ACID-BASE, ELECTRON DONATING AND CATALYTIC PROPERTIES OF SULFATED ZIRCONIA

S. Sugunan, C.R.K. Seena and T.M. Jyothi
Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India

Received June 10, 1998
In revised form November 11, 1998
Accepted January 26, 1999

Abstract

The electron donating properties of sulfated zirconia were studied from the adsorption of electron acceptors of various electron affinity. The surface acidity and basicity of the oxides have also been determined by titration method using a set of Hammett indicators. The data have been correlated with the catalytic activity of the oxide towards esterification of acetic acid using n-butanol, reduction of cyclohexanol in 2-propanol and oxidation of cyclohexanol with benzophenone.

Keywords: Sulfated zirconia, solid acids, electron donating properties

INTRODUCTION

The use of sulfated zirconia is of increasing interest because of the superacidic properties induced by the presence of SO$_4^{2-}$ [1,2]. They have been exploited in a variety of reactions of industrial importance [3]. Though a number of studies have been reported about sulfated zirconia the origin of superacidic properties of sulfated zirconia still remains controversial. The aim of the present work is to understand the sources of increased acidity after sulfate modification. That is to find out whether the increase in acidity due to sulfation is at the expense of basic sites already present on the surface or it can be due to the generation of new acid sites. The electron donor properties of the oxides are a measure of surface basicity. Hence the change in electron donating properties and surface acidity
SUGUNAN et al.: SULFATED ZIRCONIA

and basicity are measured. Esterification of acetic acid using n-butanol, reduction of cyclohexanol in 2-propanol and oxidation of cyclohexanol with benzophenone are test reactions to find out catalytic activity.

EXPERIMENTAL

Zirconia was prepared from zirconium nitrate by hydroxide method using a standard procedure [4]. The oxide was sieved to samples below 75 μ mesh size. Sulfation was carried out by impregnation method using 0.2 M ammonium sulfate solution [5]. Samples activated at different temperatures (300, 500 and 700°C) were used. The surface area was determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The acidity and basicity were determined by standard procedures [6], using the following indicators (pKa values are given in parentheses): crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroaniline (18.4). The strength distribution of electron donor sites on the oxide surface was determined by the adsorption of the following electron acceptors (EA) in acetonitrile as solvent (the electron affinity values are given in parentheses): 7,7,8,8-tetracyanoquinodimethane (TCNQ, 2.84 eV), 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil, 2.40 eV), p-dinitrobenzene (PDNB, 1.77 eV) and m-dinitrobenzene (MDNB, 1.26 eV). The method for adsorption studies is described elsewhere [7]. The amount of EA adsorbed was determined by UV-visible spectrophotometry and the adsorbed state of EA was studied by EPR spectroscopy (Varian E-112 X/Q band) and reflectance spectra (Shimadzu UV-160A UV-visible spectrophotometer with a 200-053 reflectance attachment). IR spectra of the oxides were taken on a Shimadzu IR-470 spectrophotometer. Catalytic activities for reduction, oxidation and esterification reactions were determined in liquid phase by standard procedures reported earlier [8,9].

RESULTS AND DISCUSSION

The acidity and basicity were determined on a common Ho scale, where strength of the basic sites was expressed as Ho of the conjugate acid. Results are given in Table 1. The acid base distribution curves intersect at a point on the abscissa where acidity = basicity = 0 and it is termed Ho,max [10]. It is a practical parameter to represent acid base properties of solids which is very sensitive to surface structure.