Green Chemistry

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Selective conversion of microcrystalline cellulose into hexitols on nickel particles encapsulated within ZSM-5 zeolite†

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A highly active and selective Ni/ZSM-5 catalyst was prepared by a simple method. A selectivity of 91.2% to hexitols was obtained at intermediate conversion in the hydrolytic hydrogenation of cellulose.

Cellulose is the most abundant form of biomass on earth, and is considered as an alternative resource of fuels and chemicals.[1] Considerable work has been devoted to develop various processes for the efficient transformation of cellulose to valued chemicals.[2] One-pot conversion of cellulose into polyols *via* hydrolytic hydrogenation is a promising approach for its greenness and energy efficiency. Fukuoka & Dhepe firstly investigated the conversion of cellulose over supported noble metal catalysts and they obtained 31% yield of hexitols (sorbitol and mannitol) with a Pt/A_2O_3 catalyst.[3] Since then, many studies have been devoted to improving hexitol yield by developing highly active and selective catalysts.[4] Recently, the combination of a supported Ru catalyst with acids was proven to be efficient for cellulose conversion.[5] The introduction of acids could significantly improve the hydrolysis rate of cellulose and the selectivity to hexitols. For example, the supported Pt, Pd and Ru catalysts showed a yield increase of sugar alcohols in the presence of dilute mineral acids, and C_4–C_6 sugar alcohols were produced in 81% yield by combining heteropoly acids and Ru/C in their further research. Ru-loaded zeolites and trace amounts of mineral acid presented >90% yield of hexitols for the conversion of cellulose. In addition, our previous study showed that about 50% yield of isosorbide was obtained for cellulose conversion over a Ru/C catalyst with dilute hydrochloric acid.[6]

Although the above results are extremely promising, the use of large amounts of noble metal catalyst means that the above approaches are too expensive to be applied in the large scale production. Non-noble metal catalysts, such as Ni, Cu and tungsten carbide catalysts may be more suitable for the practical hydrogenation of cellulose because of fast turnover rates, availability and low cost.[7] Most recently, the catalytic activity of nickel

supported on a variety of supports (Al_2O_3, TiO_2, SiO_2, AC, ZnO, ZrO_2 and MgO) was evaluated for the conversion of cellulose, in which the supports played an important role in product distribution and selectivity.[8] The nickel catalysts favored the formation of 1,2-propanediol, ethylene glycol, 1,2-butanediol and 1,2-hexanediol, suggesting the superior hydrogenolysis activity of Ni catalysts on cellulose conversion. Simultaneously, mesoporous carbon supported Ni-based bimetallic catalysts were reported to be effective for the conversion of cellulose to hexitols, as nearly 60% yield of hexitols was obtained at the complete conversion of cellulose over a modified Ir-Ni/MC catalyst.[9] The above results suggested that the nickel-based catalyst was comparable to the noble metal catalysts for the conversion of cellulose under similar conditions, and of a potential significance from the points of research and utilization.

Herein, we developed a highly active monometalitic Ni-based catalyst for the conversion of cellulose in hot water. Approximately 91% selectivity of hexitol was obtained at intermediate conversion. Moreover, approximately 60% yield of hexitols was obtained under the optimum conditions, which is comparable to the best results over Ir-Ni/MC catalysts.[9] The excellent catalytic performance of the Ni/ZSM-5 catalyst is intriguing since the mesoporous materials have been considered to be the most promising catalyst supports for the conversion of cellulose, in contrast to materials with micropores such as ZMS-5.[7a,9,10] Therefore, the present work exhibited unexpected results, including the use of ZMS-5 in the conversion of cellulose and the dependence of product distribution on the support. Active species and metal morphology have been discussed in detail by combining the experimental data and catalyst characterizations.

All the supported Ni catalysts were prepared by a modified incipient impregnation method[11] and their catalytic performance on cellulose conversion were summarized in Table 1. The HPLC analysis demonstrated that hexitols and C_2–C_3 polyols (glycerol, ethylene glycol and propanediol) are produced as the main products. The previous research showed that the transformation of cellulose contains several consecutive reactions, such as (1) the hydrolysis of cellulose to glucose and the hydrogenation of glucose producing hexitols, as well as (2) the subsequent hydrogenolysis of hexitols to produce small molecular alcohols.[4,5] Meanwhile, the overall conversion is determined by the cellulose hydrolysis which is considered as the rate determining step for the hydrolytic hydrogenation of cellulose under hydrothermal conditions. Similar conversions (~84%) were obtained over all the catalysts independent of which was used, indicating that the

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Table 1 Results for the conversion of cellulose and sorbitol on the supported Ni catalysts[a]

Catalyst[b]	Substrate	Conversion[c]/%	Yield[d]/% (based on carbon)			
			Hexitols	Glycerol	EG	1,2-PDO
Ni/Al$_2$O$_3$	Cellulose	84.7	14.2	5.6	4.3	7.2
Ni/SiO$_2$	Cellulose	84.4	15.8	2.8	3.1	5.0
Ni/ZSM-5	Cellulose	85.5	48.6	1.0	2.1	1.2
Ni/bentonite	Cellulose	82.9	10.2	10.6	5.0	8.3
Ni/kieselguhr	Cellulose	84.4	5.8	9.5	5.1	13.2
Ni/TiO$_2$	Cellulose	82.3	13.8	5.3	3.8	4.6
Ni/Al$_2$O$_3$	Sorbitol	96.3	—	16.9	11.4	11.5
Ni/SiO$_2$	Sorbitol	86.5	—	7.9	5.4	5.3
Ni/ZSM-5	Sorbitol	34.4	—	5.4	2.9	2.0
Ni/bentonite	Sorbitol	58.1	—	11.5	8.7	13.2
Ni/kieselguhr	Sorbitol	18.6	—	4.2	5.1	9.1
Ni/TiO$_2$	Sorbitol	63.1	—	5.2	4.2	5.5

[a] Reaction conditions: 513 K, H$_2$ 4.0 MPa (RT), microcrystalline cellulose 0.2 g, H$_2$O 10 ml, 4 h, catalyst 100 mg. [b] Ni loading = 40%, ZSM-5 was in H type with Si/Al = 25. [c] Conversion was calculated by the initial weight of cellulose and catalyst divided by the residual solid weight after reaction. [d] The yield of product = (moles of carbon in the product)/(moles of carbon in the substrate).

catalysts used have a similar influence on cellulose hydrolysis under our reaction conditions. However, the product distribution was largely different among the Ni catalysts on various types of supports, and the highest selectivity to hexitol was obtained over the Ni/ZSM-5 catalyst. Compared to other catalysts, the acidity of the solid supports should not affect the hexitol selectivity as the strength of the surface acid sites is not the predominate factor for affecting the production of hexitols. The factors concerning the selectivity of hexitols were discussed from the following two aspects: (i) if the nickel catalysts have a high activity for glucose hydrogenation, the first route is the predominate reaction, resulting in a higher selectivity to hexitol, otherwise glucose is seriously decomposed to complex degradation products. (ii) hexitols may suffer subsequent hydrogenolysis to yield smaller molecular polyols during the reaction, resulting in a decrease in selectivity. Herein, sorbitol was used as the starting substrate to characterize the extent of the hydrogenolysis under identical reaction conditions (Table 1, entries 7–12). The conversion of sorbitol over different catalysts was in the order of Ni/Al$_2$O$_3$ > Ni/SiO$_2$ > Ni/TiO$_2$ > Ni/bentonite > Ni/ZSM-5 > Ni/kieselguhr, yielding glycerol, ethylene glycol and propanediol as main products. The Ni/ZSM-5 catalyst presented lower activity for the hydrogenolysis of sorbitol, which was related to the high hexitol yield maintained in the hydrolytic hydrogenation of cellulose under identical conditions.

The performance of Ni/ZSM-5 catalyst in cellulose conversion and sorbitol hydrogenolysis is intriguing compared to other catalysts. For further discussion, the activity of three Ni/ZSM-5 catalysts with different Ni loadings was compared in Fig. 1. The hexitols were produced with a 91.2% selectivity at 48.9% cellulose conversion under the optimized reaction conditions (503 K, 4.0 MPa H$_2$ and 6 h). To the best of our knowledge, this is the highest cellulose conversion over Ni catalysts reported. The conversion of cellulose obtained over these catalysts was not much different; however, hexitol yield depended largely on Ni loading. 17% Ni/ZSM-5 gave the highest yield of 58.2%, while the 5% Ni/ZSM-5 and 40% Ni/ZSM-5 catalysts gave 24.7 and 40% yield, respectively. Based on the above analysis, we concluded that Ni/ZSM-5 catalyst had a high
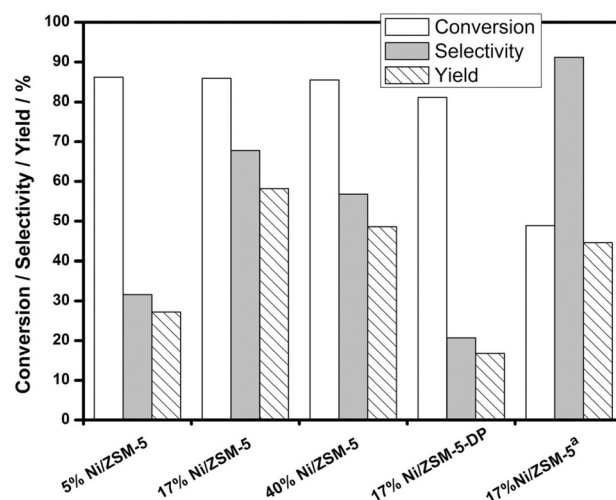
Fig. 1 Conversion and selectivity of cellulose hydrogenation on Ni based catalysts. The reaction conditions are the same as that in Table 1. [a]503 K, 6 h.

catalytic ability, while the decrease in yield over the 5% Ni/ZSM-5 and 40% Ni/ZSM-5 catalysts may be preliminarily due to the hydrogenolysis of hexitols. However, the experimental data showed that hexitol was converted at only 2.6, 7.8, and 8.6% respectively over the 5, 17, and 40% Ni/ZSM-5 catalysts under similar reaction conditions (503 K, 4.0 MPa H$_2$, 6 h). This suggested that the Ni/ZSM-5 catalysts have inferior activity for hexitol hydrogenalysis, irrespective to the Ni loading. Comparing the catalytic performance of 5% Ni/ZSM-5 on cellulose hydrogenation and sorbitol hydrogenolysis, it is concluded that 5% Ni/ZSM-5 had low activity for the hydrogenation of glucose formed from cellulose hydrolysis, inducing a large amount of glucose to degradate to smaller molecules in aqueous phase. Moreover, a 17% Ni/ZSM-5-DP catalyst prepared by precipitation method showed a quite a low yield (16.8%) of hexitols, even lower than that over the 5% Ni/ZSM-5 catalyst (27.2%).

Therefore, the selectivity to hexitols over Ni/ZSM-5 catalysts was proposed to depend on several factors such as active species, particle distribution, interaction between metal particles and support, the correlation between catalytic performance, and the nature of the catalyst. The XRD patterns for the Ni/ZSM-5 catalysts exhibited similar characteristic diffraction peaks for the metallic Ni species (Fig. 2), as for the 5% Ni/ZSM-5 catalyst. The diffraction peaks of nickel were relatively weak, suggesting that the nickel species was not well crystallized and mostly in the amorphous phase. In contrast, the 17 and 40% Ni/ZSM-5 samples presented sharp diffraction peaks of metallic nickel with better crystal facets especially with a rich Ni(111) facet compared to the 17% Ni/ZSM-5-DP and 5% Ni/ZSM-5 samples, which may relate to their catalytic activity and will be discussed later. The analysis of the TPR results showed only one single major reduction peak presented on the 17% Ni/ZSM-5-DP catalyst (Fig. 3), suggesting that only one nickel species existed in the Ni/ZSM-5-DP prepared by precipitation. However, two peaks were observed at relatively higher temperatures for the other Ni/ZSM-5 samples prepared *via* the impregnation method, indicating that the interaction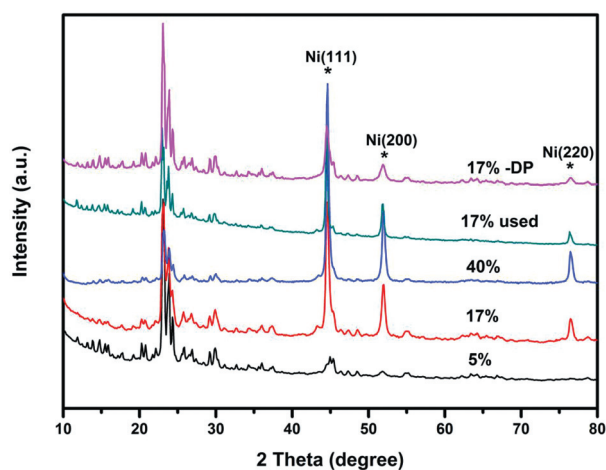 between the nickel particles and the support was stronger, in addition to two active species presented on the Ni/ZSM-5 samples prepared by impreganation. In the literature, Ni(111) was demonstrated to be active for the hydrogenation reaction.[12] Thus, taking this into account, along with the experimental data in Fig. 1, we can deduce that the nickel particles with a rich Ni(111) facet, having a higher reduction temperature, were more active for the hydrogenation of glucose. Therefore, the lack of Ni(111) facets should be responsible for the low activity of the 5% Ni/ZSM-5 catalyst in glucose hydrogenation.
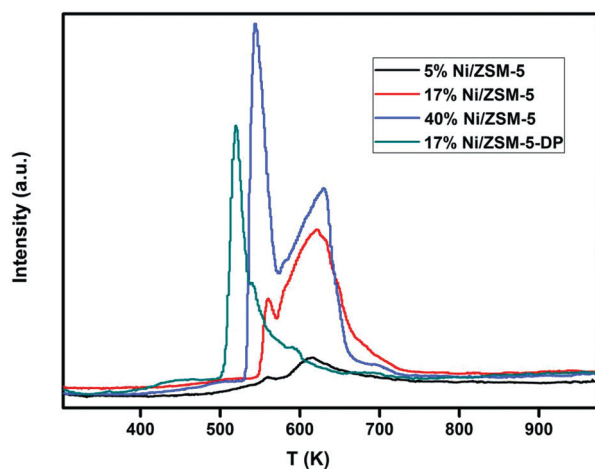
In addition, the TEM images of the Ni/ZSM-5 catalysts (Fig. 4a, 4a′) showed that the nickel was highly dispersed throughout the 5% Ni/ZSM-5 catalyst with a particle size of approximately 4–8 nm. For the 17% Ni/ZSM-5-DP catalyst, the particle size is approximately 8–15 nm (Fig. 4c, 4c′). Meanwhile, most of the nickel particles on the 17% Ni/ZSM-5 sample are spherical in shape with a narrow size distribution and the average particle size is ~19 nm (Fig. 4b, 4b′). The nickel particles presented are uniformly spherical, looking like spheral flower buds with loose leaves. Further observation showed that those "leaves" were mainly composed of Ni(111) facets (Fig. S1†). The difference in the reducibility and morphology of nickel particles was attributed to the preparation methods, which were also related to the selectivity of hexitols. When the catalyst was prepared by a deposition–precipitation method, the nickel species was mainly precipitated on the outer surface of the ZSM-5 zeolite, and so a reduction peak was observed at a relatively low temperature in the TPR spectra. For the catalysts prepared by the impregnation method, the nickel species were not only adsorbed on the outer surface but mostly immersed into the channels of ZSM-5, having a stronger interaction with the ZMS-5 zeolite, thus the catalysts presented two reduction peaks in the TPR spectra. As all Ni/ZSM-5 catalysts prepared by the impreganation method gave low conversions in sorbitol hydrogenolysis, we could propose that nickel particles encapsulated within the ZSM-5 zeolite had an inferior activity for hexitol hydrogenolysis.

The hydrolytic hydrogenation of cellulose involved several basic steps, such as cleavage of glycosidic bonds, hydrogenation of C═O bonds and cleavage of C–C and C–O bonds. Being
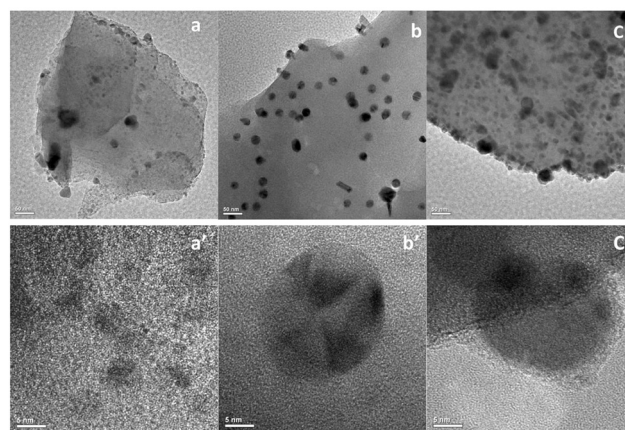

Fig. 2 XRD pattern of the Ni/ZSM-5 catalysts.

Fig. 3 H$_2$-TPR profiles of the Ni/ZSM-5 catalysts.

Fig. 4 TEM images for (a, a′) 5% Ni/ZSM-5 catalysts; (b, b′) 17% Ni/ZSM-5; and (c, c′) 17% Ni/ZSM-5-DP catalysts. 100 particles were counted for analysis.

different from the other Ni catalysts, Ni/ZSM-5 catalyst could suppress the cleavage of C–C and C–O bonds, maintaining high hexitol selectivity at elevated temperatures. The above results indicated that the microstructure of the nickel particles had a major influence on the activity and selectivity of the Ni/ZSM-5 catalysts in cellulose conversion. The excellent selectivity to hexitols was obtained with 17% Ni/ZSM-5 catalyst due to its petaloid-like (a flower bud-like structure) microcrystallinity with a rich Ni(111) crystal plane which had a stronger metal-support interaction with the ZSM-5 zeolite. This unique structure could favor the formation of hexitols from the hydrogenation of glucose produced from cellulose, but not the further hydrogenolysis of hexitols. The adsorption behavior of glucose and hexitols on the nickel particles may allow us to understand the reaction mechanism and will be further investigated in our future work. However, the Ni/ZSM-5 catalyst deactivated remarkably in the second recycling. The stability analysis and improvement of Ni/ZSM-5 is an important issue and also a challenge for Ni-based catalyst utilization in aqueous phase catalysis.[13]

In conclusion, we developed an effective Ni/ZSM-5 catalyst, which could catalyze the hydrolytic hydrogenation of cellulose into hexitols with high activity and selectivity. The nickel particles encapsulated within the ZSM-5 zeolite have a unique flower bud-like structure, and the catalyst demonstrated a high selectivity toward hexitols (91.2%)—the highest for cellulose hydrogenation by heterogeneous catalysts reported to date. The present results reveal that Ni-based catalysts may replace noble metal catalysts in the transformation of biomass. This work will encourage subsequent research on non-noble metal catalysts in the field of the biomass conversion, and it is expected that some innovative results will be obtained using low-cost nickel based catalysts.

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