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Temperature programmed desorption studies on a new active zinc oxide catalyst

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Abstract

The present work describes the characterisation of a new active zinc oxide catalyst by combined study of temperature programmed desorption (TPD) of adsorbed ammonia and infrared (IR) spectroscopy of ammonia adsorbed at different levels. This zinc oxide showed an unusually high acidity ~7.0145 mmol/g in terms of adsorbed ammonia. TPD profile gave three distinct regions at 433, 573 and 673 K unlike other zinc oxide sample which showed only two distinct peaks at low and medium temperatures. Attempts are made to classify these peaks into strong and weak B and L acid sites, with complementary evidence from IR spectroscopic studies.

Keywords: Temperature programmed desorption; Infrared spectroscopy; Zinc oxide catalyst

1. Introduction

Zinc oxide is a well-known catalytic material in a large number of industrial processes. It is known that the acidity and catalytic activity of a zinc oxide catalyst is very much dependent on the method of its preparation [1,2]. The active zinc oxide described in this work showed unusually high acidity and also a higher catalytic activity compared with zinc oxides prepared by conventional routes. Zinc oxide is basically a dehydrogenating catalyst on which dehydration can also take place [3]. In the present investigation, acidity of ZnO prepared from $Zn(NO_3)\cdot 6H_2O$, urea and oxalic acid is determined by temperature programmed desorption (TPD) and infrared spectroscopy (IR) studies using ammonia as a probe molecule. The studies showed the presence of both Brønsted and Lewis acid sites above 673 K. These acid sites are responsible for the higher dehydration [3,4] activity of this ZnO catalyst in acetamide dehydration and in propan-2-ol decomposition reactions.

2. Experimental

Synthesis of the zinc oxide catalyst is described previously [3], and involved heating an intimate solid mixture of $Zn(NO_3)\cdot 6H_2O$, oxalic acid and urea in the molar ratio 1:1:2 at 653 K for 6 h. In the present study, TPD was carried out using NH_3 as a probe molecule. Before adsorption of ammonia, the catalyst was activated at 393 K in a stream of oxygen gas. Dried ammonia gas was then passed over the catalyst for 30 min at a flow rate of 5 ml/min. The amount of ammonia desorbed at various temperatures measures

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catalyst acidity which was expressed in mmol/g of catalyst. In another experiment, the catalyst sample was evacuated and exposed to ammonia for 20 min followed by outgassing at 393 K for 1 h. The ammonia adsorbed sample was heat treated at various predetermined temperatures to attain selective desorptions and their IR spectra subsequently recorded in KBr pellets.

3. Results and discussions

One of the widely used techniques for characterisation of acid sites and their distribution on solid acid catalysts is TPD of adsorbed bases such as pyridine or ammonia. Characterisation of the catalyst by IR spectroscopy after various stages of desorption is often useful to identify the nature of acid sites, and is a

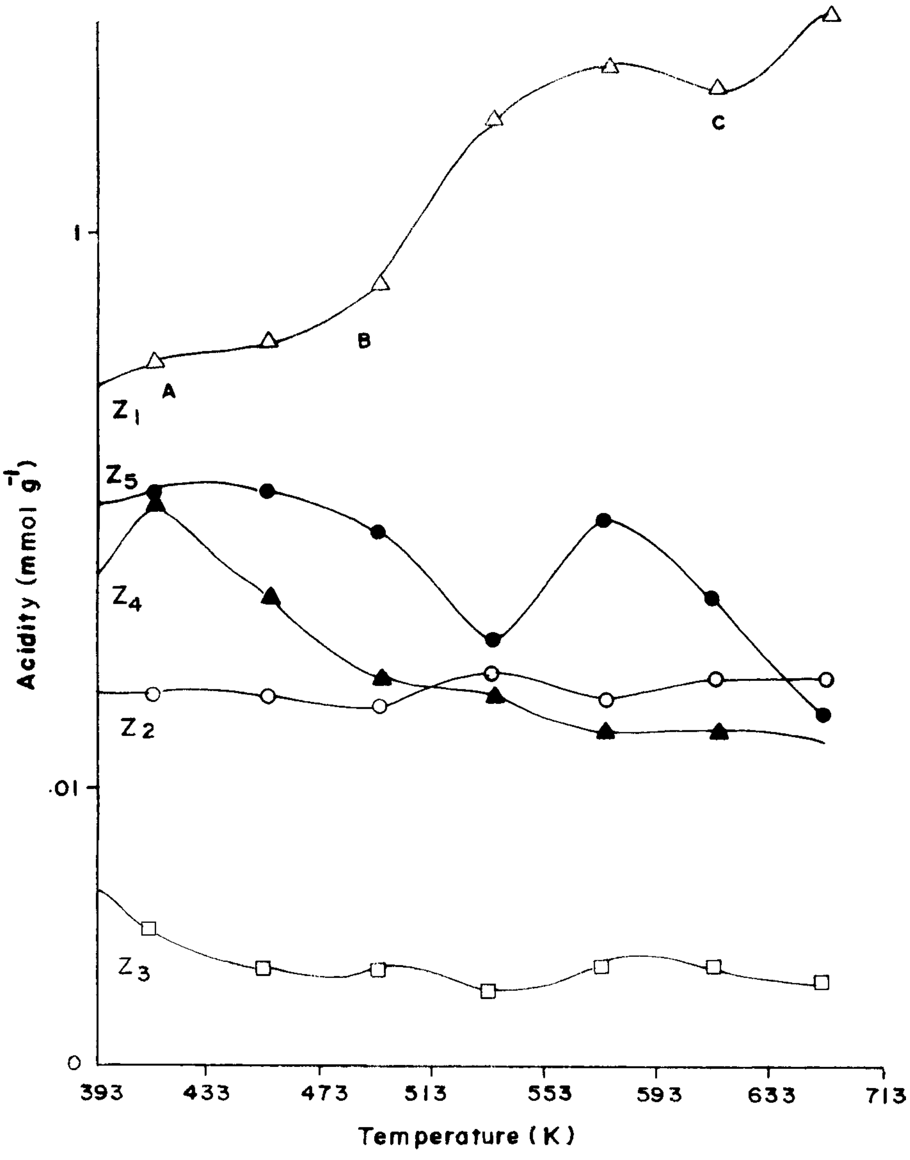

Fig. 1. TPD profiles of zinc oxides using adsorbed ammonia.

complementary technique to TPD. For ammonia adsorbed on ZnO, the following IR absorptions are reported [4] for B and L sites, 3420, 1630, and 1220 cm^{-1}. Yin et al. [5] reported IR absorptions at 1240 and 1285 cm^{-1} due to ammonia coordinated to two kinds of L sites. The N–H stretching range of adsorbed ammonia is characterised by broad but less resolved bands between 2400 and 3400 cm^{-1}. Below 1800 cm^{-1} resolved N–H bending modes of NH_4^+ adsorbed on different B and L sites are observed. Issao and coworkers [6] have reported high acidities (~2 mmol/g) for a zinc oxide precipitated from chloride medium.

The TPD profiles of the zinc oxide catalyst is given in Fig. 1; it is clear that the sample Z_1 has much higher acidity as compared to the other samples; the total acidity of Z_1 is estimated to be ~7 mmol/g. Also Z_1 shows three distinct acidity regions while all other samples showed at most two peaks in the TPD profiles, analogous to zeolite catalysts. In the TPD spectra of ammonia adsorbed zeolites, usually two peaks at temperature maxima around 457 and 725 K (known as low temperature (LT) and high temperature (HT) peaks) are observed [7,8]. High peak temperatures correspond to higher acid strength. The desorption of ammonia from HT peak is often due to ammonia bound to strong structural B sites. It is also possible that some of the desorbed ammonia from strong L sites is included in the HT peak. That overlap between B and L site peaks (both weak and strong) is possible, is reported earlier. Careful analysis of TPD profiles of H-mordenites (ammonia adsorbed) show that the two main peaks are a composite of four different types of acid sites, i.e. weak and strong B and L sites. [9] The results of the present work are discussed in the above context.

The TPD profiles of ZnO catalysts of the present work show two peaks; the LT peak around 433 K and

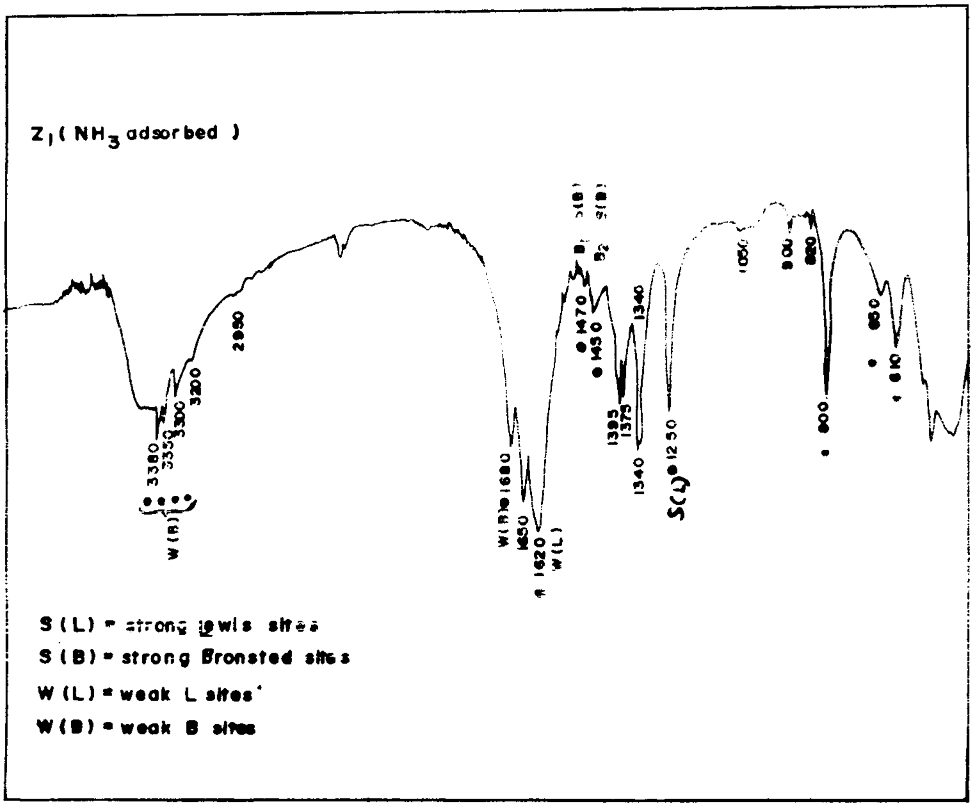

Fig. 2. IR spectra of ammonia adsorbed on Z_1 at room temperature.

HT peak around 573 K. Both these peaks may therefore be tentatively assigned to weak and strong L sites, respectively. The TPD profile of Z_I may be divided into three distinct regions. AB region around 453 K could be associated with weak L sites. BC, the main acidity region of ZnO with a maximum around 573 K, may be ascribed to the presence of large number of catalytically active L sites. This sample of zinc oxide also shows another distinct acidity region CD with T_{max} ~673 K, that may be associated with strong B

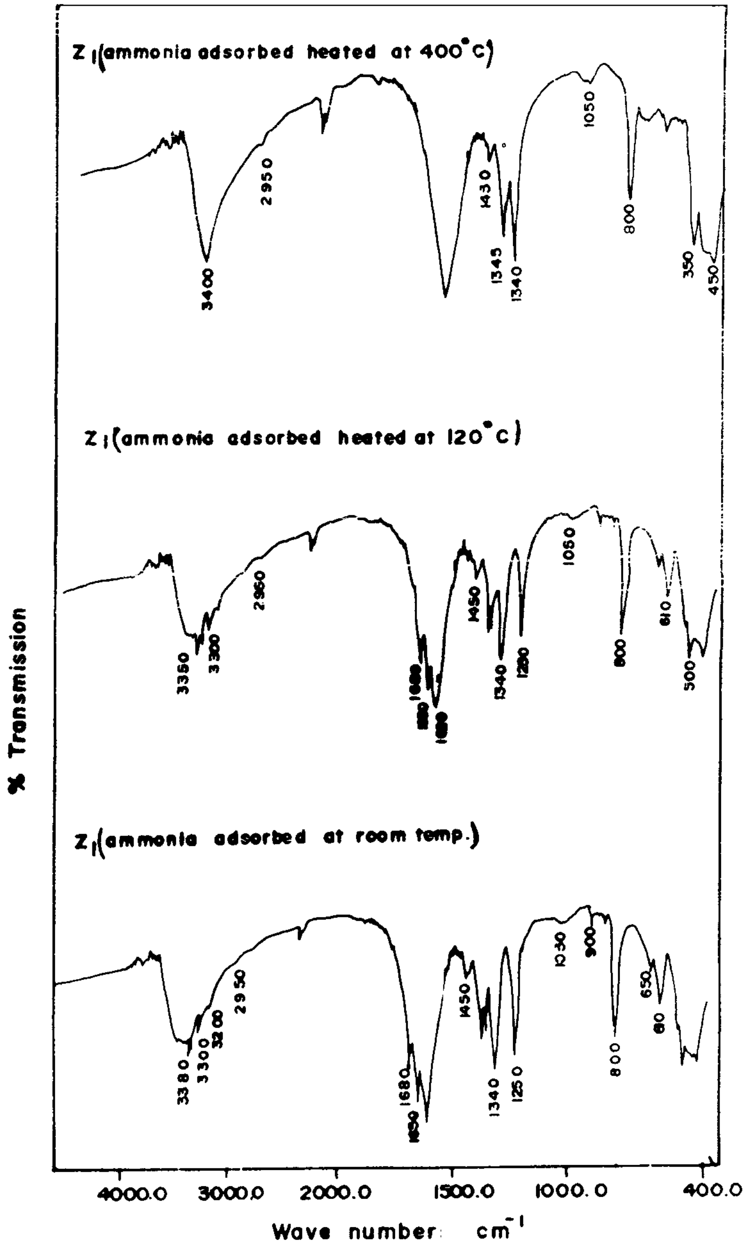

Fig. 3. IR spectra of ammonia adsorbed on Z_I at different temperatures.

sites. In order to get better insight into the nature of the acid centres of this highly active zinc oxide, the IR spectra of samples containing adsorbed and partly desorbed ammonia were analysed. The data are presented in Figs. 2 and 3. Fig. 2 gives the IR spectrum of Z_1 containing adsorbed ammonia. Fig. 3 gives the IR spectrum of the same sample heat treated at 393 K, to drive away any physisorped ammonia. There is no difference in the two spectra indicating that the additional peaks following ammonia adsorption, are only due to chemisorped ammonia on B or L sites. These additional peaks are marked as •, while peaks marked **e**, represent enhanced intensities of the existing absorptions following ammonia adsorption. The additional absorptions are identified and labeled as per literature assignments [4,10,11].

Thus, the LT (or AB) region in TPD of Z_1 could be an overlap of weak B and L sites, the weak L sites identified by the absorptions at $1620\,cm^{-1}$, which manifests by splitting of the main $1650\,cm^{-1}$ absorption of the pure ZnO. The prominent absorption at $1250\,cm^{-1}$ is due to strong sites which should obviously be in high concentration. This is reflected in the main TPD region BC. The absorptions at $1680\,cm^{-1}$ could be N–H bending deformation mode of ammonia adsorbed on weak B site, while the small absorptions between 3200 and $3400\,cm^{-1}$ are the corresponding stretching N–H modes, indicative of a narrow energy distribution of the weak B sites. The figure also shows two small absorptions at 1470 and $1450\,cm^{-1}$. Bands around this value are most characteristic of NH_4^+ due to asymmetric deformation of N–H. These absorptions, particularly the one at $1450\,cm^{-1}$ persists even after heat treatment of the sample at 673 K (Fig. 3). Hence these bands are due to two types of strong B sites, of slightly differing strength. It may be noted that below 673 K, peaks due to weak B and L sites as well as due to strong L sites, all disappear.

These strong B sites should correspond to the HT peak in the region CD of its TPD profile. These sites could be associated with structural hydroxyls. Existence of such hydroxyls which could be removed by heat treatment beyond 723 K has been earlier reported [12].

Acknowledgements

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