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Catalytic properties of $NiSO_4/ZrO_2$ promoted with Fe_2O_3 for acid catalysis

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Abstract

A series of catalysts, $NiSO_4/Fe_2O_3$–ZrO_2, for acid catalysis were prepared by the impregnation method, where support, Fe_2O_3–ZrO_2 was prepared by the co-precipitation method using a mixed aqueous solution of zirconium oxychloride and iron nitrate solution followed by adding an aqueous ammonia solution. No diffraction line of nickel sulfate was observed up to 20 wt.%, indicating good dispersion of nickel sulfate on the surface of Fe_2O_3–ZrO_2. The addition of nickel sulfate (or Fe_2O_3) to ZrO_2 shifted the phase transition of ZrO_2 from amorphous to tetragonal to higher temperature because of the interaction between nickel sulfate (or Fe_2O_3) and ZrO_2. 15-$NiSO_4/Fe_2O_3$–ZrO_2 containing 15 wt.% $NiSO_4$ and 5 mol% Fe_2O_3, and calcined at 700 °C exhibited maximum catalytic activities for both reactions, 2-propanol dehydration and cumene dealkylation. The catalytic activities for both reactions were correlated with the acidity of catalysts measured by the ammonia chemisorption method. The addition of Fe_2O_3 up to 5 mol% enhanced the acidity, thermal property, and catalytic activities of $NiSO_4/Fe_2O_3$–ZrO_2 gradually due to the interaction between Fe_2O_3 and ZrO_2 and consequent formation of Fe–O–Zr bond.

Keywords: A. Oxides; C. Infrared spectroscopy; C. X-ray diffraction; D. Catalytic properties; D. Surface properties

1. Introduction

Solid acid catalysts are finding numerous applications in many areas. Liquid superacids based on HF, which are efficient and selective at room temperature, are not suitable for industrial processes due to separation problems tied with environmental regulations [1]. Many catalysts were reported in the literature including $AlCl_3$ with additives like $SbCl_3$ and HCl, chlorinated alumina, transition metal-exchanged zeolites, heteropoly acids and some bifunctional catalysts [2]. Most of these catalysts suffer from different drawbacks such as high working temperature, continuous supply of chlorine, and a high hydrogen pressure. Conventional industrial acid catalysts, such as sulfuric acid, $AlCl_3$ and BF_3, have unavoidable drawbacks because of their severe corrosivity and high susceptibility to water. Thus, the search for environmentally benign heterogeneous catalysts has driven the worldwide research of new materials as a substitute for current liquid acids and halogen-based solid acids. Among them sulfated oxides, such as sulfated zirconia, titania, and iron oxide exhibiting high thermostability, superacidic property, and high catalytic activity, have

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evoked increasing interest [3–5]. The strong acidity of zircona-supported sulfate has attracted much attention because of its ability to catalyze many reactions such as cracking, alkylation, and isomerization.

In recent years, promoted zirconia catalysts have gained much attention for isomerization reactions due to their super acidity, non-toxicity, and a high activity at low temperatures [3,6]. Sulfated zirconia incorporating Fe and Mn has been shown to be highly active for butane isomerization, catalyzing the reaction even at room temperature [7,8]. Such promotion in activity of catalyst has been confirmed by several other research group [8–10]. Coelho et al. [11] have discovered that the addition of Ni to sulfated zirconia results in an activity enhancement comparable to that caused by the addition of Fe and Mn. It has been reported by several workers that the addition of platinum to zirconia modified by sulfate ions enhances catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen [12,13]. The high catalytic activity and small deactivation can be explained by both the elimination of the coke by hydrogenation and hydrogenolysis, and the formation of Brönsted acid sites from H_2 on the catalysts [12]. Recently, it has been found that a main group element Al can also promote the catalytic activity and stability of sulfated zirconia for *n*-butane isomerization [14,15].

Many metal sulfates generate fairly large amounts of acid sites of moderate or strong strength on their surfaces when they are calcined at 400–700 °C [4,16]. The acidic property of metal sulfate often gives high selectivity for diversified reaction such as hydration, polymerization, alkylation, cracking, and isomerization. Structural and physicochemical properties of supported metal sulfates are considered to be in different states compared with bulk metal sulfates because of their interaction with supports [17–19]. In our previous work [20], it has been shown that NiO_4 supported on ZrO_2 is very active for ethylene dimerization. It came to our attention that nickel sulfate catalysts supported on ZrO_2 promoted with Fe_2O_3 have not been reported up to now.

In view of the above reasons, we were interested to investigate the role of promoter, Fe_2O_3 on the acidity of catalyst, and its application to acid catalytic reactions. In this study, an Fe_2O_3–ZrO_2 mixed oxide was prepared by a co-precipitation method and impregnated with nickel sulfate. The catalytic activities of the Fe_2O_3-promoted catalysts for acid catalysis, 2-propanol dehydration, and cumene dealkylation with relation to Fe_2O_3 content were investigated. The characterization of the samples was performed by means of Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and surface area measurements.

2. Experimental

2.1. Catalyst preparation

The Fe_2O_3–ZrO_2 mixed oxide was prepared by a co-precipitation method using aqueous ammonia as the precipitation reagent. The co-precipitate of $Fe(OH)_3$–$Zr(OH)_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of iron nitrate and zirconium oxychloride (Junsei Chemical Co.) at room temperature with stirring until the pH of the mother liquor reached about 8. Catalysts containing various nickel sulfate contents were prepared by the impregnation of $Fe(OH)_3$–$Zr(OH)_4$ powder with an aqueous solution of $NiSO_4$, followed by calcining at different temperatures for 1.5 h in air. This series of catalysts is denoted by the mole percentage of Fe_2O_3 and the weight percentage of nickel sulfate. For example, 15-$NiSO_4$/5-Fe_2O_3–ZrO_2 indicates the catalyst containing 5 mol% of Fe_2O_3 and 15 wt.% of $NiSO_4$.

2.2. Procedure

FTIR spectra were obtained in a heatable gas cell at room temperature using a Mattson Model GL6030E spectrophotometer. The self-supporting catalyst wafers contained about 10 mg cm^{-2}. Prior to obtaining the spectra, we heated each sample under vacuum at 25–500 °C for 1 h. Catalysts were checked in order to determine the structure of the prepared catalysts by means of a Philips X'pert-APD X-ray diffractometer, employing Ni-filtered Cu Kα radiation. DSC measurements were performed by a PL-STA model 1500H apparatus in air; the heating rate was 5 °C min^{-1}. For each experiment 10–15 mg of the sample was used. Temperature-programmed NH_3 desorption experiments were performed as follows. Before introducing NH_3, the catalyst was activated at 400 °C for 1 h in He flowing at 50 cm^3 min^{-1}. After adsorption of NH_3, the He flow was continued for an additional 30 min to remove the excess of NH_3. The reactor temperature was raised at a rate of 10 °C min^{-1} to 600 °C.