Construction of an *operando* dual-beam fourier transform infrared spectrometer and its application in heterogeneous catalysis characterization

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Abstract: An *operando* dual-beam Fourier transform infrared (DB-FTIR) spectrometer was successfully developed using a facile method. The DB-FTIR spectrometer is suitable for the real-time study of the dynamic surface processes involved in gas/solid heterogeneous catalysis under real reaction conditions because it can simultaneously collect reference and sample spectra. The influence of gas-phase molecular vibration and heat irradiation at real reaction temperatures can therefore be eliminated. The DB-FTIR spectrometer was successfully used to follow the transformation of alkenes over nano-sized HZSM-5 and Zn promoted HZSM-5 zeolites under real reaction conditions.

Keywords: *Operando* DB-FTIR, Real-time spectrum, Real reaction condition.

1. Introduction

Currently, in situ transmission IR spectroscopy (TIRS), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, and Fourier transform infrared attenuated total reflection (FTIR/ATR) spectroscopy are very popular tools in the study of heterogeneous catalysis. All of these commercial FTIR spectrometers operate in the single-beam (SB-FTIR) mode, and require the measurement of reference (background) spectra to remove variations caused by changes in background absorption and instrument conditions. They are not suitable for real-time study of the dynamic processes involved in gas/solid heterogeneous catalysis because they cannot collect the reference and sample spectra simultaneously. Another major problem with SB-FTIR spectrometers is that they are strongly influenced by gas-phase molecular vibration and heat irradiation at high temperatures. However, there is an urgent need for real-time surface characterization methods in the field of heterogeneous catalysis. This is because the fundamental understanding of heterogeneous catalytic processes, and thus the rational design of advanced catalysts, requires information related to the transient species involved in the reaction. These transient species can be captured only under real reaction conditions. In principle, a dual-beam Fourier transform infrared spectrometer (DB-FTIR) could simultaneously eliminate the influence of both gas-phase molecular vibration and heat irradiation at real reaction temperatures. This technique is therefore expected to be a useful *operando* characterization method for heterogeneous catalysis. Kuehl, Dignam and Debreczeny et al [1-3] have tried to develop a DB-FTIR spectrometer by redesigning the optical layout of a commercial spectrometer to simulate dual-beam conditions. However, this is too difficult to be practical use.

Here, we report a facile method for the development of an *operando* DB-FTIR spectrometer and its application in heterogeneous catalysis. The DB-FTIR spectrometer can perform time-resolved collection of both reference and sample spectra, and thus produce real-time spectra of the catalyst surface species under real heterogeneous reaction conditions (continuous gas flow and temperatures of up to 550 ℃) by simultaneous subtraction of the reference spectra from the sample spectra.

2. Experimental

The IR reactor cell was developed to have identical CaF_2 windows to ensure total elimination of the background interference. Two Nicolet 10s infrared spectrometers equipped with mercury cadmium telluride (MCT) detectors were used to construct the DB-FTIR spectrometer. Special software was designed to ensure that the two spectrometers collected the spectra simultaneously. The catalysts were pressed into selfsupporting thin wafers (1 cm^2) that were placed in the sample beam, and the reference beam was vacant. The sample was activated in the IR reactor cell at 400 ℃ for 4 h under vacuum (10^{-3} Pa), and the spectra were recorded at a resolution of 4 cm^{-1} with 64 scans in the region of $\tilde{\nu}$ =4000–1000 cm^{-1}. The intensities of the reference and sample beams were adjusted to the same level. NaZSM-5 zeolite with crystal size of 20-50 nm used was manufactured by Dalian Ligong Qiwangda Chemical Technology (Dalian, China). The SiO_2/Al_2O_3 molar ratio of ZSM-5 zeolite was 26. HZSM-5 zeolite was obtained by exchanging the NaZSM-5 zeolites twice at 80℃ with 1 M solution of ammonium nitrate. The Zn modified sample was obtained with incipient wet impregnation (IWI) method.

3. Results and discussion

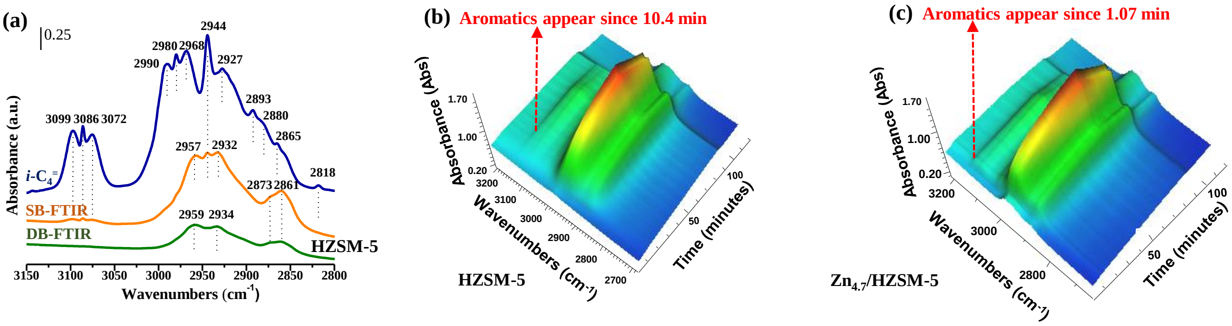

Figure 1. a. FTIR spectra of isobutene adsorption on nano-sized HZSM-5 zeolite using the DB-FTIR spectrometer and an ordinary SB-FTIR spectrometer at 150 ℃, SB-FTIR spectrum without the catalyst at 0.1 MPa and in a flowing mixture of isobutene and nitrogen gas (6 % isobutene - 94 % nitrogen); **b-c**. FTIR spectra of propene adsorption on nano-sized HZSM-5 and Zn promoted HZSM-5 zeolites using the DB-FTIR spectrometer at 0.1 MPa in a flowing mixture of propene and nitrogen gas (6 % propene - 94 % nitrogen)

To demonstrate the advantages of the DB-FTIR instrument as an *operando* spectrometer, an ordinary SB-FTIR spectrometer was compared with the DB-FTIR spectrometer by studying isobutene adsorption on nano-sized HZSM-5 zeolite, as shown in **Figure 1(a)**. During the adsorption of isobutene, the DB-FTIR spectrum contained only four obvious absorption bands, which could be attributed to the species adsorbed on the surface of the zeolite. In contrast, when the ordinary SB-FTIR spectrometer was used, the obtained spectrum exhibited interference from gas-phase molecular vibration absorptions. The example indicates that, owing mainly to the influence of the gas-phase molecular spectrum, it is difficult to obtain the correct spectrum of the catalyst surface species under real reaction conditions using an ordinary SB-FTIR spectrometer. In contrast, the spectrum is easily obtained from the DB-FTIR spectrometer because the influence of the gas-phase molecular vibrations is completely eliminated by simultaneous subtraction of the reference spectrum.

Zn/ZSM-5 zeolites are among the most efficient catalysts of short-chain hydrocarbon transformations under non-oxidative conditions. Understanding of the mechanism of such transformations and the role of acidic and Zn sites at the different stages of the reaction is of key importance for further improvement of catalyst activity, selectivity and lifetime. As shown in **Figure 1(b-c)**, the dynamic process of propene aromatization over HZSM-5 and Zn/HZSM-5 could be followed by DB-FTIR under real-reaction conditions. We firstly observed that the function of Zn ion incorporation was accelerating the formation of aromatics in propene transformation.

4. Conclusions

In summary, an *operando* DB-FTIR spectrometer has been developed using a facile method. This spectrometer is expected to be a powerful tool for the in-situ study of heterogeneous catalysis. It is very convenient for eliminating the effects of gas-phase molecular vibration and heat irradiation, and can provide important information on surface active sites, intermediate or spectator species and the reaction mechanism under real reaction conditions.

References

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