

CHAPTER II

LITERATURE REVIEW

2.1 Reviewed literature

Papers that concern with the characterization of basic sites on catalyst are shown as follows.

Scokart and Rouxhet (1980) investigated the adsorption of pyrrole on various metal oxide by infrared spectroscopy. They found that the shift of the NH stretching band due to H bonding allowed the detection of basic sites on the surface and estimation of their strength. They also showed that pyrrole may be used to probe molecule for Lewis acid sites and the polymerization or decomposition of pyrrole did not affect the interpretation of spectra and the assignment of NH bands.

Huang and Kaliaguine (1992) showed that the basicity of alkali-metal cation X, Y, mordenite and ZSM-5 could be characterized by the bathochromic shift of the IR NH-stretching vibration on which it was used to monitor the framework oxygen basicity. It was shown that the basic sites detected by pyrrole adsorption in zeolite were Lewis bases. This was in agreement with the view that the basic sites in zeolites were the framework oxygens adjacent to the cations. Moreover the coexistence of two NH-stretching bands in the spectrum of pyrrole chemisorbed in a zeolite containing two kinds of cations indicated that the basicity of these sites was determined mainly by the local environment rather than by the bulk zeolite composition. The basicity in higher Si zeolites became weaker both in basic strength and the density of basic sites, as indicated by the high NH-stretching frequency and the weak band intensity. A pyrrole species associated with acid sites was also detected.

Xie *et al.* (1994) investigated adsorption of pyrrole on alkaline earth exchanged X zeolites using FTIR spectroscopy. They found that Lewis basic, Lewis acidic (cations) and also Brönsted acidic sites coexisted in these zeolites. The NH stretching frequencies of pyrrole adsorbed on both basic and acidic sites were related with the charge on the oxygen and cations. This relationship supported their idea that the alkaline earth cations in faujasite existed in the form of $(\text{MOH})^+$. These cations would then be the Lewis acidic sites in these zeolites, while the adjacent framework oxygens were the basic sites. Brönsted acid sites were also produced due to the dissociation of water, however, the portion of these Brönsted acid sites that could be detected by pyridine adsorption was relatively small.

Davydov *et al.* (1995) studied basic sites of various oxide catalysts for oxidative methane coupling with the IR spectra of CO_2 probe molecules since it was possible to determine the concentration and strength of surface basic sites. Since the surface structure was non-uniform, its oxygen ions carried different negative effective charges and thus produced carbonates, exhibiting different IR spectra. A correlation between the site strengths and carbonate's spectral behaviour found earlier, allowed them to distinguish the sites rather well. The catalytic activity of oxide catalysts was found to depend on the presence and concentration of the strongest basic sites on the oxide surface.

Binet *et al.* (1996) studied pyrrole adsorption on various metal oxides: reduced or unreduced ceria, alumina dehydroxylated to varying extents and in NaX zeolite. Pyrrole adsorption was found to be either non-dissociative or dissociative on the more basic adsorption sites), the pyrrolate anion being formed in the latter case. When bound to surface hydroxy groups through an H-bond, the pyrrolate anion was thought possibly to be non-planar; complex progressions of IR bands were then observed involving the combination of CH-stretching modes with a ring-deformation vibration. When pyrrole was non-dissociatively adsorbed through an $\text{NH}\cdots\text{O}$ bridge with O^{2-} moderately basic surface centers, the shift of the NH-stretching frequency reflected the O^{2-} basicity. Interaction with surface hydroxy groups led to $\text{NH}\cdots(\text{OH})$ hydrogen-

bridged species, which have been found to be either cyclic or linear according to whether the hydroxy groups were monodentate or bidentate, respectively.

Kaßner and Baerns (1996) studied the surface basicity and acidity of alkaline earth metal oxides which had earlier been tested as catalysts for the oxidative coupling of methane. For determining the acid-base properties two probe reactions, i.e., the decomposition of 2-propanol to acetone and propene and the retroaldolization of diacetone alcohol, further the temperature-programmed desorption (TPD) of CO₂, the benzoic acid titration with Hammett indicators and DRIFT spectroscopic investigations of the adsorption of CO₂ and pyridine were applied. The decomposition of 2-propanol was found to be of restrictive applicability for determining the basicity of a metal oxide.

Murphy *et al.* (1996) investigated the use of pyrrole as an IR spectroscopic probe. It was found that the overall Lewis basicity in EMT zeolites increased as the cation was exchanged from LiEMT to CsEMT in the alkali cation series. The shift in the $\nu(\text{NH})$ stretching frequency of adsorbed pyrrole correlated with the oxygen charge in the respective EMT samples. Computer deconvolution of the main and broad $\nu(\text{NH})$ band of pyrrole chemisorbed on basic sites was performed using a band simulation program. This analysis revealed that the broad $\nu(\text{NH})$ band is actually composed of four individual $\nu(\text{NH})$ component bands in Li, Na, Rb, and CsEMT, each one representing pyrrole adsorbed on a distinct basic site. These four bands evidence the intrinsic heterogeneity of basic sites existing in the EMT zeolite. This heterogeneity is shown to depend on both the nature and the location of the exchanged cations.

Lavelly (1996) reviewed infrared spectra analysis of species formed by acid probe adsorption on divided metal oxides and alkaline zeolites which could lead to information on their surface basicity, particularly on the nature and strength of basic sites. Results obtained from carbon monoxide, carbon dioxide, sulfur dioxide, pyrrole, chloroform, acetonitrile, alcohols, thiols, boric acid trimethyl ether, ammonia and pyridine were critically reviewed. It was concluded that no probe would be

universally used. Pyrrole in the case of alkaline zeolites, CO₂ for weakly basic metal oxides and for basic OH groups and CO for the characterization of highly basic structural defects on metal oxides activated at high temperature appeared quite suitable probes. When other methods were used (TPD, microcalorimetry, volumetry, etc.) IR spectroscopy was a complementary method necessary for the knowledge of the type of sites involved; in particular, data obtained from CO₂ and SO₂ adsorption had to be carefully used since both probes which led on highly basic metal oxides to polydentate species which did not result from their adsorption but from their reaction with the given oxide. Ammonia and pyridine, generally used as probes for the acidity of catalysts, also adsorbed on basic oxides through a dissociative chemisorption.

Yang *et al.* (1997) investigated zeolite β (with a Si/Al ratio of 15.2) aluminated with NaAlO₂ solution. The basicities of the aluminated samples were investigated by FTIR spectroscopy using pyrrole as a probe molecule. It was found that the NH-stretching frequency of pyrrole adsorbed on the sample shifted towards lower wavenumbers as the Si/Al ratio was decreased and correlated well with the negative charge on the framework oxygen calculated from the Sanderson electronegativity equalization principle. These results revealed that zeolite β possesses a stronger overall basicity after alumination; hence, the alumination was an effective method to improve the basicity. It was furthermore found that the strength of the basic sites was heterogeneous and that stronger basic sites were created by the alumination procedure.

Kustov (1997) reviewed modern trends in IR-spectroscopic characterization of acid and basic sites in zeolites and oxide catalysts. Besides the enhancement of the sensitivity of IR spectroscopy due to application of Fourier-transform techniques, the progress in characterization was shown to be related to the broadening of the spectral range (investigation of overtones, combination bands, and low-frequency modes) and the use of new non-traditional probe molecules for identification of acid and basic sites.

Scire and coworkers (1998) studied effect of the addition of calcium as promoter on the basic properties of Pd/Al₂O₃ system by FTIR of pyrrole in order to clarify performance of palladium supported catalysts in the selective hydrogenation of phenol to cyclohexanone. The obtained results showed that the addition of calcium caused an increase in the number and strength of the basic sites. They suggested that the promoter enhanced the catalytic performance of Pd/Al₂O₃ through a variation of the acid-base characteristics of the support leading to a modification of the electronic surroundings of Pd sites on which hydrogen is activated.

Zecchina *et al.* (1998) reviewed a very general definition of acids and basis, following both Brønsted and Lewis theories, since the starting point in order to introduce the concept of the acid and basic strength of surface sites. The surface of an oxide was described as a bidimensional organization of acid-base pair (AB), whose strength could be measured by probe molecules. It was shown that in order to obtain a reasonable scale of surface acidity and basicity, probe molecules characterized by minimal interaction energy had to be used. Among the probe molecules, which could be employed to measure surface acidity, carbon monoxide was the most useful. On the contrary, a probe molecule specific and highly sensitive for basic sites was missing.

Binet *et al.* (1999) studied surface properties of high surface area ceria samples, either in the reduced or unreduced state, using FTIR spectroscopy. Upon reduction, detailed features in the background spectrum of unreduced samples, which may be assigned to surface, vanished while weak bands due to electronic transitions appeared. One of these bands was assignable to Ce³⁺ as point defect in the core. Adsorption of probe molecules was used to characterize the Lewis acid-base strength of surface sites. Adsorption of a proton donor (pyrrole) or an electronic acceptor (CO₂) was indicative of the high basicity of surface O²⁻ ions for ceria either reduced or not. The acid strength of cerium ions was weak; its decreased upon reduction may be shown by adsorbing weak Lewis bases (CO, acetonitrile) but not by stronger ones (pyridine, dimethylether).

Matsumoto *et al.* (1999) investigated adsorption characteristics and polymerization of pyrrole on Y-zeolites of different cation types in connection with adsorption behaviour using in situ IR spectroscopy, and EPR spectroscopy. Adsorption of pyrrole on NaY was physisorption giving no significant changes in IR and EPR spectra. In the adsorption on HY and CuY, the formation of pyrrole oligomers or polymers was observed.

2.2 Comment on previous work

From the above reviewed literature, it can be seen that as a probe molecule, pyrrole possesses various advantages: its vapour pressure is suitable for studying adsorption from the vapour phase. Another important feature, which may be an advantage or disadvantage, is probably its amphoteric character allowing it to interact with both basic and acidic sites (Lewis and Brønsted acids). Generally, the adsorption of pyrrole on basic sites causes a relatively large bathochromic shift of its NH stretching frequency, because the hydrogen atom of the NH bond interacts directly with the basic sites. On the other hand, the adsorption on acid sites causes just a relatively small bathochromic shift in NH stretching frequency, because the acid sites interact with the pyrrole ring rather than the hydrogen atom of the pyrrole molecule. However, the characteristic IR band of pyrrole for basic sites was very weak due to the lower density of basic sites in catalysts. Furthermore, there are some problems about interpretation of FTIR data because the position of NH-FTIR bands interfere with the OH bands of the adsorbents.

Although the basicity measurement by using pyrrole as a probe molecule has been received much attention rather than other probe molecules, there are many problems with interpretation of IR bands and experimental procedures which are listed to depend on samples to be characterized. In order to investigate the difference of two types of basic sites, this research intends to distinguish IR adsorption bands between Brønsted basic sites and Lewis basic sites by adsorption of pyrrole on two types of catalysts: metal oxide and metal hydroxide. Magnesium oxide and calcium

hydroxide are the representative of metal oxide and metal hydroxide respectively. In the same way, NaY and Na-mordenite are the representative of zeolite that is used for testing by pyrrole adsorption.