_3OH, the end-of-pulse (7 ns-pulse at 308 nm) conductivity of various powdered or coated TiO_2 was higher and also the conductivity decay was slower, indicating hole scavenging [7].

Unlike time-resolved microwave conductivity, time-resolved IR spectroscopy can be very useful to detect directly very instable intermediate species formed in the course of a photocatalytic reaction. Fig. 4 shows an example. After irradiation of Pt/TiO_2 with a 355 nm-pulse in the presence of propan-2-ol, the carbonyl band of acetone, the main intermediate product of propan-2-ol oxidation, appeared and its intensity remained stable on the time scale

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