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Benzene hydrogenation over oxide-modified MCM-41 supported ruthenium–lanthanum catalyst: The influence of zirconia crystal form and surface hydrophilicity

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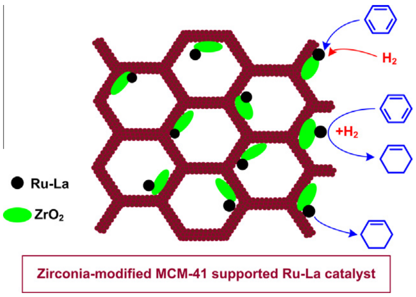
HIGHLIGHTS

- Different crystal form ZrO_2 modified MCM-41 were tested in benzene hydrogenation.
- Tetragonal ZrO_2-MCM-41 with higher hydrophilicity increase cyclohexene selectivity.
- Monoclinic ZrO_2-MCM-41 with more Brønsted acid sites reduce cyclohexene selectivity.
- ZrO_2-MCM-41 with larger pore size and volume is better for cyclohexene selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of the preparation conditions on the crystal form and surface properties of zirconia were studied. Mesoporous MCM-41 modified by tetragonal and monoclinic zirconia were synthesized by hydrothermal and precipitation methods. Then MCM-41 and zirconia-modified MCM-41 supported ruthenium–lanthanum catalysts were prepared via cyclohexane–water double solvent impregnation method. The obtained supports and catalysts were characterized by powder X-ray diffraction, transmission electron microscopy, energy dispersive X-ray spectroscopy, N_2 adsorption–desorption, thermogravimetric and differential scanning calorimetry, temperature programmed desorption of NH_3, static water/benzene adsorption techniques. It has been found that MCM-41 modified by tetragonal zirconia with exclusive Lewis-acidic sites exhibits more surface hydroxyl groups and higher hydrophilicity than MCM-41 modified by monoclinic and amorphous zirconia. Tetragonal zirconia-modified MCM-41 supported ruthenium–lanthanum catalyst shows better catalytic performance in benzene hydrogenation to cyclohexene with benzene conversion of 54.4% and cyclohexene selectivity of 84.7%.

1. Introduction

Cyclohexene can be used to produce caprolactam and adipic acid, the principal precursors of nylon-6 and nylon-66 [1,2]. The production routes for caprolactam and adipic acid based on cyclohexene have the advantages of higher yield, environmental friendliness and atomic economy. However, the conventional manufacture methods of cyclohexene from cyclohexanol, cyclohexane and halogenated cyclohexane have the drawbacks of complicated operations, poor efficiencies and high costs [3]. Hence, in recent decades, researchers have been focusing on developing suitable catalyst for the novel route of selective hydrogenation of benzene to cyclohexene.

From the point of view of thermodynamic analysis, we can see that benzene hydrogenation tends to produce cyclohexane which

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has smaller standard formation free-energy than cyclohexene [4–9]. It has been found that the key point for benzene hydrogenation to cyclohexene with high selectivity lies in how to promote the desorption of the produced cyclohexene from the catalyst and inhibit its adsorption so as to prevent the further hydrogenation to cyclohexane. Numerous literature reports liquid phase hydrogenation of benzene to cyclohexene over unsupported ruthenium based alloy catalyst [10–20]. Unsupported Ru–Zn catalysts were prepared and tested in benzene hydrogenation in the solution of $ZnSO_4$ and additives (diethanolamine or PEG-1000) [10,11]. The synergism of the additives and $ZnSO_4$ can enhance the hydrophilicity of the catalyst and stabilize the formed cyclohexene, thus increasing the selectivity to cyclohexene. For improving the utilization rate of noble ruthenium metal and catalyst lifetime, the development of the efficient supported ruthenium based catalyst has been the research focus in the field of partial hydrogenation of benzene [21–37]. The hydrophilic supports are more likely to form a stagnant water layer on its surface which may promote the desorption of the formed cyclohexene and inhibit its adsorption [38]. Suppino et al. [34] have investigated the effects of organic additives on the partial hydrogenation of benzene over Ru/Al_2O_3 and Ru/CeO_2 catalsyts. The effects of additives based on the interactions between additive and catalyst and also between the additive and the stagnant water film on the surface of Ru are discussed. The organic additive containing N atoms may bond to the Ru active site to block the planar adsorption of benzene and lower the activity. And the presence of the additive with hydroxyl groups may enhance the hydrophilicity aroud the ruthenium particles to increase the yield of cyclohexene. Zirconia has attracted considerable attention as a potential support in partial hydrogenation of benzene to cyclohexene for its good hydrophilicity [27,30,31,38–41]. However, many researches only focus on its structural properties, such as the BET surface area, the pore size distribution and the particle size distribution. There are very few reports concerned with the effects of the crystal forms and surface properties of zirconia on the performance of ruthenium catalyst. Because of the amphoteric character of the surface hydroxyl groups, the surface acid–base property of zirconia also plays an important role in the catalytic performance [42,43]. Velu et al. [44] have prepared a series of palladium catalyst supported on ZrO_2, CeO_2, Al_2O_3 and MgO for selective hydrogenation of phenol to cyclohexanone and the results show that the special acid–base properties of CeO_2 and ZrO_2 can induce a non-planar adsorption of phenol on catalysts surface giving rise to form cyclohexanone. Jung and Bell [45] have proposed that the higher rate of methanol synthesis from CO/H_2 over Cu supported on monoclinic zirconia than that of tetragonal zirconia is due to the H-atom spillover from Cu to monoclinic ZrO_2 caused by the Brønsted acid sites.

It also has been found that molecular sieves with regular mesoporous structure show good performance in benzene hydrogenation to cyclohexene [46–49]. In these researches, the effects of the promoters, the kind of the ruthenium precursors and the reaction solvents on the performance of ruthenium catalyst were discussed. In our previous work [50], Ru–La catalysts supported on zirconia-modified mesoporous molecular sieve MCM-41 were tested in benzene hydrogenation. The results show that the cyclohexene selectivity increases in a certain degree based on the hydrophilic modification of zirconia to MCM-41. However, the effects of the crystal forms and surface properties of zirconia on the catalytic performance have not been discussed in depth. In this paper, MCM-41 modified by zirconia with different crystal forms, surface hydroxyl groups, surface acid–base properties and textural properties were characterized and the effect of zirconia property on hydrophilic index and catalytic performance in benzene hydrogenation were discussed.

2. Experimental

2.1. Materials

$RuCl_3 \cdot xH_2O$ (Ru wt.% = 37.1%) and cyclohexene were purchased from Shanghai Jiuyue Chemical Industry Corporation Limited. Benzene, cyclohexane, $ZrOCl_2 \cdot 8H_2O$, $ZnSO_4 \cdot 7H_2O$, $La(NO_3)_3 \cdot 6H_2O$, tetraethoxysilane (TEOs, SiO_2 wt.% = 28%), cetyl trimethyl ammonium bromide (CTAB), mesitylene (TMB), $NaAlO_2$, ammonia solution (25–28 wt.%) and ethanol were purchased from Tianjin Guangfu Fine Chemical Research Institute. All reagents were analytical grade. H_2 (99.99%) was provided by Zhuzhou Diamond Gas Company.

2.2. Catalyst preparation

MCM-41 was prepared by hydrothermal synthesis method. Typically, 2.76 g of CTAB was dissolved in 80 g of deionized water, and 2.74 g of TMB was added to the solution. After the pH of the solution was adjusted to 11 by ammonia solution (25 wt.%), 5 g of TEOs was added slowly to the solution over a period of 10 min with vigorous stirring and a white gel was obtained. And then 12 mL of 0.1 M $NaAlO_2$ aqueous solution was dropwise added into the gel. The mixture was stirred for 1 h followed by transferring to a Teflon-lined autoclave for crystallization at 413 K for 2 days. The aged sample was filtered and washed with deionized water and ethanol. Finally, the sample was dried at 363 K for 12 h and calcined at 1023 K for 5 h in air with a heating rate of 1 K min^{-1}.

The zirconia-modified MCM-41 supports were synthesized by hydrothermal and precipitation method, which are marked as ZrO_2-MCM-41-HS and ZrO_2-MCM-41-PS respectively. The mass ratio of zirconia to MCM-41 is 0.05. As to ZrO_2-MCM-41-HS, MCM-41 powder was dispersed in 0.01 M $ZrOCl_2$ aqueous solution with stirring for 30 min. Ammonia solution (25 wt.%) was dropped to adjust the pH to 10. After dispersing under ultrasonication for 30 min, the slurry was transferred to a Teflon-lined autoclave for crystallization. Then it was filtrated, washed with distilled water and ethanol and dried at 333 K for 12 h. According to the crystallization temperature and time, the samples were marked as ZrO_2-MCM-41-HS-*T*-t (*T* represents crystallization temperature with unit of degree Celsius, t represents crystallization time with unit of hour). As to ZrO_2-MCM-41-PS, MCM-41 powder was dispersed in 15 mL of 0.025 M $ZrOCl_2$ aqueous solution with stirring for 30 min. Then 20 mL of 0.05 M ammonia solution was dropped into the above aqueous solution. After aging for 1 h, the slurry was filtrated, washed with distilled water and ethanol. Finally, it was dried at 373 K for 12 h and calcined at 773 K for 4 h in air with a heating rate of 5 K min^{-1}.

Ru–La/ZrO_2-MCM-41 catalysts were prepared by double solvent impregnation method. Typically, 1.0 g of ZrO_2-MCM-41 was dispersed in 24 mL of cyclohexane with stirring for 15 min. Then 2 mL of aqueous solution containing 0.2696 g of $RuCl_3 \cdot xH_2O$ and 0.0438 g of $La(NO_3)_3 \cdot 6H_2O$ was dropped into the above solution and stirred for 10 min. After the decantation of the supernatant, the remnant black solid was dried at 373 K for 12 h, and then reduced at 573 K for 4 h under 40 mL min^{-1} of 20 vol.% of H_2/N_2. Ru–La/MCM-41 catalyst was prepared by the similar method except that the support was unmodified MCM-41.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were determined under a D/max2500 TC diffractometer using Cu Kα radiation (λ = 1.542 Å). The tube voltage was 40 kV, the current was 30 mA,