



Catalytic hydrogenation of xylose to xylitol using ruthenium catalyst on NiO modified TiO₂ support

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ABSTRACT

The activity of Ru catalyst on a new class of NiO modified TiO₂ support, Ru/(NiO–TiO₂), was studied in the liquid phase catalytic hydrogenation of xylose to xylitol. The TiO₂ support was modified by simple impregnation method using nickel chloride precursor and subsequent oxidation. Various catalysts with different targeted compositions of Ru (1.0 and 5.0 wt%) and NiO (1.0, 5.0 and 10 wt%) in NiO–TiO₂ were prepared. These catalysts were 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 novel catalysts are evaluated for selective hydrogenation of xylose and the results compared with those obtained from conventional Raney Ni, Ru/C and Ru/TiO₂ catalysts carried out under identical reaction conditions. The effect of NiO additive in the catalyst Ru/(NiO–TiO₂), clearly found to enhance the conversion, yield and selectivity to xylitol. Furthermore, the order of catalytic activity may be given as Ru (1.0%)/NiO (5.0%)-TiO₂ > Ru (1.0%)/TiO₂ > Ru (1.0%)/C > Raney Ni. The effects of Ru and NiO loading, xylose concentration (2.5, 15 and 30 wt%) and temperature (100, 120 and 140 °C) were studied. Although at higher temp 140 °C, the conversion of xylose was increased to optimum level, xylose to xylitol selectivity decreased due to formation of by-products.

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1. Introduction

The selective catalytic hydrogenation of naturally occurring sugar molecules to their corresponding sugar alcohols is an environment friendly route for the production of alternative sweeteners: solid metal-based catalysts are used in an aqueous environment and the hydrogen addition is brought about through catalytic reactions, thus avoiding the use of stoichiometric reducing agents and the subsequent formation of inorganic salts as waste material [1–3]. Xylitol, a penta carbon sugar alcohol with interesting properties, is an excellent artificial sweetener gaining large importance in recent years. The annual xylitol market is estimated to be around \$340 million priced at ~\$5/kg indicating its significance in many food and other value added chemical industries. It is highly soluble in water, does not caramelize at elevated temperatures, its sweetening capacity exceeds that of sugar and has lower insulin requirements, thus being especially suitable for usage by diabetics. Over the last few years, the demand for xylitol has increased enormously [4–7]. Xylitol also finds applications in several other industries such as in pharmaceutical, cosmetic, and synthetic resin [8–11]. The hydrogenation of xylose to xylitol is

traditionally carried out in a three-phase slurry batch reactor over Raney nickel catalysts [12]. The principal advantages of the use of nickel catalysts are its lower price, ease of use as suspended slurry in typical batch reactions, good activity and selectivity [11,13]. Nevertheless, the major drawback of Raney Ni catalysts, usually, is their relatively fast deactivation due to accumulation of organic impurities (from the starting material) on the catalyst surface, leading to poisoning of the active sites, and metal leaching [1,14–16]. Consequently, conversion rates and process selectivity are jeopardized. In addition, it is most important that Ni must be completely removed from hydrogenated xylitol solution when it is used in the food industry, or as medicine or cosmetics, which adds further costs since expensive purification steps such as ion-exchange, filtering and crystallization are involved [15]. The past few years have seen a variety noble (Pt, Pd, Ru) metals with some supports, but among them Ruthenium based catalysts which show much less or no deactivation, have been found as alternative to Ni based catalysts for hydrogenation processes in recent years [17–21]. Investigations are under progress for proper metal-support systems for the direct hydrogenation of xylose-rich solutions (Scheme 1) leading to high activity and selectivity levels towards xylitol production, while being less sensitive to the deactivation of catalyst surface by fouling species. Although some reports are available on the applications of Ru on activated carbon and TiO₂ support, there is no systematic study using modified TiO₂ support.

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