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Comprehensive IR study on acid/base properties of metal oxides

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ABSTRACT

Acid/base properties (type, strength, number) of a wide range of metal oxides were studied by IR (infrared) spectroscopy. Ammonia, pyridine and CD_3CN were used as probe molecules for acidity measurement. CO_2, $CHCl_3$, benzaldehyde and nitrobenzene were used for basicity measurement. Pyridine for the nature and number of acid sites, CD_3CN for the strength of acid sites, $CHCl_3$ for the strength of basic sites and nitrobenzene for the number of basic sites were found to be suitable probes. The absorption coefficients of pyridine for acidic sites and nitrobenzene for basic sites, estimated for various metal oxides by IR coupled with mass spectrometry, were within ±10% of the average value, which indicates that the integrated molar extinction coefficients could be used for semi-quantification of acid/base sites of various oxides samples. The comprehensive IR results in this study will be available to characterize properties of Lewis and Brønsted acid sites and basic sites on metal oxides by a simple IR experiment.

1. Introduction

Solid catalysts, including solid acid, solid base and supported metal catalysts, are important from both academic and industrial viewpoints [1–5]. Solid acid and base catalysts are mainly metal oxides, and many of the supported metal catalysts are bifunctional catalysts composed of transition metals and metal oxides with different acid/base properties. Therefore, catalytic properties of many heterogeneous catalysts depend strongly on their acid/base properties [6–12]. In order to design new catalysts, a convenient index for acid/base properties of a wide range of metal oxides is needed. Physical parameters such as electronegativity have been used as a conventional index, but a chemical index is more preferable. The titration of acidic and basic sites using indicators in aprotic solvents such as benzene or hexane is a classical method to obtain a chemical index of acid/base properties of solids [13–15], but this method have at least three problems. First, the titration cannot be conducted in aqueous suspension, because this would eliminate the differences in acid strength of the various sites. Second, bulky indicator molecules are hindered from diffusing into the interior of the metal oxides, which may cause the miss judgment because visual observation of the indicator molecules and their change upon protonation by acid sites is restricted to the surface. Third, generally used indicators are not selective for either Brønsted or Lewis acid sites. Temperature-programmed desorption (TPD) has been used for analysis of acid/base properties of solids [16,17]. Other techniques, including the measurements of adsorption isotherms and isobars and calorimetric measurements, have also being used for the characterization of the acid/base properties of solids [16,18,19]. However, these methods cannot be used for discrimination of the type (Brønsted or Lewis type) of acid sites except for a method by Matsuhashi et al. [20,21]: comparison of adsorption hearts of N_2 and Ar.

IR spectroscopy is a powerful tool for identifying the nature (type and strength) of acid/base sites [22–34]. It can easily distinguish between Brønsted and Lewis acids by using probe molecules such as ammonia or pyridine [27–30]. Acid and base strength of metal oxides can be estimated from peak shift values of adsorbed probe molecules [35–37] or from the profile of absorbance versus desorption temperature [35]. Experimental determination of the integrated molar extinction coefficient enables us to estimate the number of acid and basic sites [27,31–34]. For example, Niwa and co-workers reported that IR combined with NH_3-TPD method simultaneously gave the information about acid-type (Brønsted and Lewis) and strength and number of acid sites of zeolites and sulfated ZrO_2 [38–40]. However, in the case of metal oxides such as SiO_2, the main fingerprint band of Lewis acid sites overlaps with the absorption of SiO_2, indicating that NH_3 cannot be widely applied. Although other basic probes (pyridine and CD_3CN) and acidic probes (CO_2, $CHCl_3$, and benzaldehyde) have been applied to characterize acid/base properties of a specific metal oxide, there are few IR studies on a wide range of metal oxides under the same

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