FULL LENGTH ARTICLE

Characterization and catalytic activity of NiO/mesoporous aluminosilicate AlSBA-15 in conversion of some hydrocarbons

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Abstract Mesoporous aluminosilicate AlSBA-15 was synthesized and adopted as a support for NiO with 3, 6 and 9 wt.% loadings. Characterization of various samples was performed through XRD, FTIR, DSC-TGA, TPR, SEM and TEM techniques. Textural and morphological characteristics were examined using N_2 adsorption–desorption isotherms. Catalytic activities were measured in cumene cracking for parent AlSBA-15 and in *n*-hexane and toluene cracking and cyclohexane dehydrogenation for supported NiO samples. Uniformity of the ordered 2D-hexagonal structure of AlSBA-15 was evident even after loading with NiO. NiO and NiOOH phases could be detected particularly in the sample containing 9 wt.% NiO. TPR profile of solid loaded with 3 wt.% NiO sample showed negative peaks at 400 and 600 °C, related to hydrogen spillover on reduced sample. Selectivity towards *n*-hexane and toluene cracking increased with both temperature and metal oxide loading, achieving 100% at 350 °C. In cyclohexane dehydrogenation, the sample loaded with 3 wt.% NiO was the most active and selective one towards benzene formation.

1. Introduction

Highly ordered large pore mesoporous silica molecular sieves SBA-15 with considerably thicker pore walls as compared to MCM-41 have been recently synthesized using an amphiphilic triblock copolymer as the structure directing agent in highly acidic media [1–4]. SBA-15 exhibits improved hydrothermal stability as compared to MCM-41 [4,5]. The incorporation of aluminum into SBA-15 by post synthetic and direct methods has been reported [6–11]. During materials preparation via post synthetic methods often metal oxides are formed in the channels or on the external surface. Metal oxides formed in the mesopores will block the pores partially or fully, thereby

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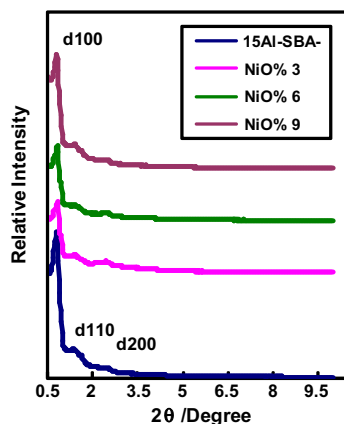E-mail address: hebagobara@yahoo.com.

Figure 1a Low-angle XRD of Al-SBA-15 support and NiO/Al-SBA-15 catalysts.

reducing surface area, pore volume, and pore diameter, or play a negative role in catalysis [12] Yue et al. [6] have studied the direct synthesis of AlSBA-15 and found that the catalytic activity of AlSBA-15 in cumene cracking is higher as compared to AlMCM-41.

It has been found that the extent of Al incorporation and substitution in the tetrahedral framework [13] of AlMCM-41 and the catalytic activity [14] are greatly dependent on the Al source used in the preparation of these materials [15–20]. Janicke et al. [15] and Reddy and Song [18,20] have reported that Al isopropoxide is the best source for the incorporation of Al (III) in MCM-41. Hartmann et al. [21] have investigated the effect of Al source on the incorporation of MCM-48 and found that a maximum incorporation of Al and large pore diameter on the MCM-48 were achieved by using Al isopropoxide as the Al source. Materials with uniform and tunable pore sizes are expected to play an important role in a number of applications in catalysis, molecular separations and sorption of very bulky molecules [22], and to the fabrication of semiconductors, semiconductor nanowires, and low dielectric devices [23,24].

Ni catalysts have been used for many years for different catalytic processes such as hydrogenation/dehydrogenation, cracking, hydrodesulfurization (HDS) and hydrodechlorination (HDC). However, relatively few papers have been published on applications of nickel supported on mesoporous materials [25]. The most widely used method for the preparation of these catalysts is the use of an incipient wetness impregnation process [26,27]. However, other methods have been reported for preparing mesoporous silica, MCM-41, as a support for nickel catalysts. These methods include ion-exchange with $NiCl_2$ or $Ni(NH_3)_4(NO_3)_2$ solutions, and direct Ni^{2+}

incorporation during the fabrication of the support using a sol–gel method especially small extend Ni loading (< 5 wt.%) [28].

The present work aims at the synthesis of mesoporous AlSBA-15 as mesoporous support material for nickel catalyst samples prepared by wet impregnation technique. The prepared catalysts were characterized using XRD, N_2 physisorption, FT-IR and SEM techniques. The acidity of the employed support was tested through cumene cracking. The prepared catalysts were applied in the catalytic of n-hexane and tolune cracking and cyclohexane dehydrogenation reactions.

2. Experimental

2.1. Synthesis of AlSBA-15 and Ni/AlSBA-15 catalysts

AlSBA-15 was synthesized using a triblock copolymer poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (Pluronic P123, molecular weight) 5800, EO_{20}-$PO_{70}EO_{20}$, Aldrich) as a structure directing agent. In a typical synthesis, 4 g of Pluronic P123 was added to 30 mL of water. After stirring for few hours, a clear solution was obtained. Thereafter, the required amount of HCl was added, and the solution was stirred for another 2 h. Then, 9 g of tetraethyl orthosilicate and the required amount of the desired Al isopropoxide were added, and the resulting mixture was stirred for 24 h at 40 °C. The sample was prepared by using 70 mL of 0.29 M HCl and a Si/nAl ratio of 7 [29]. The solid product was recovered by filtration, washed several times with water, and dried overnight at 100 °C. The sample was calcined at 540 °C to remove the template.

NiO samples were deposited into the mesoporous AlSBA-15 by wet impregnation method using an aqueous solution of Ni $(NO_3)_2 \cdot 6H_2O$. The calculated amount of nickel nitrate precursor was added to 1 g of ALSBA-15, in order to obtain 3, 6 and 9 wt.% Ni in the final catalysts. The solid catalysts samples were dried at 120 °C for 16 h and then calcined at 200 °C in a stream of air. The oxide samples obtained were reduced by heating at 450 °C in a current of pure hydrogen.

2.2. Characterization

The materials were characterized by powder X-ray diffraction recorded on a Brucker D8 advance X-ray diffractogram with Cu Kα radiation ($\lambda = 1.5418$ Å). IR experiments were performed using AT1 Mattson model Genesis Series (USA) infra red spectrophotometer adopting KBr technique. For all samples, the KBr technique was carried out approximately in a quantitative manner since the weight of the sample and that of KBr were always kept constant.

Table 1 Physicochemical properties of SBA-15 and Ni–Al SBA-15 materials with different Ni contents.

Catalyst samples	α_0[a] (nm)	S_{BET} (m²/g)	V_t (cm³/g)	S_{micro} (m²/g)	V_{micro} (cm³/g)	W_{BJH} (nm)	T_W[b] (nm)
AlSBA-15 support	12.55	810	1.186	141	0.0340	10.13	2.42
3% NiO	12.34	668	1.025	70	0.0120	10.10	2.24
6%NiO	12.51	551	0.882	23	0.0076	10.16	2.35
9% NiO	12.86	619	0.959	58	0.0076	10.09	2.77

[a] α_0: The length of the hexagonal unit cell $\alpha_0 = 2d_{100}/(3)^{1/2}$.
[b] T_W: The wall thickness = $\alpha_0 - W_{BJH}$.