Short communication

Influence of transition metals on the surface acidic properties of titania prepared by sol–gel route

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Abstract

A series of titania catalysts containing chromium, molybdenum as well as tungsten has been prepared by colloidal sol–gel route using metatitanic acid as the precursor. Structural characterization of the prepared catalysts was done with Energy dispersive X-ray analysis, X-ray diffraction, BET surface area and pore volume measurements. The influence of different transition metals like chromium, molybdenum and tungsten on the surface acidic properties of titania is investigated in detail. Two independent methods have been used to study the surface acidity of these catalyst systems: temperature programmed desorption of ammonia which is a measure of total acidity and thermodesorption studies using 2,6-dimethyl pyridine which is a measure of Bronsted acidity. Cumene cracking reaction is carried out over the prepared systems for further characterizing the acidity of the prepared catalysts. Remarkable enhancement in the surface acidity is observed after transition metal incorporation. The catalytic activity of the prepared catalysts was tested towards the dehydrogenation of cyclohexane.
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1. Introduction

The replacement of liquid acids by solids is now considered as highly desirable in order to design clean processes for better protection of the environment [1]. Most of the solid acid catalysts used in various chemical transformations are based on inorganic oxides. In most cases, these oxides are to be modified chemically or physically so as to get the desired catalytic activity for a particular reaction. Oxides, because of their ability to take part in the exchange of electrons, protons or oxide ions are used as catalysts in both redox as well as acid base catalysis [2]. In metal oxides, coordinative unsaturation is principally responsible for the ability towards adsorption and catalysis of various reactions. The exposed cations and anions of the metal oxide surfaces form acidic and basic sites as well as acid–base pairs. Besides this, the variable valency of the cation results in the ability of the oxides to undergo oxidation and reduction. The catalytic activities of the solid acids are not only related to the surface concentration of acid sites, but also depends on their nature (i.e. Bronsted or Lewis type) and strength [3].

Titania is now the object of increasing interest in the field of heterogeneous catalysis. The interactions between metal oxides and the oxide supports have attracted much attention because of the wide application of the supported metal oxide systems. It is well known that the supported oxides of transition metals are widely used as catalysts for

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various reactions. There are three common titania polymorphs—anatase, brookite and rutile. Both anatase and rutile have been extensively studied for photocatalytic applications with the former found to be the most suitable for photocatalytic reactions [4]. One of the most important applications of the sol–gel method can be found in the field of catalysis. The properties of catalysts and support materials strongly depend on the preparation procedures [5–11]. The high porosity and large specific surface area of materials prepared by sol–gel route make them very attractive from a catalytic point of view. The relatively low surface area as well as poor stability of titania structure at high temperature is the main disadvantage of titania while using as a catalyst or a catalyst support [12]. The sol–gel synthesized titania and its modification with other metals overcomes these limitations.

The aim of the present work is to prepare titania and their transition metal modified analogues through colloidal sol–gel route and to characterize its structure using various physico-chemical techniques. Furthermore, a detailed investigation on the surface acidic properties of the prepared catalysts is also carried out using different independent techniques.

2. Experimental

Transition metal modified titania catalysts (2, 6 and 10 wt. %) were prepared by sol–gel method. The precursor used is metatitanic acid i.e., hydrated titania (Travancore Titanium Limited, Kerala). Titanyl sulphate is obtained by dissolving the precursor in concentrated sulphuric acid. Ammonia is added to this until complete precipitation of titanium hydroxide occurs. The sulphate freed precipitate is suspended in hot water and added 10% HNO_3 drop wise until a stable sol is obtained at a pH of around 1.5. Calculated amounts of the metal to be incorporated is added to the clear sol before gelation. Gelation is done chemically by slightly perturbing the pH of the sol by the addition of drops of ammonia. The gel is oven dried at 383 K for 12 h and subsequently calcined at 773 K for 5 h in air atmosphere. The catalysts are denoted as TiXy where X is the symbol of the incorporated metal and y is its corresponding weight percentage.

XRD patterns of the samples were recorded between $10°$ and $70°$ 2θ on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu Kα radiation source ($\lambda = 1.5406$ Å). The BET surface area and pore volume measurements were carried out by nitrogen adsorption at 77 K using a Micromeritics Gemini-2360 surface area analyzer. The precalcined samples were outgassed for 4 h at 400 °C in nitrogen atmosphere prior to the sorption measurement. EDX spectra of the samples were recorded in an EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si-Li detector). To determine the total acidity of the catalysts, temperature programmed desorption was done using NH_3 as the probe molecule. Prior to the experiment, the catalysts were activated inside the reactor at 300 °C for 30 min with continuous flow of nitrogen. After cooling to the room temperature, a specific volume of ammonia was injected in the absence of the carrier gas and allowed to attain equilibrium. Excess physisorbed ammonia was removed by the flow of nitrogen. Then the temperature program is done from room temperature to 600 °C in a stepwise manner. The ammonia desorbed at each interval of 100 °C was collected in a known volume of dilute sulfuric acid and estimated volumetrically by titration with standardized NaOH. 2,6-Dimethyl pyridine (2,6-DMP) adsorbs strongly on Bronsted acid sites and forms weak bonds with Lewis acid sites. The 2,6-dimethyl pyridine weakly bound to the Lewis acid sites get desorbed below 300 °C. Hence thermodesorption study of 2,6-dimethyl pyridine adsorbed sample beyond 300 °C can give the measure of Bronsted acid sites. The samples were activated at 500 °C for 1 h and kept in a dessicator saturated with 2,6-dimethyl pyridine for 48 h. It is then subjected to TG analysis at a heating rate 20 °C/min. in nitrogen atmosphere. The percentage of weight loss in the temperature region 300–600 °C is divided into weak (300–400 °C), medium (400–500 °C) and strong (500–600 °C) acid sites. Gas phase cumene cracking reaction is carried out in a vertical down flow glass reactor under the flow of nitrogen using 0.5 g of the catalyst. The catalysts were placed in the reactor and supported on either side with a thin layer of glass wool and ceramic beds. The reactor was heated to the reaction temperature with help of a tubular furnace provided with a temperature controller. The catalyst was activated at 500 °C for 2 h before the catalytic runs. Reactants were fed into the reactor using a syringe pump. The bottom of the reactor was connected to a coiled condenser and receiver to collect the products. The products obtained in the first hour were discarded and the products collected after different times-on-stream was analyzed. The activities and selectivities considered for comparison of the behaviour of the different catalysts are those obtained after 2 h. The same reaction set up is used for the catalytic dehydrogenation of cyclohexane. The products were analyzed by gas chromatography (Chemito GC 1000) using BP1 capillary column (12 m × 0.32 m) with FID detector.