Simple and Novel Co-precipitation Method of Synthesis of 3D Pyramidal Hierarchical Ni@ CeO_2-Al_2O_3 Nanocatalyst for Cyclohexane Dehydrogenation

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KEYWORDS

Ceria-alumina, 3D hierarchical structure, benzene production, micro-mesopores structures, boehmite.

SHORT SUMMARY

Hierarchical CeO_2-Al_2O_3 nanocomposites with 10 and 20% ceria content as well as γ-Al_2O_3 were synthesized by modified co-precipitation method without using any template. The as-synthesized nanocomposites were characterized using several techniques such as XRD, BET, TEM, TGA, XPS, FE-SEM and AFM. The synthesized nanocomposites were loaded by 5% NiO via ultrasonic method and successfully investigated for cyclohexane dehydrogenation. The XRD results ensured the formation of crystalline cubic γ-alumina and cubic CeO_2 with fluorite structure. Additionally, a solid-solution has been formed in all CeO_2-Al_2O_3 nanocomposites with retaining the ceria fluorite structure. Moreover, a large fraction of dispersed CeO_2 phase over the nanocomposites surface accompanied by $CeAlO_3$ cubic phase was observed. Different techniques emphasized the development of totally novel 3-dimensional hierarchical pyramidal structure nanocomposites which newly synthesized with a facile preparation procedure. Finally, the synthesized nanocomposites achieved high benzene yield of 98.9 and 99%, at LHSV of 1 h^{-1} whereas, 100% selectivity was achieved at LHSV of 3 h^{-1} towards benzene production up to 350 °C of reaction temperature. At higher reaction temperature, a considerable amount of methane is clearly detected in the product gas suggesting the occurrence of cyclohexane hydrogenolysis.

EXTENDED ABSTRACT

The cyclohexane dehydrogenation to benzene is one of the promising catalytic bi-functional reaction where, it can be made reversibly to produce benzene and/or for CO-free hydrogen storage for PEM fuel cells [1]. most of the studies have concentrated on alumina supported platinum as a catalyst [2]. While, because of process economic a specific interest to use other metals such as nickel has been reported as effective for hydrocarbon reforming including dehydrogenation reaction [3]. Also, the catalytic activity of supported metal nanocatalyst is strongly dependent on the shape, size and size distribution of the metal particles and the support [4]. Porous alumina has attracted a great attention due to its highly desirable properties. Tthe porous materials with defined hierarchical structures are generally efficient and preferred for many applications that operated under high pressure and/or diffusion rate. These hierarchical morphologies have been synthesized through various strategies that relied on several theories and materials such as applying templating [5]. In this study are reported a new, simple and cheap procedure to synthesize template-free hierarchical CeO_2/Al_2O_3 with micro/nanostructure by modifying of the co-precipitation method. The applied technique produces a porous 3D pyramidal morphology and crystalline mixed oxide with uniform pore sizes. In addition, a homogenous well-defined porous structure has been obtained. As an application to these materials, the synthesized hierarchical supports were loaded with 5% NiO and investigated as catalysts for the cyclohexane dehydration reaction

Experimental

Synthesis of porous Al_2O_3 by modified co-precipitation method,

Synthesis of hierarchical CeO_2-Al_2O_3 oxides and NiO loading by ultrasonic technique

Table 1: Textural properties of Al_2O_3, CeO_2/Al_2O_3 and Ni/ CeO_2-Al_2O_3 nanocomposites

Samples	S_{BET} (m^2g^{-1})	Total pore volume V_P (cm^3g^{-1})	Average pore Radius r_p (nm)
Alumina	254	0.58	22.5
10% Ce-Al	239	0.41	15.6
20% Ce-Al	229	0.33	15.6
Ni/10%Ce-Al	177	0.24	05.1
Ni/20%Ce-Al	156	0.23	05.7

Catalytic activity

Prior to the catalytic activity experiments, the loaded NiO samples were reduced to Ni^0 in a flow system. The catalyst was loaded into the reactor of 30 x 1.5 cm (length x diameter) and heated up to 450 °C with heating rate of 2 °C/min under hydrogen flow of 100 sccm. The reduction procedure was continued for 4 h. The cyclohexane liquid was then pumped to the reactor with flow rate of 6 and 2 ml/h the evolved gasses analyzed through GC tool.

Cyclohexane conversion (wt %) = $Cyclohexane_{in}$- $Cyclohexane_{out}$/ $Cyclohexane_{in}$. (1)

Component yield (wt %) = quantity of the componen t/ ∑ of the produced components (2)

Fractional component selectivity (wt %) = yield (wt %) / Total conversion x100. (3)

Tables and Figures

The FE-SEM images of the prepared samples in Fig.1(a-d) a distinguishable regular pyramidal shape for all the prepared samples with almost 150 µm height and 250 µm length. While some other smaller size of 20 µm were detected. The images depicted those specimens exhibited multi-layer porous sheets structure with smooth surface for the neat supports. While it possessed a rough surface in the NiO loaded samples. Fig. 1c, d demonstrated small black spots of around 30 nm diameter on the pyramids surface. This indicated the successive loading of NiO on the pyramidal surface.

The derived surface parameters such as surface area (S_{BET}), total pore volume (V_p) and the pore radius (r_p) are summarized in Table 1. S_{BET} of the neat alumina was found to be 254 m^2/g, which is much greater than that illustrated in literature. The total pore volume and the average pore radius were 0.58 cm^3/g and 22.5 nm, respectively were calculated to Al_2O_3. in addition, the obtained pore size distribution curve (PSD) revealed the presence of narrow lower and wide moderate mesopores binary systems that centered at 5 and 23 nm

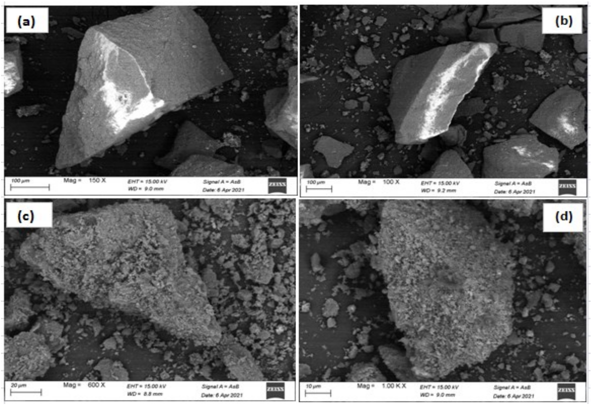

Fig.1 :FE-SEM images of (a) 10% Ce-Al, (b) 20% Ce-Al, (c) Ni/10%Ce-Al and (d) Ni/20%Ce-Al

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