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Selective hydrogenation of D-glucose to D-sorbitol over Ru/ZSM-5 catalysts

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ABSTRACT

Ru particles were introduced into the zeolite ZSM-5 (MFI) by either a conventional impregnation method or a one-step template-free process. The resultant materials were characterized by X-ray diffraction, N_2 adsorption-desorption, scanning electron microscopy, transmission electron microscopy, NH_3 and CO_2 temperature-programmed desorption. The results indicated that the Ru species in ZSM-5 catalysts prepared via the latter approach (designated as Ru/ZSM-5-TF) were highly dispersed in the ZSM-5 framework structure and this material exhibited high catalytic performance during the hydrogenation of D-glucose to D-sorbitol. The conversion of D-glucose was as high as 99.6% with D-sorbitol selectivity reaching 99.2%, exceeding the performance of Ru/ZSM-5 catalysts prepared by the conventional impregnation method with microporous or desilicated ZSM-5 supports. More importantly, this catalyst showed high stability against leaching and poisoning and could be reused several times. The extensive dispersion of the Ru species, strong interaction between the Ru species and the ZSM-5, and the suitable surface acidity-basicity balance of the Ru/ZSM-5-TF were all critical factors leading to excellent catalytic behavior and stability.

1. Introduction

Approximately 700,000 tonnes of D-sorbitol are synthesized each year worldwide by the catalytic hydrogenation of D-glucose, which represents an inexpensive, abundant feedstock obtainable from renewable resources such as starch-containing crops or cellulose [1–4]. D-sorbitol has many applications in the food, pharmaceutical, cosmetic and paper industries, and it can also be used as a building block in the synthesis of various fine chemicals, including vitamin C [5–7].

Most of the industrial processes for the synthesis of this compound are based on the batch-wise hydrogenation of D-glucose to D-sorbitol over Raney Ni catalysts, promoted by various transition metals [8]. Although Raney Ni has several advantages, such as low cost, excellent setting and high activity, the risk of leaching of the Ni or of the metal promoter reduces the economic benefits of the process [9]. The more stable supported Ru catalysts have demonstrated good activity and excellent selectivity during the hydrogenation of sugars, but have the drawback of high cost. To reduce this cost, Ru nanoparticles have been dispersed on different solid supports, including silica [10,11], multi-wall carbon nanotubes [12], activated carbons [13,14], alumina oxides [15–17], and some synthetic materials such as synthetic zeolites [18], which have also been studied

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for the dehydration of D-glucose. However, these catalysts are typically prepared using conventional methods such as impregnation followed by H_2 reduction. These supported catalysts also suffer from the disadvantage of rapid deactivation, likely resulting from the relatively weak interaction between the metal and the support as well as the limited diffusion of reactants/products within the support materials [19], leading to aggregation/sintering and leaching of Ru particles during use [20]. In addition, there is no way to precisely control the size and location of metal particles on the solid supports through the conventional synthetic approaches [21].

ZSM-5 zeolites with appropriate acidity and good shape-selectivity are widely used as supports in hydrogenation reactions [22]. Recently, more direct, template-free syntheses of Ru-containing ZSM-5 composites have been described [23–25], which provide control over both the texture and Si/Al ratio without any requirement for additives. RuO_2 clusters of uniform size (ca. 1 nm) have been deposited predominantly in MFI (ZSM-5) channels during hydrothermal synthesis and subsequently exhibit high reactivity for 1-hexene hydrogenation after reduction [26]. More importantly, encapsulation of metal or oxide clusters within zeolites can protect such clusters against sintering and also reduce their contact with toxic impurities, while concurrently allowing the active sites to select reactants and transition states on the basis of molecular size [25].

To date, the fabrication of highly dispersed metal nanoparticles within molecular sieve materials with tunable pore-sizes, and their subsequent use as catalysts for the hydrogenation of sugar alcohols, has not been reported in the literature. In the work reported herein, uniform Ru nanoparticles with an average diameter of less than 1 nm and encapsulated in ZSM-5 were prepared by a one-step, template-free method using $RuCl_3$ as the Ru precursor. The preparation method was simple and fast and allowed the prepared Ru clusters to be finely dispersed in the ZSM-5 support. We report herein that the materials prepared in this manner resulted in significant improvements in the D-sorbitol yields during the hydrogenation of D-glucose.

2. Experimental

2.1. Materials

Ru/C (5 wt%) was purchased from Aladdin Reagent Co., Ltd., while $RuCl_3 \cdot xH_2O$ (AR, 37.5 wt% Ru), NaOH (AR, 96 wt%), $NaAlO_2$ (54 wt% Al_2O_3, 41 wt% Na_2O, 5 wt% H_2O), D-glucose and D-sorbitol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The colloidal silica sol Ludox HS-40 (40 wt% in water, average particle size ~ 12 nm) was purchased from Aldrich. Commercially available ZSM-5 (Si/Al = 38) was acquired from the Catalyst Plant of Nankai University and was dried at 120 °C for 24 h before use.

2.2. Catalyst preparation

The incorporation of the Ru was realized by two different methods: an impregnation process and an in situ one-step process. In the first method, MFI-type zeolites were synthesized by a modified version of Weitkamp's method [24], with the molar composition $nRuO_2{:}nSiO_2{:}nAl_2O_3{:}nNa_2O{:}nH_2O$ = 0.65~2.81:38:1:11.5:2800. A solution of 2.35 g NaOH and 0.7112 g sodium aluminate in 90 g H_2O was added to 21.71 g Ludox HS-40 with stirring, after which 25 mL of a solution containing the desired amount of $RuCl_3 \cdot xH_2O$ was added to the initial mixture. This combined mixture was then stirred at 50 °C for 3 h followed by crystallization in a rotating stainless-steel autoclave (100 cm^3) for 4 d at 160 °C. Upon completion, the template-free zeolite Ru/ZSM-5-TF was obtained.

ZSM-5 with framework Si/Al ratios in the range of 25–50 has been shown to be an eligible structure for the introduction of mesoporosity via desilication. In this work, alkali-treated ZSM-5 samples (Si/Al = 38), denoted as ZSM-5-AT, were fabricated by immersing the zeolite in a 0.3 mol/L NaOH solution at 65 °C for 120 min. The treated samples were subsequently filtered, washed with distilled water, dried at 80 °C, ion-exchanged with NH_4NO_3 solution (0.1 mol/L) three times and finally calcined in static air at 550 °C for 4 h at a heating rate of 1 °C/min.

For comparison purposes, Ru/ZSM-5 catalysts were also prepared by the incipient wetness impregnation method at ambient temperature, employing an aqueous $RuCl_3$ solution as the Ru precursor. The preparation procedure associated with the impregnation method involved impregnating the dry supports (commercial microporous ZSM-5 zeolites with Si/Al = 38, denoted as ZSM-5-MS, and mesoporous ZSM-5 created by desilication in alkaline medium, denoted as ZSM-5-AT) with an aqueous solution of $RuCl_3$. To achieve incipient wetness, a liquid ($RuCl_3/H_2O$ solution of 20.1 mg/mL) to solid ratio of 2.0 mL/g was used. Following impregnation and subsequent ultrasonic treatment (600 W) for 2 h, the mixture was continuously stirred under ambient conditions to allow slow evaporation of water. The samples were then dried overnight at 110 °C, followed by reduction in H_2 at 350 °C for 3 h. The obtained sample was designated as Ru/ZSM-5-MS and Ru/ZSM-5-AT.

2.3. Catalyst characterization

The X-ray powder diffraction (XRD) patterns of catalysts were obtained with a Bruker D8 Advance X-ray diffraction instrument, using Ni-filtered Cu-K_α radiation. N_2 adsorption-desorption experiments were performed with a Micromeritics ASAP 2020 surface area and porosity analyzer and ICP analyses were carried out on a Thermo IRIS Intrepid II XSP atomic emission spectrometer to determine the chemical composition of catalysts and to examine metal leaching during reactions. NH_3 temperature-programmed desorption (NH_3-TPD), CO_2 temperature-programmed desorption (CO_2-TPD) and H_2 temperature-programmed reduction (H_2-TPR) data were acquired using a Micromeritics Autochem II chemisorption analyzer. Transmission electron microscopy (TEM) images were taken using a field emission H-7600 electron microscope at 120 kV, while scanning electron microscopy (SEM) analysis was conducted on a Hitachi S-4800 electron microscope working at 200 kV.