An Infrared Spectroscopic Study on the Lewis Base Properties of Metal Oxides by using a Novel Probe Molecule: Boric Acid Trimethyl Ester

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Surface Lewis base sites and their basic strength of MgO, CaO, ZrO_2, TiO_2, SnO_2 and Sb_2O_5 have been differentiated with an infrared (IR) spectroscopic approach by using boric acid trimethyl ester as a probe molecule.

Surface acid–base properties are important characters of a solid, in particular, of metal oxides. The acid–base catalysts have been used widely in chemical industry and the acid–base theory has been a big component of current catalysis.[1] The studies on surface acid–base properties have received much attention in catalysis and surface science. In the past decades, the surface acid properties have been well characterized. There have been several successful approaches to characterize surface acid sites and acidic strength. For instance, pyridine and NH_3 have been frequently used to distinguish surface acid sites.[2,3] However, the surface base properties, particularly Lewis base properties of solids are poorly understood. There lacks an effective approach to characterize the surface Lewis base sites even though base catalysts have been increasing their importance in catalysis.[4,5] Although CO_2 has been used to measure surface base sites of oxide catalysts,[6] it is difficult to identify the fine difference of Lewis base sites with the adsorption of CO_2. Recently, pyrrole has also been tried to detect surface base sites,[7–9] even though pyrrole is not a typical conjugate Lewis acid.

In this communication, we report a new method to characterize surface Lewis base sites and strength by using a novel probe molecule, boric acid trimethyl ester (hereafter referred to as BATE). The boron atom of BATE has one empty p_z-orbital which is horizontal to the plane of the molecule. Since the empty orbital of the boron atom has a tendency to accept an electron pair, BATE is a kind of typical Lewis acid. Therefore BATE could selectively interact with surface Lewis base sites. Our results show that the IR spectrum of adsorbed BATE is simplicity, and especially the IR bands related to B–O bonds are very intense and sensitive to surface Lewis base sites. BATE might be an ideal probe molecule for detecting the surface Lewis base sites. In fact, this probe molecule has been successfully used to differentiate the Lewis base properties of metal oxides in this work.

The metal oxides chosen were examples of a strong base oxide (MgO, CaO), a medium base oxide (ZrO_2, TiO_2) and a weak base oxide (SnO_2, Sb_2O_5), respectively. All samples were pressed into self-supporting discs and put in a quartz-made IR cell where the sample can be treated *in vacuo*. The IR cell was connected to a vacuum system and a gas reservoir of BATE. Prior to BATE adsorption, MgO was outgassed at 773 K, CaO was treated in pure O_2 at 973 K to remove surface carbonate species, and the rest of the samples were outgassed at 573 K to remove adsorbed H_2O. After the pretreatment the sample was cooled down to room temp., and then the vapour of BATE was introduced onto the sample. The IR spectra were recorded before and after the adsorption of BATE, and the absorbance given minus the background. The IR spectra were taken on a Perkin–Elmer 580 B IR spectrometer with a 3600 data station.

Fig. 1 gives the IR spectra of adsorbed BATE on MgO, ZrO_2 and SnO_2 together with that of BATE gas phase [Fig. 1(*c*)]. The IR spectra of adsorbed BATE on CaO, TiO_2 and Sb_2O_5 are not shown here since their spectra are almost similar to those for MgO, ZrO_2 and SnO_2, respectively. The IR bands in the vibrational regions of B–O (1420–1250 cm^{-1}) and C–O (1100–1000 cm^{-1}) bonds are sensitive to the surface sites, however, the bands at 3000 cm^{-1} region of the C–H stretch remain almost unchanged for the adsorbed BATE on these oxides. It is believed that the surface Lewis sites, *i.e.* surface oxygen anions, coordinate to a boron atom of BATE, so the B–O bond is firstly affected by the surface coordination. For the sake of brevity, Fig. 1 shows only the bands in the 1800–800 cm^{-1} region. In Fig. 1(*c*) the IR bands at 1480, 1360 and 1030 cm^{-1} of BATE can be assigned to the vibrations of the deformation of methyl, the stretch of the B–O bond and the stretch of C–O bond, respectively. The IR band of methyl at 1480 cm^{-1} is nearly unchangeable for adsorbed BATE on these oxides probably because the methyl is far from the boron atom, however, the IR bands of B–O and C–O vary considerably as seen in Fig. 1(*a*), 1(*b*) and 1(*d*). The Ir band at 1360 cm^{-1} splits into two bands at 1410 and 1300 cm^{-1} for the adsorbed BATE on MgO, and the band splitting can also be observed for the adsorbed BATE on CaO. The band of C–O vibration for adsorbed BATE shifts to higher wavenumbers compared with that of gaseous BATE. This implies that the BATE molecule interacts strongly with surface Lewis base sites so that the degenerated vibration involving the B–O bond splits and shifts significantly. The shift of the IR band of the C–O bond confirms further the coordination interaction not only changes the B–O bond but also the C–O bond. The

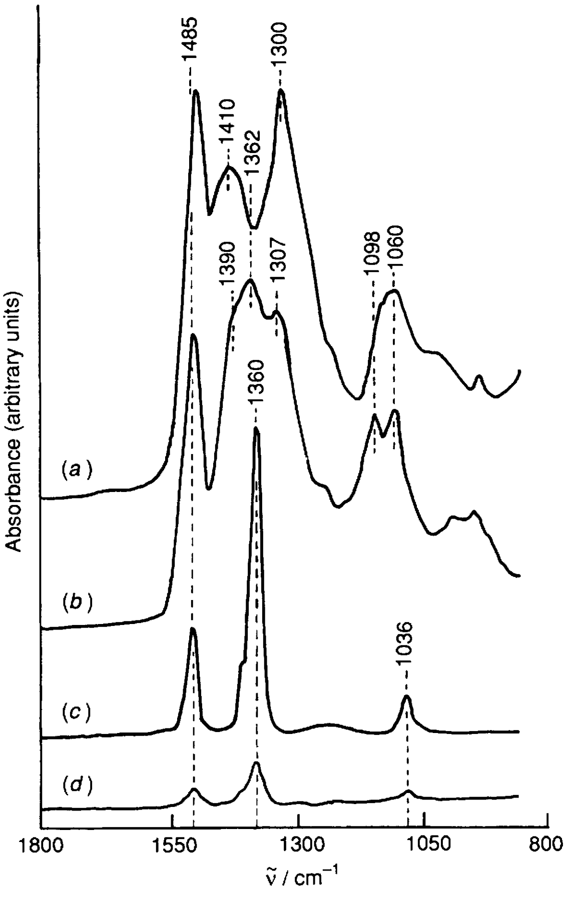

Fig. 1 IR spectra of adsorbed BATE on MgO (*a*), ZrO_2 (*b*) SnO_2 (*d*) and BATE gas phase (*c*), (BATE = boric acid trimethyl ester)

splitting of band at 1360 cm^{-1} together with the large violet-shift of band at 1030 cm^{-1} indicates that the adsorbed BATE interacts strongly with surface Lewis base sites so that the strength of the B–O and C–O bonds are changed dramatically. For the adsorbed BATE on ZrO_2, three bands at 1390, 1362 and 1307 cm^{-1} appear as shown in Fig. 1(*b*). The three bands can be tentatively attributed to two types of adsorbed BATE, one giving the splitting bands at 1390 and 1307 cm^{-1} is similar to that on MgO while the other has the band at 1362 cm^{-1}. The two bands at 1098 and 1060 cm^{-1} of the C–O vibration also reflects that there are two types of adsorbed BATE on ZrO_2 indicating that the surface possesses two types of sites with quite different strengths of Lewis base. This is in accordance with the amphoteric properties of ZrO_2 because there are at least two types of surface oxygen anions which may have different coordination environments or/and different electron densities. In Fig. 1(*d*), the adsorption of BATE on SnO_2 gives very weak bands and the adsorbed BATE is removed easily by outgassing at room temp. The position of these weak bands is identical to the gaseous BATE indicating that the interaction between adsorbed BATE and SnO_2 surface is very weak. While the intensities of adsorbed BATE on MgO are much stronger than that on ZrO_2 and SnO_2, and the adsorbed BATE on MgO and ZrO_2 is difficult to remove *via* evacuation at room temp.

The results in Fig. 1 clearly suggests that the different Lewis sites on metal oxides can be differentiated by the BATE adsorption because the surface oxygen anion with a different electron density has a different electron donating ability towards the boron atom of BATE. The planar structure of $[BO_3]$ in BATE may convert to a pyramidal structure when it interacts strongly with a Lewis site as that for MgO, the E-degenerate mode related to the B–O vibration may split into two bands. For medium strength Lewis base sites adsorbed BATE still keeps its planar structure and the electron donation of Lewis base sites weakens the B–O bond, and as a result, the vibrational frequency of the B–O bond shifts to a lower frequency. The strength of the Lewis base site on SnO_2 is very weak, accordingly the IR spectrum of adsorbed BATE retains the identity of the gas phase [Fig. 1(*c*) and 1(*d*)]. This means that the types of surface Lewis base sites can be distinguished by the IR spectra of the adsorbed BATE on them. On the basis of the IR results, the Lewis base strength of above metal oxides should be in the following order, MgO, CaO > ZrO_2, TiO_2 > SnO_2, Sb_2O_5.

In this study, BATE is found to be a sensitive probe molecule to detect and distinguish the surface Lewis base sites, surface oxygen anions. BATE interacts selectively with surface Lewis sites and its IR spectrum supplies the direct information of both the types of Lewis base sites and the strength of Lewis base of metal oxides.

This work was supported by the Natural Science Foundation of China (NSFC).

Received, 19th July 1993; Com. 3/04229D

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