

The potential of ATR-FT-IR spectroscopy as an analysis tool for heterogeneous (photo)catalysis

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Introduction

The amount of infrared studies dealing with the analysis of heterogeneous catalysts is enormous. The reasons are numerous: the technique is non-invasive, it can be applied in many reaction conditions, from high vacuum to high pressure, and provides unique information on the state of adsorbed molecules on the surfaces of catalysts. While the *in situ* spectra recorded during the eighties and nineties are mainly related to gas phase heterogeneous catalytic studies in steady state reaction conditions, recently the number of papers devoted to ATR spectroscopy for liquid phase applications has significantly increased [1,2].

Also, but only in recent years, the photocatalytic community embarks on the use of infrared spectroscopy for analysis of photocatalytic processes, in particular ATR spectroscopy, to analyze contaminant oxidation in waste water streams: the small volume probed by the ATR methodology circumvents the strong absorption modes of water. To the best of our knowledge, fundamental ATR studies of selective photo-oxidation, however, do not yet exist.

During this presentation the use of ATR spectroscopy for analysis of liquid phase selective catalytic reactions will be discussed, i.e. photocatalytic selective oxidation of cyclohexane over TiO₂, and cyclohexene over V-based catalysts, respectively. The first example discusses long term activity profiles and the deactivation mechanism, the second rapid scan time resolved experiments (ms) for mechanism elucidation.

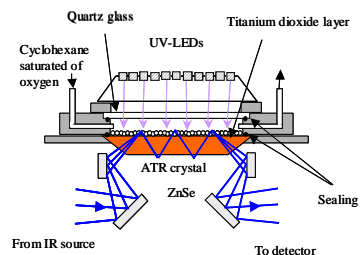


Figure 1. Schematic representation of the ATR flow cell equipped with UV LEDs

Materials and Methods

TiO₂-Cyclohexane

An overview of the used flow cell and illumination device (UV-LEDs) is depicted in Figure 1. The UV-LEDs have an emission peak at 375 nm. The ZnSe ATR-crystal was coated with 2 mL of a sonicated 1.5 g/L TiO₂ suspension (Hombikat anatase), followed by removal of water by evacuation in a dissicator. Cyclohexane oxidation was performed at 25 °C for 4 hours. The initial volume was 50 ml.

V-TUD 1 - Cyclohexene

The catalyst used was vanadia incorporated in the 3-dimensional mesoporous material TUD-1 with a loading of 2 wt-% vanadia. The ATR spectra were recorded with an ASI systems model Dicomp ATR accessory equipped with a three reflection diamond ATR crystal and incorporated in the sample compartment of a Bruker Model IFS 66v/S spectrometer. The catalyst was deposited on the ATR crystal using 3 microliter of a suspension containing 25 mg of the ground catalyst (mortar) in 1 ml of demineralized water, and evaporation to dryness applying a reduced pressure of about 100 mTorr. A home made teflon liquid cell was assembled over the coated diamond crystal, after which oxygen and an aliquot of 0.2 ml pure cyclohexene were introduced. Spectral development was recorded in rapid scan mode during, and after sending a laser pulse of 458 nm (480 ms, 200 mW) to the V-TUD1 catalyst.

Results and Discussion

Anatase TiO₂ in cyclohexane oxidation

Spectra recorded during illumination of TiO₂ (Hombikat, anatase) and cyclohexane (not shown) contain increasing intensities at 1710 cm⁻¹ (cyclohexanone), and 1680 cm⁻¹ and 1420 cm⁻¹ (carboxylates). Furthermore, the vibrational bending mode of water (~1630 cm⁻¹) is contributing to the spectra. Build up of carboxylates takes place in the first hour of reaction, after which the vibrational modes are no longer increasing, suggesting that the catalyst surface becomes saturated. The dynamics of the relative intensities (cyclohexanone and carboxylates) indicate that carboxylate formation is a parallel processes to cyclohexanone formation, and that carboxylates significantly deteriorate the formation rate of cyclohexanone. A detailed spectroscopic analysis (including the use of isotopically labelled Cyclohexane – D₁₂), as well as a mechanism for catalyst deactivation will be discussed during the presentation.

Vanadia/TUD-1 in cyclohexene oxidation: time resolved spectroscopy

Without providing a detailed spectral interpretation, the spectra obtained during rapid scan analysis indicate that under pulsed illumination at 458 nm a significant amount of product, i.e. cyclohexenone (1695 cm⁻¹), was formed, demonstrating for the first time that hydrated vanadia centers in mesoporous materials can be activated by visible light to induce oxidation reactions (dehydrated entities only absorb UV light). Using the rapid scan technology, a direct involvement of V-OH groups, causing dynamic changes in the 1100-500 cm⁻¹ region, in the selective oxidation process could be revealed. The spectral changes will be extensively discussed and a reaction mechanism proposed during the presentation.

Significance

(Time resolved) ATR-FT-IR spectroscopy is a very powerful tool for mechanism elucidation in heterogeneous liquid phase selective photocatalytic processes.

References

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2. Mul, G., Hamminga, G.M., Moulijn, J.A. *Vib. Spec.* 34, 109 (2004)