Selective hydrogenation of adipic acid to 1,6-hexanediol by atomically dispersed Ni on silica

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Abstract: This study investigated one-step hydrogenation of adipic acid (AA) to 1,6-hexanediol (HDO) by atomically dispersed Ni/SiO_2 catalyst (Ni-ad). Significant high HDO yield (~94%) with complete conversion of AA could be achieved at 220 ^oC and 50 bar initial H_2 pressure with a 12-h reaction time compared to the HDO yield (~56%) of the benchmark catalysts, 5 wt% $RuSn/Al_2O_3$ (RuSn). Proper physicochemical properties of tested catalysts were performed. The reaction network of AA hydrogenation was established as well. The outstanding performances of Ni-ad is because of its finely dispersed $Ni^0/Ni^{\delta+}$ paired sites, which are effective in C=O bond weakening and hydride insertion.

Keywords: adipic acid, hydrogenation, 1,6-hexanediol, nickel, silica.

1. Introduction

Adipic acid (AA) is an important chemical used as a comonomer in polymer synthesis (such as nylon 6/6) and as an additive in food industry. The growing productivity of AA propelled by coal utilization in China stimulates the upgrading of AA into more valuable chemicals. 1,6-Hexanediol (HDO), a versatile chemical used in polyurethanes, coatings, and adhesives manufacturing, can be derived from AA. Conventional way to upgrade AA to HDO is through a two-step process: AA esterification with methanol to form dimethyl adipate (DMA), followed by DMA hydrogenation to HDO. However, distillation is required to remove water and side products to facilitate the slow and reversible esterification step.[1]

Atomically-dispersed metal catalysts with high weight loading (~15%) have gained great attentions because of its potential of being easily synthesized and large-scale manufactured. Moreover, finely dispersed metal particles in nano-scale range can be formed and strongly integrated in silica support, allowing a long-term operation in harsh reaction conditions.[2]

This study, for the first time, reports a one-step hydrogenation process of AA to HDO using Ni-ad, and was compared with the benchmark catalysts, 5 wt% $RuSn/Al_2O_3$ (RuSn) and 20wt% Ni/SiO_2 (Ni-im) under the same reaction platform. A head-to-head comparison showed that Ni-ad is more active and selective in AA to HDO than its counterparts. Moreover, spent Ni-ad can be recycled for more than 3 times in the same reaction condition with negligible loss of hydrogenation activity. Such an outstanding catalytic behavior is attributed to the unique and finely dispersed $Ni^0/Ni^{\delta+}$ paired sites in Ni-ad.

2. Experimental

Ammonia evaporation combined with hydrothermal method was used to synthesize Ni-ad with a Ni loading of 15 wt%.[2] The incipient wetness impregnation was used to fabricate RuSn and Ni/SiO_2 (Ni-im) with the same Ni loading. Physicochemical properties were characterized by N_2 physisorption, XRD, HR-TEM, XPS, UV-vis, pyridine-IR, CO chemisorption/desorption, H_2-TPR, and NH_3-TPD. A mixture containing 0.1 g AA, 60 mL 1,4-dioxane, and 0.1 g of catalyst were used in catalytic testing. Hydrogenation of AA was conducted in a H_2-pressured, 300 mL batch-type reactor (Parr model 4561) at 220 ^oC and 50 bar with a 500 rpm stirring rate. The resulting polar and non-polar compounds were quantitative analyzed by a gas chromatograph (GC, Shimadzu 2010 plus) with a 0.32 mm x 30 m SH-Rtx-Wax capillary column and a GC/MS (Agilent 5890 II / 5972) with a 0.25mm x 60 m Agilent DB-5MS capillary column.

3. Results and discussion

Scheme 1 shows the reaction network of AA hydrogenation based on product distribution. The main route for HDO synthesis is onset by AA hydrodeoxygenation to hydroxycarboxylic acid (HA), followed by HA dehydration to caprolactone and caprolactone hydrogenation.

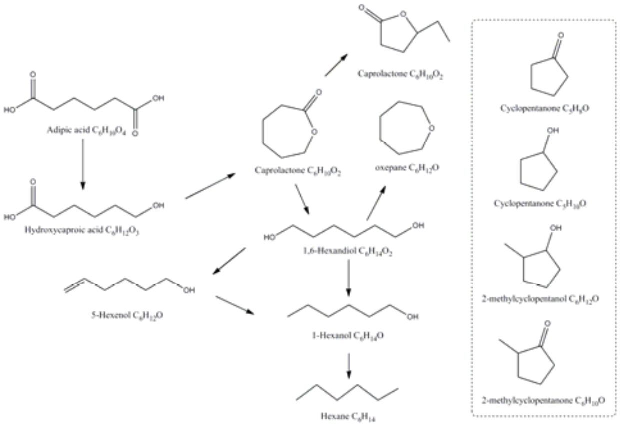

Figure 1. Reaction network of AA hydrogenation.

Figure 1 (A) and (B) displays the conversion of AA and product yields over RuSn and Ni-ad, respectively, as a function of time. Conversion of AA increased from 50% to 100% for RuSn from 0.5 h to 3 h, while that of Ni-ad reached 100% at 6 h. This indicates that RuSn is more active than Ni-ad in AA conversion. However, product yields were quite different: merely 56% yield of HDO was produced by RuSn with considerable amount of over-hydrogenated product, i.e.,1-hexanol (8%) and unidentified species (~30%). Conversely, an outstanding yield of HDO (94%) could be achieved over Ni-ad, with negligible side products. Catalyst characterization performed by TEM observed Ni particle in the range of 2 to 7 nm for Ni-ad; 10-20 m, Ni-im. XPS profiles showed that the oxidation state of Ni cations close to +1 for as-prepared Ni-ad, whereas Ni/SiO_2 prepared by impregnation has its oxidation state close to +2. H_2-TPR also revealed a multi-peak response below 250 °C, and CO desorption after chemisorption showed a lower higher CO desorption temperature of Ni-ad than Ni-im. All the characterization results revealed that Ni-ad contains small Ni particles in silica sheet. Moreover, metallic Ni coupled with higher oxidation states Ni cations formed a paired active site, which allows selective deoxygenation of AA conversion to HDO.

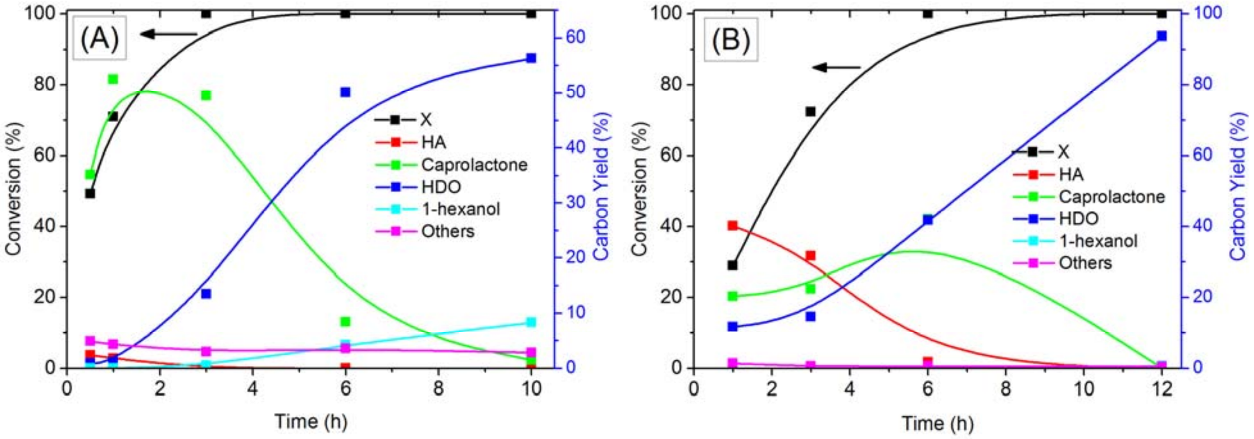

Figure 1. Conversion and product distribution as a function of time of (A) RuSn and (B) Ni-ad catalysts in AA conversion at 220 °C with initial H_2 pressure of 50 bar (autogenous pressure of ~68 bar).

4. Conclusions

AA can be selectively hydrogenated into HDO via atomically-dispersed Ni on silica with exceptional high yield (94%). The explanation for the outstanding performance of Ni-ad is because of the highly dispersed $Ni^0/Ni^{\delta+}$ paired sites in silica sheet. The partial positive charged Ni cation can weaken carboxyl group of AA, while finely dispersed metallic Ni facilitate hydride transfer for C=O bond hydrogenolysis.

References

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2. Y. Zhu et al., J. Catal. 353 (2017) 315-324.