



Nanosized iron and nickel oxide zirconia supported catalysts for benzylation of benzene: Role of metal oxide support interaction

Tarek T. Ali^{a,b}, Katabathini Narasimharao^{a,*}, Nesreen S. Ahmed^a, Sulaiman Basahel^a, Shael Al-Thabaiti^a, Mohamed Mokhtar^{a,c,**}

^a Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

^b Chemistry Department, Faculty of Science, Sohag University, P.O. Box 82524, Sohag, Egypt

^c Physical Chemistry Department, National Research Centre, El Buhouth St., Dokki, Cairo, Egypt

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ABSTRACT

Nanocrystalline Fe₂O₃ and NiO mesoporous ZrO₂ supported catalysts were prepared and thermally treated at 500 °C. The efficacy of catalysts for catalyzing the benzylation of benzene using benzyl chloride was studied. The mesoporous ZrO₂ alone showed only benzyl chloride conversion of 44% after a reaction time of 600 min at 75 °C. An increase in the conversion of benzyl chloride to 49% was observed after loading 10 wt% of NiO on ZrO₂. The conversion was further increased to 58% with the increase of NiO loading to 20 wt%. However, a drastic increase of conversion was observed after loading 10 wt% Fe₂O₃ on ZrO₂, the conversion reached to 78% under identical reaction conditions. The increase of Fe₂O₃ loading to 20 wt% led to a significant increase in conversion of benzyl chloride to 91%. The characterization results showed that ZrO₂ support is mesoporous comprising monoclinic and tetragonal phases. The loading of the NiO or Fe₂O₃ led to phase transformation of ZrO₂ into cubic phase. Diffraction peaks due to Fe₂O₃ were not observed; in contrast, the presence of segregated NiO phase was observed in case of NiO supported ZrO₂ samples. The mesoporous ZrO₂ support maintained the stability of catalytically active Fe₂O₃ species after six reaction cycles. The enhanced catalytic activity of this catalyst is attributed to the presence of a greater degree of dispersion of Fe₂O₃ over ZrO₂, higher redox potential and a greater degree of accessible surface Lewis acid sites.

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1. Introduction

Diphenylmethane, also known as benzyl benzene, is a valuable intermediate in chemical industry due to its use in the dye and perfume manufacturing processes [1]. Friedel–Crafts benzylation of benzene using benzyl chloride to afford diphenylmethane is a well-known method to synthesize diphenylmethane. The commonly used homogeneous catalysts such as AlCl₃, BF₃, H₃PO₄ and H₂SO₄ suffer from several disadvantages including difficulty in separation, recovery, disposal of used catalyst, their corrosive nature and high toxicity. The development of reusable heterogeneous catalysts is necessary to overcome the problems associated with homogenous catalysts [2]. Clark et al. reported that Zn modified montmorillonite and nickel chlorides were highly active catalysts for Friedel–Crafts

alkylation [3]. Coq et al. indicated that highly acidic zeolite catalysts, such as HY and H-ZSM-5, show poor activity for the benzylation reaction, because of diffusion limitation caused by their microporous nature [4]. Choudhary et al. [5] has studied benzylation of benzene by benzyl chloride over Fe-, Zn-, Ga- and In-modified ZSM-5 type catalysts and the performance of the catalysts were attributed to their improved properties. The same authors also observed that Fe-containing mesoporous molecular sieves were active in benzylation of benzene and have better stability than the Fe-pillared clays [5].

Subsequently, research has been directed towards the preparation of mesoporous materials for the benzylation reaction [6]. Mesoporous catalysts exhibited better benzylation activity than microporous catalysts. However, the reported mesoporous materials possessed poor stability and weak acidity compared with zeolites. Therefore, development of mesoporous catalysts with high stability and strong acidity for benzylation reaction is a topic of interest [7].

Zirconium dioxide (ZrO₂) is an important material that has been used extensively for heterogeneous catalytic reactions and

* Corresponding author. Tel.: +966 500558045; fax: +966 26952292.

** Corresponding author. Tel.: +966 500558045; fax: +966 26952292.

E-mail addresses: katabathini@yahoo.com (K. Narasimharao), mmokhtar2000@yahoo.com (M. Mokhtar).

in other applications because of its versatile structural and surface chemical properties as well as good thermal stability [8]. Furthermore, ZrO₂ has been reported to be a better catalyst and catalyst support than classical materials such as Al₂O₃, SiO₂ and TiO₂ [9]. Very few studies have been devoted to use catalysts that contain iron oxide, nickel oxide and for benzylation of benzene. Koyande et al. performed benzylation of benzene and other aromatic compounds over sulfated ZrO₂ and Fe₂O₃ catalysts [10]. Shinde et al. [11] used different ferrites such as CuFe₂O₄, NiFe₂O₄, CoFe₂O₄, ZnFeO₄ and MgFe₂O₄ for the benzylation of benzene.

Decades ago, Mizuno et al. [12] reported that highly dispersed ZrO₂-supported Fe, Co, Cr and Cu oxides show very high catalytic activities for the reduction of NO by CO. It was evident that the superior performances of these catalysts are considered to be a consequence of specific metal oxide–ZrO₂ interactions [13]. The nature of interaction between metal/metal oxide and ZrO₂ has been much less extensively studied than the interaction involving other supports such as Al₂O₃, SiO₂ and TiO₂. Yamaguchi [14] have observed distinctly three different iron species on the surface of ZrO₂ support; two kinds of highly dispersed Fe³⁺ species and bulk Fe₂O₃ particles.

Dongare et al. [15] synthesized NiO–ZrO₂ by the sol–gel method and they used the catalysts for methane oxidation. The authors observed that increasing of NiO content to 20 mol% was accompanied by an increase of catalytic activity. They also indicated that solid solutions of Ni–Zr–O and highly dispersed NiO particles were present in the catalysts and responsible for high activity of these catalysts. The activity of the catalysts decreased when NiO content was further increased to 40 mol%. They suggested the decrease of activity was due to the formation of coarse NiO particles possessing the properties of bulk NiO.

It is well known that the high dispersion of catalytically active transition metal oxides and their uniform volume distribution is necessary to increase the interface between the phases. It was observed in the literature that a NiO–ZrO₂ sample with 20 wt% nickel oxide loading retained its cubic phase even after calcination at 1000 °C, indicating thermal stability of cubic NiO–ZrO₂ phase [15].

In a recent publication [16], we reported synthesis of nano-sized iron oxide supported on mesoporous ZrO₂ using a modified co-precipitation method. We observed that addition of 20 wt% of iron oxide to ZrO₂ led to formation of amorphous Fe₂O₃ on the surface of the ZrO₂ support and migration of Fe cations from the surface to the crystal lattice of ZrO₂ to stabilize the tetragonal phase. In continuation of our effort to develop stable solid acid catalysts for production of fine chemicals, it is our interest to synthesize, characterize nanosize supported mesoporous ZrO₂ materials and utilize them as catalysts for benzylation. In this paper, we synthesized nanocrystalline iron oxide and nickel oxide supported ZrO₂ catalysts and studied physico-chemical properties of catalysts to investigate the nature of interaction between metal oxide and ZrO₂ and its role in benzylation of benzene reaction.

2. Experimental

2.1. Materials

All reagents were analytical grade and used as received without purification. Zirconyl chloride octahydrate [(ZrOCl₂.8H₂O)], ferric nitrate nonahydrate [Fe(NO₃)₃.9H₂O], nickel nitrate hexahydrate [(NiNO₃)₂.6H₂O], aqueous ammonia solution and ethylenediamine [C₂H₄(NH₂)₂] were purchased from Aldrich, U.K.

2.2. Synthesis of nanocrystalline mesoporous iron and nickel oxide-supported ZrO₂ materials

The nanocrystalline mesoporous ZrO₂ support was prepared by a modified sol–gel method using ethylenediamine (EDA) as gel protection agent. Iron and nickel support on nanocrystalline mesoporous ZrO₂ were prepared by conventional impregnation.

2.2.1. Method of preparation

In this method, EDA was used as gel protecting agent to prepare ZrO₂ support. Hundred milliliter of 0.88 molar EDA solution was added drop wise to the solution containing 26.1 g of ZrOCl₂.8H₂O in 100 mL of distilled water. The solution (pH of 10) was maintained at 50 °C in a water bath and subjected to ultrasonication for 5 h. Then the solution was kept for aging at 80 °C for 100 h to obtain a gel. The obtained gel was then washed with ethanol for four times and dried at 100 °C for 24 h.

Iron and nickel oxide supported ZrO₂ nanomaterials were prepared by impregnating the calculated amount of dried ZrO₂ powder with solutions of Fe (NO₃)₃.9H₂O or Ni(NO₃)₂.6H₂O that corresponded to 10.0 wt% and 20.0 wt% of iron or nickel oxide. The excess water was removed by slow drying and the dried materials were washed four times with distilled water. Portions of the synthesized materials were calcined at 500 °C with a ramp rate of 1 °C min⁻¹ and kept at this temperature for 3 h. The calcined materials were annotated using the following nomenclature: 10-FeZr, 20-FeZr, 10-NiZr and 20-NiZr for 10 wt% and 20 wt% iron and nickel oxides loaded ZrO₂ samples.

2.3. Characterization

The elemental composition of the catalysts was determined by ICP-AES, Optima 7300DV, Perkin Elmer Corporation, USA. The sample preparation for ICP-AES was as follows: about 100 mg of catalyst was placed in a PTFE beaker and then complete dissolution of the sample was achieved by adding 8 mL of 40% HF, 2 mL of HNO₃ and 2 mL of HCl and to this 15 mL of ultra-pure water was added and then PTFE beaker was placed in an ultrasonic bath for 10 min to obtain homogeneous dissolution. The solution was then rinsed into a centrifuge tube and centrifuged at 3000 rpm for 3 min. The clear supernatant was decanted and used to prepare 250 mL stock solution.

X-ray powder diffraction (XRD) studies were performed for all of the prepared solid samples using a Bruker diffractometer (Bruker D8 advance target). The patterns were obtained using copper Kα₁ and a monochromator (λ = 1.5405 Å) at 40 kV and 40 mA. The crystallite size of the zirconia phase was calculated using Scherrer equation (1):

$$D = B\lambda / \beta_{1/2} \cos \theta \quad (1)$$

where D is the average crystallite size of the phase under investigation, B the Scherrer constant (0.89), λ the wavelength of the X-ray beam used (1.5405 Å), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the diffraction peak and θ is the diffraction angle. The identification of different crystalline phases in the samples was performed by comparing the data with the Joint Committee for Powder Diffraction Standards (JCPDS) files. The Raman spectra of samples were measured with a Bruker Equinox 55 FT-IR spectrometer equipped with an FRA106/S FT Raman module and a liquid N₂ cooled Ge detector using the 1064 nm line of an Nd:YAG laser with an output laser power of 200 mW. SEM measurements were carried out using a JEOL JSM840A system. For SEM, each of the powders was attached to an aluminum block using double sided carbon tape. The samples were then coated in gold to make them conductive and compatible with the SEM technique.

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