

# HYDROGENATION OF GLUCOSE TO SORBITOL OVER NANOPARTICLE Ni/Al<sub>2</sub>O<sub>3</sub> CATALYSTS

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## Introduction

Hydrogenation of glucose to sorbitol is an industrially important chemical process because of wide applications of sorbitol in food, drug and cosmetics.<sup>1</sup> For example, D-sorbitol is an intermediate in the synthesis of vitamin C. Also, hydrogenation of glucose to sorbitol followed by aqueous phase reforming has been recently suggested as a route for the production of H<sub>2</sub> and fuels from biomass.<sup>2</sup> Nickel-based supported catalysts containing 50-60 wt% Ni are typically being used in the commercial scale hydrogenation of glucose as well as fats and oils. However, the high Ni content makes these catalysts very expensive, and undergo deactivation due to Ni leaching during the reaction. Stable and highly active Ni-based catalysts with lower Ni content are therefore needed to reduce catalyst cost and improve the efficiency of the hydrogenation process. This work investigates the catalytic performance of novel Ni/Al<sub>2</sub>O<sub>3</sub> nanoparticle catalysts containing 15 to 30 wt % Ni for the hydrogenation of glucose to sorbitol.

## Materials and Methods

Ni/Al<sub>2</sub>O<sub>3</sub> supported catalysts with nickel metal loading between 15 and 30 wt% were synthesized by three different methods, namely homogeneous alkalization (HA), layered double hydroxide coating (LC) and citrate process (CP).<sup>3</sup> They were characterized by ICP, BET surface area, TPR, XRD, and TEM.<sup>4</sup> The Ni metal surface area and dispersions were determined by both H<sub>2</sub>-TPD and static chemisorption methods. Batch hydrogenation tests of glucose were performed in a 600 mL high pressure Parr reactor using 1g of several pre-reduced and passivated Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. About 100g of 20% aqueous solution of glucose was loaded into the reactor for the tests at 580 psig hydrogen pressure and 120°C. Pressure drop as a function of time was monitored at a stirring rate of 1200 rpm. The product mixture after 4h was recovered and analyzed by HPLC.

## Results and Discussion

A series of over sixteen Ni/Al<sub>2</sub>O<sub>3</sub> catalyst samples have been synthesized employing the three different synthetic methods mentioned above. The Ni metal surface area, dispersion and particle size of a few selected samples determined by H<sub>2</sub>-TPD and static chemisorption experiments are shown in **Table I**. The results indicate that some of the samples, especially Ni/Al<sub>2</sub>O<sub>3</sub> – 6, Ni/Al<sub>2</sub>O<sub>3</sub> – 11, and Ni/Al<sub>2</sub>O<sub>3</sub> – 14 containing about 15 wt% Ni exhibit relatively higher Ni metal surface area (Ni SA) and dispersion (D), and smaller Ni metal crystallite sizes (dp) compared to a commercial Ni/Al<sub>2</sub>O<sub>3</sub> catalyst containing a similar Ni loading.

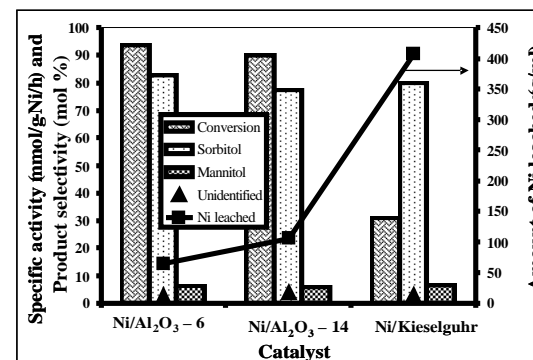
Hydrogenation of glucose has been performed as a test reaction over these catalysts and the results are shown in **Figure 1**. The catalysts Ni/Al<sub>2</sub>O<sub>3</sub> – 6 and Ni/Al<sub>2</sub>O<sub>3</sub> – 14 containing about 15 wt% Ni exhibit higher specific activity of over 90 mmol/g Ni/h with a selectivity of greater than 80 mol% to sorbitol, compared to the commercial Ni/Kieselguhr catalyst containing about 60 wt% Ni, which exhibits a specific activity of only about 30 mmol/g Ni/h. It is also interesting to note that the amount of Ni leached during hydrogenation reaction as measured by

ICP analysis of the reactor effluent is very low, about 60 µg/ml in the case of Ni/Al<sub>2</sub>O<sub>3</sub> – 6 catalyst developed in the present study compared to a very high Ni leaching of over 400 µg/ml observed for the commercial Ni/Kieselguhr catalyst. These results clearly highlight that novel nanoparticle Ni/Al<sub>2</sub>O<sub>3</sub> catalysts exhibiting high activity, selectivity and stability have been developed in the present study. Kinetic analysis of the batch reactor data for the catalysts tested will be presented.

**Table 1** Physicochemical properties of Ni/Al<sub>2</sub>O<sub>3</sub> hydrogenation catalysts

Catalyst	Synthesis Method	Ni loading (wt%)	Ni SA (m <sup>2</sup> /g-Ni)	D (%)	dp (nm)
Ni/Al <sub>2</sub> O <sub>3</sub> – 5	HA	25.5	131 (133)	19.6 (19.9)	5.2
Ni/Al <sub>2</sub> O <sub>3</sub> – 6	HA	15.6	170 (133)	25.5 (19.9)	4.0
Ni/Al <sub>2</sub> O <sub>3</sub> – 10	LC	26.9	159 (141)	23.8 (21.2)	4.3
Ni/Al <sub>2</sub> O <sub>3</sub> – 11	LC	15.6	142 (127)	21.4 (19.1)	5.2
Ni/Al <sub>2</sub> O <sub>3</sub> – 14	CP	16.9	128 (129)	19.2 (19.3)	5.3
Ni/Al <sub>2</sub> O <sub>3</sub> – Commercial	-	15.2	110	16.5 (16.3)	6.2
Ni/Kieselguhr	-	60.0	61.4	9.2	11.0

Data in parenthesis are obtained from static H<sub>2</sub> chemisorption



**Figure 1** Hydrogenation of glucose over nanoparticle Ni/Al<sub>2</sub>O<sub>3</sub> catalysts

## Significance

The alternative Ni/Al<sub>2</sub>O<sub>3</sub> hydrogenation catalysts of the present study with lower Ni loading, high dispersion and high stability compared to that of the commercial Ni-based hydrogenation catalyst could significantly reduce the cost of the catalyst and improve the efficiency of various industrially important hydrogenation processes, including hydrogenation of glucose, fats and oils.

## References

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