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Viewpoint

Far reaching potentials of far infrared spectroscopy in catalysis research



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1. Introduction

Fourier transform infrared (FTIR) spectroscopy has played an important role in identifying molecular finger prints of reactants, products and intermediates, in elucidating the mechanisms of a broad range of reactions, and in probing the fundamental nature of active sites of many catalysts by both *in-situ* and *ex-situ* measurements [1,2]. Specifically, FTIR spectroscopy measures the absorption of chemical bonds or groups in the 10–12500 cm^{-1} spectral region. The study of FTIR is commonly performed in three spectral segments, near infrared (NIR, 4000–12500 cm^{-1}), middle infrared (MIR, 400–4000 cm^{-1}), and far infrared (FIR, 10–400 cm^{-1}) (Fig. 1). MIR spectroscopy has been well established and most widely applied to study various bonds among C, H, O, N, S, B, X (halides). MIR application covers a wide range of fields [3–6], including chemicals, food safety, environmental monitoring, materials, etc. The application of MIR in catalysis is relatively mature in following the transformation of chemical bonds and groups involved in reactions and over catalyst surfaces.

However, for structural investigation of chemical bonds involving heavier elements, particularly those in inorganic compounds such as metal oxides or salts, spectroscopy in the MIR and NIR regions is not applicable, because the vibration energies of these bonds fall in the FIR spectral region. Therefore, FIR spectroscopy can be used for the characterization of some inorganic compounds [7,8] and some metal coordination complexes [9,10] that may be catalytically active. FIR in the low spectral energy region has been shown to be well suited to

study lattice vibrations [11], hydrogen bonds [12], as well as the skeleton vibration of aromatic molecules [13]. It should be emphasized that FIR remains much under developed and the least applied infrared tool, especially in the study of catalytic mechanisms. This mini review is therefore intended to draw attentions to the potential applications of FIR in catalysis research by discussing some important features of early studies and of some recent literatures. Potential future directions are suggested in the development of FIR for catalysis studies.

2. FIR characterization of catalyst structures

Catalysts are commonly categorized according to their physical state in corresponding reaction systems. Homogeneous catalysts refer to those that are fully miscible and disperse molecular level, while heterogeneous catalysts refer to those in which only surfaces contribute to catalytic activity. When organometallic complexes are used as homogeneous catalysts in solvent media in which reactions take place, such complexes and the reactants are both dissolved in the solvents. Although enzymes as catalysts are also homogeneous in aqueous reaction media together with reaction substrates, absorption bands by water in the IR spectral region (both MIR and FIR) is so intense that IR is not a suitable tool for such systems. Inorganic solid catalysts are mostly present as a heterogeneous phase in either liquid or gaseous reaction phase. Bonds among heavier elements, mostly metals in metallic or higher oxidation states often play major roles during catalysis. Techniques such as extended X-ray absorption fine structure (EXAFS), X-ray crystallography, mass spectrometry, nuclear magnetic resonance (NMR), UV-Vis spectroscopy, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and other specialized methods are often used for characterization of homogeneous catalysts or heterogeneous catalyst [14,15]. These techniques have been proven versatile and informative pertaining to obtain critical mechanistic insights on the role of the catalysts in catalyzing reactions of interest. However, it should be noted that some of these tools are only available in specialized laboratories that are not readily accessible to many researchers.

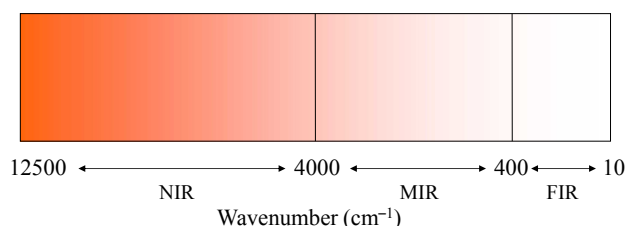


Fig. 1. The regions of infrared spectra.

Even though FIR has not been widely applied as a catalyst characterization tool, like other IR tools, it is simple to operate, and is suited for the characterization of a wide variety of solid catalysts and organometallic complexes. As an underdeveloped spectroscopic tool, FIR offers the potentials to become a low-cost technology to provide structural information related to catalyst functions.

FIR is suited to study organometallic structural configurations. FIR studies of square planar trialkylphosphine complexes of the types *cis* and *trans* MX_2L_2 ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{Me}_3\text{P}, \text{Et}_3\text{P}$) have shown that metal-phosphorus stretching frequencies $\nu(\text{M}-\text{P})$ occur in the narrow range $400\text{--}440\text{ cm}^{-1}$ [16]. Metal-halogen $\nu(\text{M}-\text{X})$ frequencies however, are found in a wider frequency range and are markedly dependent on the *cis* or *trans* geometry of the complex [17]. Boorman et al. [18] studied tetrahedral and square planar adducts of nickel (II) halides with tertiary phosphines and di-phosphines with FIR. Correlations of $\nu(\text{Ni}-\text{X})$ and $\nu(\text{Ni}-\text{P})$ with stereo-chemistry indicate that FIR is a useful technique to distinguish tetrahedral from *cis* or *trans* square planar complexes.

Metal clusters consisting of several metal atoms show spectra unique for each cluster size and exhibit fingerprints of the cluster's structure [19–21]. Fielicke et al investigated the FIR spectra of neutral and cationic niobium clusters of $\text{Nb}_5^{0/+}$ to $\text{Nb}_9^{0/+}$. The experimental spectra were recorded in the $85\text{--}600\text{ cm}^{-1}$ region that covered the structure-specific vibrational fingerprint range for these metal clusters. A comparison of the experimental and calculated Far-IR spectra allows for the identification of the cluster structures. The comparison with theory revealed that the overall geometries for the cations and neutrals are very similar [21].

Important to heterogeneous catalysts, FIR was shown to be able to differentiate structures of solid state catalysts [22–24]. For examples, the alumina phases, boehmite, diaspore, gibbsite and bayerite, can be distinguished by FIR spectroscopy because the low-frequency modes of FIR are generally the most sensitive to the changes of AlO_4 units. Boehmite has two characteristic FIR bands at 366 and 323 cm^{-1} , while diaspore has five bands at $354, 331, 250, 199$ and 158 cm^{-1} . Gibbsite shows three characteristic FIR bands at $371, 279$ and 246 cm^{-1} , whereas bayerite shows six bands at $383, 345, 326, 296, 252$ and 62 cm^{-1} [22]. Thus FIR allows for the study and the differentiation of the stretching of AlO_4 units to characterize these four alumina phases in bauxites.

Microporous materials, particularly zeolites, are widely used as selective adsorbents for separations and as heterogeneous catalysts for catalytic processes. IR spectroscopy of adsorbed probe molecules is a widely used technique for zeolite characterization [25]. CO is the most frequently used molecule to probe zeolite structural and surface properties by monitoring the variation of its IR absorption wavenumber in reference to that of CO in gas phase. Otero Areán et al. [26] studied the stretching vibration of weak $\text{M}^+\cdots\text{CO}$ bond ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) formed upon CO adsorption in different alkali-metal exchanged zeolites at 77 K . As shown in Fig. 2, the wavenumber of the cation-carbon bond vibration $\nu(\text{M}-\text{C})$ increases linearly with increasing the inverse of the square of the cation radius. The ab-

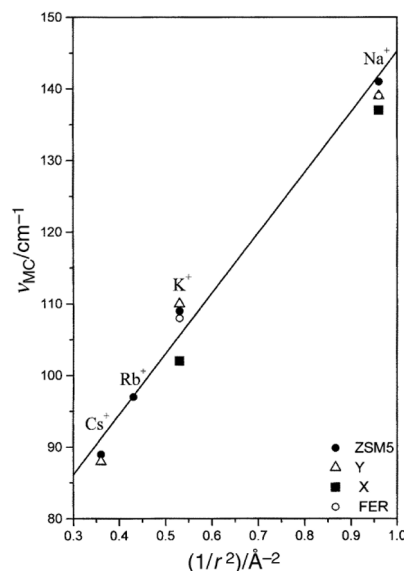


Fig. 2. Plot of the wavenumber of the cation-carbon stretching vibration versus the inverse of the square of the cation radius. Reproduced with permission from Ref. [26].

sorption wavenumber of CO on an alkali ion does not vary appreciably in different zeolites, such as ZSM-5, Y, X and FER. The largest Na–CO vibration wavenumber is 141 cm^{-1} . The high sensitivity of the $\nu(\text{M}^+-\text{CO})$ to the metal ions ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) in the FIR region suggests that it would be possible to quantitatively determine the relative abundance of these metal ions in zeolites.

For CO adsorbed (at 210 K) on ZnO, Saussey et al. [27] reported the $\nu(\text{Zn}-\text{CO})$ fundamental stretching at 215 cm^{-1} . The higher wavenumber of the cation-carbon bond $\nu(\text{M}-\text{C})$ observed for the CO/ZnO system than the CO/alkali-metal exchanged zeolites can be explained by the stronger Zn–CO bond strength due to the higher electric charge density of the Zn^{2+} ion. Thus FIR spectroscopy of appropriate probe molecules may reveal structural details of surface sites by accurately measuring the low energy modes. Furthermore, Engström and Ryberg [28] compared the vibrational properties of the low-energy modes of a molecular and an atomic adsorbate: CO and O on Pt(111) surface by far infrared spectroscopy. For oxygen atoms an antiabsorption dip associated with the frustrated translation was observed, while in contrast, no such dip was observed for the frustrated rotations of CO. Obviously, MIR, FIR spectroscopies become complementary in studying gas adsorption process in catalysis [25,26]. They can be used to study a wide range of energy from 10 to 4000 cm^{-1} and to track light variations of the molecular vibration of adsorbent interaction with the substrate through the whole adsorption process.

3. In-situ FIR study in catalysis

In-situ IR has been widely used for catalyst characterization to gather information about catalyst structure, concentration of reactants, intermediates and products. *In-situ* FIR could lift, to some extent, limitations in the region of middle infrared spec-

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