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Selective hydrogenation of D-mannose to D-mannitol using NiO-modified TiO_2 ($NiO\text{-}TiO_2$) supported ruthenium catalyst

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ABSTRACT

NiO-modified TiO_2 ($NiO\text{-}TiO_2$) supported ruthenium catalyst $Ru/(NiO\text{-}TiO_2)$ is prepared by simple impregnation method and characterized by using energy dispersive X-ray analysis (EDX/EDS), temperature-programmed reduction (TPR), inductively coupled plasma (ICP) mass spectrometry, transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and CO chemisorption. The catalyst $Ru/(NiO\text{-}TiO_2)$ is evaluated in D-mannose hydrogenation and hydrogenation experiments to produce a selective product D-mannitol were carried out batch wise in a three-phase laboratory scale reactor. A tentative mechanism for reduction of D-mannose is presented. The kinetics of D-mannose hydrogenation to D-mannitol using catalyst $Ru/(NiO\text{-}TiO_2)$ was studied. The kinetic data were modeled by zero, first and second-order reaction equations. A set of four experiments was also carried out to test the deactivation of the catalyst. For affording maximum D-mannose conversion, yield and selectivity to D-mannitol, the reaction conditions are optimized.

1. Introduction

Several attempts were made by researchers earlier to develop the catalysts based on nickel as an active metal (the catalysts, Raney Ni or supported/promoted nickel catalysts) [1–5] in hydrogenation of sugars to their corresponding sugar alcohols [6,7]. But, the nickel based catalysts were found to have some disadvantage (leaching) resulting in loss of activity and high metal content in the product solution [8,9]. Therefore, in recent years the catalysts based on ruthenium due their higher activities were evaluated in the hydrogenation of sugars to sugar alcohols (i.e. D-sorbitol, xylitol, lactitol, etc.) [10–17]. Off these, a sugar alcohol D-manntiol, similar to D-sorbitol, is of the industrial important since D-mannitol is also extensively used in food and pharmaceutical industries [18–22]. It has excellent properties such as non-toxic, non-hygroscopic and low caloric sugar. D-mannitol is present in small quantities in most fruits and vegetables [23–27]. Besides small amount of D-mannitol can be obtained naturally from their sources, commercial large scale production of D-mannitol was relied on catalytic hydrogenation of an appropriate starting material either D-fructose/invert sugar (D-fructose/D-glucose mixture) or D-mannose. Most of the studies were focused for the production of D-mannitol by catalytic hydrogenation of aqueous solutions either of D-fructose [28] or invert sugar (D-fructose/D-glucose mixture) [29,30] at high pressure and a high temperature. However, very little attention is paid for direct hydrogenation of D-mannose to D-mannitol and hydrogenation experiments to produce D-mannitol is scantly available in the literature [31]. Since D-mannose is a natural aldohexose and a building block of vegetable polysaccharides, therefore D-mannose possesses industrial relevance for the production of D-mannitol. It is mainly used as a sugar substitute and for pharmaceutical purposes. D-mannose is chosen here as a starting material for the production of D-mannitol (as represented in Scheme 1).

Our aim of the work was to evaluate ($NiO\text{-}TiO_2$) supported ruthenium catalyst $Ru/(NiO\text{-}TiO_2)$ in direct hydrogenation of D-mannose to D-mannitol. In kinetic study of D-mannose hydrogenation, both order of reaction and activation energy were also determined. A set of four experiments was carried out to test the deactivation of the catalyst.

2. Experimental

2.1. Materials

Ruthenium chloride ($RuCl_3{\cdot}xH_2O$) was purchased from Strem Chemicals, Newburyport, MA01950 (USA). The nickel chloride, D-mannose and D-mannitol were purchased from Sigma–Aldrich company, Inc, (USA). The support titanium (IV) oxide (rutile type) (TiO_2), purity – 99.9%, shape fine powder ca. 1– 2 micron purchased from Degussa is used after drying at 110 °C. De- ionized water was used as solvent for making all solutions.

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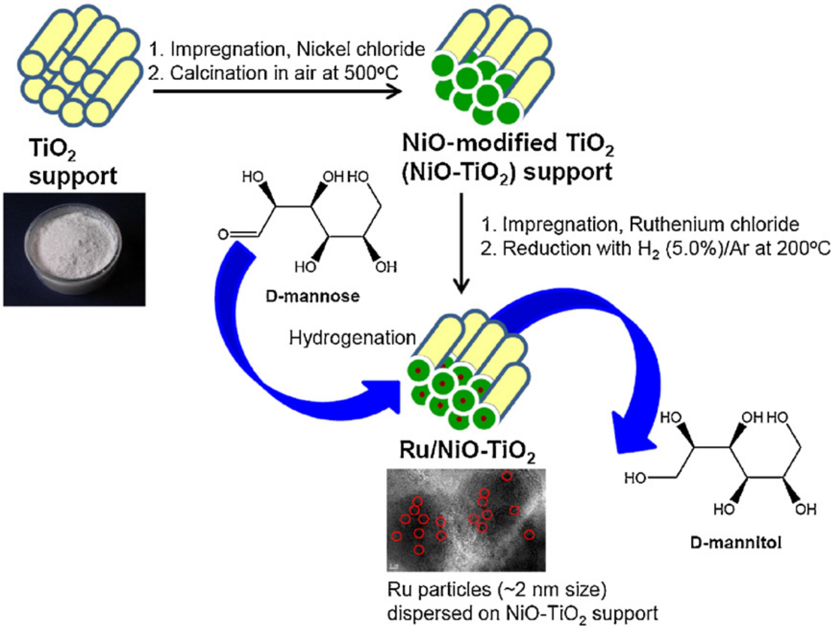

Scheme 1. A schematic approach for the preparation of active catalyst (Ru/NiO-TiO_2) used in hydrogenation of D-mannose to produce D-mannitol.

2.2. Catalyst Ru/(NiO-TiO_2) preparation

The preparation of novel catalyst Ru/(NiO-TiO_2) was carried out by impregnation method using ruthenium chloride and new class of NiO-modified TiO_2 support [11,16]. The proposed support material (NiO-TiO_2) was prepared by the following procedure: required amount (4.8 g) of TiO_2 was immersed into aqueous solution nickel chloride (0.55 g) under magnetic stirring. Then, the resulting mixture was dried at 110 °C overnight and after complete drying the sample was oxidized in air at 500 °C for 10 h to obtain NiO-modified TiO_2 support (NiO-TiO_2) (Scheme 1). The calculated amount of (NiO-TiO_2) was further re-impregnated with aqueous solution of ruthenium (III) chloride (0.52 g) and was kept in an oven at 110 °C overnight. The catalyst Ru/(NiO-TiO_2) thus prepared was reduced in a continuous flow of (5.0%) H_2/Ar at 200 °C (temperature determined from temperature-programmed reduction experiment) for 3 h and then used immediately for the hydrogenation of D-mannose.

2.3. Hydrogenation of D-mannose

10 wt% D-mannose solution was prepared by dissolving 20 g of D-mannose in 180 ml de-ionized water. This solution was mixed with 1.0 g of catalyst Ru/(NiO-TiO_2) to form the reaction slurry and thereafter the hydrogenation experiments of D-mannose were conducted in a 300 mL. The hydrogen gas was purged into the reactor at 2.0 MPa H_2 pressure to deoxygenate the reaction mixture followed by stirring (400 rpm for 30 min) at room temperature and then pressure was released. The hydrogenation was initiated by stirring the reaction mixture at constant impeller speed of 1200 rpm and was continued for 240 min at temperature of 120 °C and hydrogen (H_2) pressure of 40–55 bar. At the end of hydrogenation, the solution was cooled and the catalyst was allowed to settle at the bottom of reaction flask. The above mentioned procedure was followed with other catalyst Ru/TiO_2 which was reduced at 320 °C [11,16]. The supernatant solution was filtered and then analyzed using a HPLC (Younglin Instrument, Acme 9000) equipped with refractive index (RI) detector and Sugar-Pak column. Deionized water was used as an eluent for the analysis at a flow rate of 0.4 mL/min at 70 °C. The temperature of RI detector was maintained at 35 °C throughout the analysis.

Before starting the TPR experiments, the samples were dried at 120 °C for 1 h under Ar flow and then cooled to room temperature. The (10%) H_2/Ar was used as reducing gas at a continuous flow rate of 10 mL/min.

2.4. Catalysts characterization

The metal contents (amount of Ru loading) of the catalysts were determined by using EDX, Quantax 200 Energy Dispersive X- ray Spectrometer, Bruker. The stability of catalysts (before and after reactions) was determined with X-ray diffraction (RIGAKU, Miniflex Instruments). The amount of metal ions present in the reaction mixture after hydrogenation was analyzed with an inductively coupled plasma-atomic emission spectrometry (Thermo Scientific ICAP 6500 duo). Both, morphology and particle size were determined by the transmission electron microscopy (Maker FEI, Model Technai G2). For the electron microscopy examination, the catalyst samples were dissolved in 2-propanol, dispersed carefully in an ultrasonic bath, and then deposited on carbon-coated copper grids. BET surface area was determined by N_2 adsorption–desorption at 77 K liquid N_2 temperature with a MICROMETRICS, Tristar II analyzer. For each measurement, the sample was degassed at 250 °C for 3–4 h, then analyzed at 77 K with N_2 gas at relative pressures (P/P_0) from 0.005 to 1.0 (adsorption) and 1.0 to 0.1 (desorption). CO chemisorption was carried out by using an instrument model ASAP 2020C V1.09 G. Before adsorption of the CO, the catalysts (weighed approximately 0.12 g) were pre-treated in He for 35 min, and in O_2 for 15 min, and were then reduced for 30 min in a (5.0%) H_2/Ar gas flow of 50 mL/min, and in He gas flow for 15 min at 400 °C in a reaction chamber. After this pre-treatment, the samples were cooled down to 50 °C under He gas flow and CO pulse measurements were carried out using (5.0%) CO/He gas flow of 50 mL/min. Finally, the surface concentration and dispersion of metallic Ru were obtained from the CO pulse analysis data.