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Doping effects of B in ZrO_2 on structural and catalytic properties of Ru/B-ZrO_2 catalysts for benzene partial hydrogenation

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ABSTRACT

The B-doped ZrO_2 (B-ZrO_2) samples with different B/Zr ratios were synthesized using zirconium oxychloride and boric acid as the precursors. Their crystallographic phase retained as tetragonal ZrO_2 after the doping of B; however, the amount of the Lewis acid sites increased from 46.1 $\mu mol_{NH3}\ g^{-1}$ on ZrO_2 to 100.6 $\mu mol_{NH3}\ g^{-1}$ on B-ZrO_2(1/10) with the nominal B/Zr molar ratio of 1/10. The Ru/B-ZrO_2 catalysts were then prepared by chemical reduction, and their electronic and structural properties were systematically characterized by spectroscopic techniques. It is identified that the Ru nanoparticles (NPs) supported on these B-ZrO_2 samples exhibited similar size, chemical state, and microstructure. In the partial hydrogenation of benzene, the turnover frequency of benzene was linearly proportional to the amount of the acid sites on the supports, whereas the selectivity toward cyclohexene displayed a volcanic evolution passing through a maximum of 88% on the Ru/B-ZrO_2(1/15) catalyst. Kinetic analysis indicated that the acid sites improved the rate constants of the benzene to cyclohexene step (k_1) and the cyclohexene to cyclohexane step (k_2) to different degrees. The resulting k_1/k_2 ratio increased from $3.7 \times 10^{-2}\ l\ mol^{-1}$ (Ru/ZrO_2) to $4.8 \times 10^{-2}\ l\ mol^{-1}$ (Ru/B-ZrO_2(1/15)), and then declined to $4.1 \times 10^{-2}\ l\ mol^{-1}$ (Ru/B-ZrO_2(1/10)), which explained the volcanic evolution of the selectivity toward cyclohexene with respect to the acid amount.

1. Introduction

Cyclohexene is an important chemical as its reactive C=C bond facilitates facile conversion to value-added cyclohexanol, caprolactam, and adipic acid via typical olefin reactions. The production of cyclohexene by benzene partial hydrogenation features exceptional superiority to processes including dehydration of cyclohexanol, dehydrogenation of cyclohexane, and the Birch reduction in terms of inexpensive feedstock, succinct reaction route, and consequently, operational simplicity [1]. However, it remains a great challenge to achieve a high yield of cyclohexene from benzene owing to severe thermodynamic limitation. The standard free energy change for cyclohexene formation from benzene hydrogenation (-23 kJ mol^{-1}) is much less negative than that for cyclohexane formation (-98 kJ mol^{-1}) [2]. Therefore, the development of a highly effective catalyst that is capable of steering the product to cyclohexene has been intensively pursued not only for its fundamental interest, but also for its industrial significance [3,7].

Despite the wide acceptance of the stepwise hydrogenation mechanism of benzene (benzene to cyclohexene followed by cyclohexene to cyclohexane) [6,8], the roles of the catalyst components in the partial hydrogenation of benzene, such as the surface acid sites of the supports, remain obscure. Several reviews claimed that benzene hydrogenation was a purely metal-catalyzed reaction [9,10], while many works demonstrated that the support acidity imposed remarkable effect on the activity of the supported metal catalysts [11–14]. de Mallman and Barthomeuf found that the rate of benzene hydrogenation increased with the concentration of the acid sites on Pt–faujasites [11]. Wang et al. proposed that the presence of additional hydrogenation sites at the metal–acid interface underlay the activity enhancement of benzene hydrogenation on the Pt/Al-MCM-41 catalyst with stronger acidity [12]. Lercher and coworkers put forward a detailed reaction pathway of benzene hydrogenation involving the Brønsted acid sites [13]. They identified that benzene hydrogenation on Pt/mordenites took place along two parallel reaction pathways, i.e., hydrogenation (i) on the metal surface and (ii) on the acid sites in the vicinity of Pt particles with hydrogen dissociated on the metal. The latter reaction pathway depends on the concentration of Brønsted acid sites of the zeolite and on the metal and acid site vicinity [13]. Benzene hydrogenation has also been suggested to occur on the Lewis acid

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sites of the support [14]. The Lewis acid site is an electron-deficient center, whereas benzene with the delocalized π bonds tends to be an electron donor. On the Pt/γ-Al_2O_3 and Pt/HAl-MCM-41 catalysts with the supports having the Lewis acid sites, benzene could be adsorbed easily on the Lewis acid sites with the formation of electron-deficient aromatic intermediates, which can be hydrogenated by activated hydrogen atoms [14]. Lin and Vannice found that the intrinsic activity increased in the order of Pt/η-Al_2O_3 < Pt/SiO_2 < Pt/$SiO_2 \cdot Al_2O_3$ < Pt/TiO_2 with the same order of the acid amounts on the supports in benzene hydrogenation [15], which was attributed to the occurrence of additional hydrogenation of benzene adsorbed on the acid sites of the support with spillover hydrogen (H_{so}).

ZrO_2 is an important catalyst support in benzene partial hydrogenation [16,17]. Previous works have demonstrated that the acidic property of ZrO_2 can be adjusted by B_2O_3 [18]. In this connection, herein we synthesized a series of B-doped ZrO_2 (B-ZrO_2) with different doping levels of B with the aim to tailor the acidic property of ZrO_2. With these well-characterized B-ZrO_2 supports, the Ru/B-ZrO_2 catalysts were prepared by the wetness impregnation–chemical reduction method. The influences of the doping level of B on the textural, electronic, and structural properties of the Ru/B-ZrO_2 catalysts were investigated in detail. Correlation of the physicochemical properties of the Ru/B-ZrO_2 catalysts with the catalytic performances in the partial hydrogenation of benzene to cyclohexene was attempted. The relationships between the amounts of the Lewis acid sites on the catalytic activity and the selectivity toward cyclohexene were unveiled and discussed.

2. Experimental

2.1. Preparation

The chemicals, if unspecified, were of analytical grade (A.R.) and purchased from Sinopharm Chemical Reagent. The gases were purchased from Shanghai Youjiali Liquid Helium. The B-doped ZrO_2 samples were synthesized according to Urbano et al. with some modifications [18]. Namely, the ammonia solution (25–28 wt%) was added dropwise to a mixed aqueous solution of $ZrOCl_2 \cdot 8H_2O$ (0.5 M) and H_3BO_3 to the pH of 10 under vigorous stirring at room temperature, and then refluxed at 373 K for 24 h. The precipitates were separated by centrifugation, reslurried and washed thoroughly with deionized water until the pH of 7 and the removal of the chloride ions ($AgNO_3$ test), dried at 373 K in air for 24 h, and calcined in air at 1073 K for 5 h at a heating rate of 10 K min^{-1}. The nominal B/Zr molar ratios were 1/20, 1/15, and 1/10. The B-doped ZrO_2 was labeled B-ZrO_2(x), where x represents the nominal B/Zr ratio. Pure ZrO_2 was prepared following the same procedures described above but in the absence of H_3BO_3.

The Ru/B-ZrO_2 catalysts were prepared by wetness impregnation, followed by chemical reduction. Specifically, exactly one gram of the B-ZrO_2 sample was impregnated with 30 ml of 26.4 mM aqueous solution of $RuCl_3 \cdot 3H_2O$ (A.R., Shanghai Aoke) and stirred for 48 h at room temperature. The theoretical Ru loading was 7.4 wt% for all the catalysts. Then, 2.0 ml of the 1.58 M aqueous solution of KBH_4 was added dropwise to the slurry at room temperature under mild stirring. The molar ratio between KBH_4 and Ru^{3+} was 4/1. The black solids were washed thoroughly with deionized water until all the chloride ions were removed ($AgNO_3$ test). Surface analysis confirmed that there was no residual Cl on the catalyst surface. The obtained catalyst was denoted as Ru/B-ZrO_2(x).

2.2. Characterization

The multipoint Brunauer–Emmett–Teller surface area (S_{BET}) was measured by N_2 physisorption at 77 K on a Micromeritics TriStar3000 apparatus. The sample was loaded in a glass adsorption tube and pretreated at 523 K under flowing N_2 for 5 h. The bulk composition was determined by the inductively coupled plasma-atomic emission spectroscopy (ICP–AES; Thermo Elemental IRIS Intrepid). Powder X-ray diffraction (XRD) pattern was acquired on a Bruker AXS D8 Advance X-ray diffractometer using Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The tube voltage was 40 kV, and the current was 40 mA. The 2θ angles were scanned from 20° to 70° at 4° min^{-1}.

The nature of the acid site was characterized by the FTIR spectroscopy of adsorbed pyridine (Py-IR) on a Nicolet Nexus 470 spectrometer equipped with a DTGS detector and a temperature-control accessory to provide sequences of the temperature-dependent spectra. About 15 mg of the sample was pressed with KBr into a self-supporting wafer of 2 cm in diameter. The wafer was placed in an IR cell with CaF_2 windows, evacuated at 473 K for 4 h, and then cooled to 298 K. After the background spectrum was recorded, pyridine was introduced and balanced at this temperature for 1 h. Physisorbed pyridine was removed by evacuation at 298 K. Then, the sample was heated under vacuum to 373 K, at which the spectrum was recorded with 4 cm^{-1} resolution by signal-averaging 32 scans. The amount of the Lewis acid sites involved in adsorbing pyridine (n_{Py}) was estimated by the method proposed by Hughes and White firstly on the basis of the integrated Lambert–Beer law [19] and then transformed by Onfroy et al. to the form of $n = SA/m\varepsilon$ [20]. In this equation, S, A, m, and ε are the surface area of the wafer, the integral absorption band intensity of the Lewis acid sites-bonded pyridine (L-Py), the weight of the sample, and the integral extinction coefficient, respectively. According to Onfroy et al. [20], the ε value varied little with the types of the solids. Thus, the ε value of 2.4 cm μmol^{-1} determined by Travert et al. for the 1459 cm^{-1} band of the L-Py on the B_2O_3–SiO_2 oxides at 373 K [21] was adopted in the calculation of the n_{Py}.

NH_3-TPD was carried out on a Micromeritics 2750 chemisorption system. The weighed sample (~150 mg) was pretreated at 473 K for 1 h under He and cooled to 393 K. The 10 vol% NH_3/He mixed gas was introduced instead of He at this temperature for 1 h to ensure the saturation adsorption of NH_3 [22]. The sample was then purged with He until the signal returned to the baseline as monitored by a thermal conductivity detector (TCD). The desorption curve of NH_3 was acquired by heating the sample from 393 K to 993 K at 10 K min^{-1} under He with the flow rate of 25 ml min^{-1}. Comparison of the area of the desorption peak with that calibrated by a 500 μl-capacity loop allowed for quantifying the total amount of the acid sites per gram of the sample.

CO chemisorption was used to determine the dispersion and active surface area (S_{Ru}) of Ru, which was also performed on the Micromeritics 2750 chemisorption system. The weighed sample (~100 mg) was pretreated at 473 K for 1 h under He and cooled to 298 K. Pure CO pulses were injected until the eluted peak did not change in intensity [23]. The dispersion of Ru and S_{Ru} was calculated according to the CO uptake with the assumptions of the CO:Ru stoichiometry of 0.5:1 [24] and the Ru surface atomic density of 1.63×10^{19} atoms m^{-2} [22].

X-ray photoelectron spectroscopic (XPS) spectrum was collected on a Perkin-Elmer PHI5000C instrument with Mg Kα radiation ($h\nu$ = 1253.6 eV) as the excitation source. The catalyst protected by ethanol was mounted on the sample plate, degassed in the pretreatment chamber in vacuo at 298 K overnight, and then transferred to the analyzing chamber where the background pressure was lower than 2×10^{-9} Torr. As the Ru 3d peak partly overlapped with the C 1s peak of the contaminant carbon, all binding energy (BE) values were referenced to the Zr $3d_{5/2}$ BE of ZrO_2 at 182.2 eV with an uncertainty of ±0.2 eV.

The surface morphology, particle size, and the selected-area electron diffraction (SAED) pattern were observed by transmission