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COMMUNICATION

Catalytic conversion of cellulose to hexitols with mesoporous carbon supported Ni-based bimetallic catalysts†

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Robust and highly active Ni-based bimetallic catalysts supported on mesoporous carbon have been developed for catalytic conversion of cellulose to hexitols, over which the maximum hexitol yield reached 59.8%.

Fossil energy depletion and global warming have stimulated great interest in the study of biomass conversion due to its renewable property and low net CO_2 emission level. Cellulose is one of the most abundant sources of biomass, which accounts for 40–60 wt% of dry lignocellulosic biomass. The plentiful functional groups (*e.g.*, OH groups) of cellulose make it an ideal feedstock for sustainable production of chemicals.[1] Nevertheless, the extensive hydrogen-bonding networks and the high crystallinity of cellulose make it resistant to chemical and enzymatic degradation.[2] Great efforts have been devoted to the cellulose transformation in various ways, such as fermentation with enzyme,[3] photochemical conversion,[4] hydrolysis with acid catalysts,[5] pyrolysis at high temperatures,[6] and etherification with alcohols.[7]

One-pot conversion of cellulose with solid catalysts under hydrothermal conditions is a green and efficient process for the sustainable production of chemicals, in which several consecutive reactions proceed in one reactor and cooperate well. For example, when the hydrolysis of cellulose is coupled with the hydrogenation of glucose over a noble metal catalyst, hexitols (containing sorbitol and mannitol) are produced as the main product.[8] On the other hand, when the hydrolysis of cellulose is coupled with hydrogenolysis of sugars over a tungsten-based catalyst, ethylene glycols are yielded predominantly.[9]

Hexitols are not only used as a sweetener in food industry but also currently considered as an important platform chemical for the sustainable production of fuels and chemicals.[10] Following the pioneering work of Fukuoka for the one-pot conversion of cellulose to hexitols,[8a] there have been great efforts towards the enhancement of sorbitol yield.[11] Nevertheless, there are few solid catalysts able to arrive at a hexitol yield exceeding 50% when microcrystalline cellulose is used as the feedstock. Moreover, the harsh reaction conditions required for the conversion of cellulose exerts a great challenge on the stability of a solid catalyst.[12]

Carbon material is one of the best choices as the catalyst support due to its excellent stability under hydrothermal conditions and large surface area for dispersing active components. In particular, mesoporous carbon (MC) materials offer great advantages over conventional activated carbon (AC) owing to their well-controlled pore structures in the mesopores which are favorable to transportation of large molecules.[13] Recently, we found that the MC supported tungsten carbide catalysts exhibited much superior performance for cellulose conversion into ethylene glycol compared to the AC supported counterparts.[9d] Moreover, sulfonated MC was more active than the sulfonated AC for the hydrolysis of cellulose to glucose.[5c] Similar to our findings, Fukuoka *et al.* reported that Ru catalysts supported on mesoporous CMK-3 were water-tolerant and reusable for the catalytic degradation of cellulose to sugars.[14] All these studies demonstrate that MC is a superior support in the conversion of cellulose under hydrothermal conditions.

Herein, we report that a series of Ni-based bimetallic catalysts supported on MC are very active and highly stable for the conversion of cellulose to hexitols. Typically, Rh-Ni/MC and Ir-Ni/MC catalysts give a yield of hexitols close to 60% with complete conversion of cellulose. The modification of nickel with noble metals improves greatly the stability of catalysts, and 4%Ir-4%Ni/MC catalysts can be recycled 4 times without any loss of performance. To our knowledge, this is the best performance of heterogeneous catalysts ever reported for the cellulose conversion to hexitols.

The MC support was prepared by a nanocasting method with sucrose as the carbon precursor and a commercial silica fume as the hard template as reported previously.[9d,15] As expected, the MC support presents a high surface area (983 $m^2\ g^{-1}$) and a large pore size (9.4 nm). Interestingly, a loading of 5%Ni or Ni-based bimetallic components leads to a further increase of the surface area, up to 1106 $m^2\ g^{-1}$ (Table S1†). The preferred textural properties of the MC support provide a better dispersion of metal component than AC. As shown in Fig. 1, the Ni particles are uniformly dispersed on the 20%Ni/MC, and most of the

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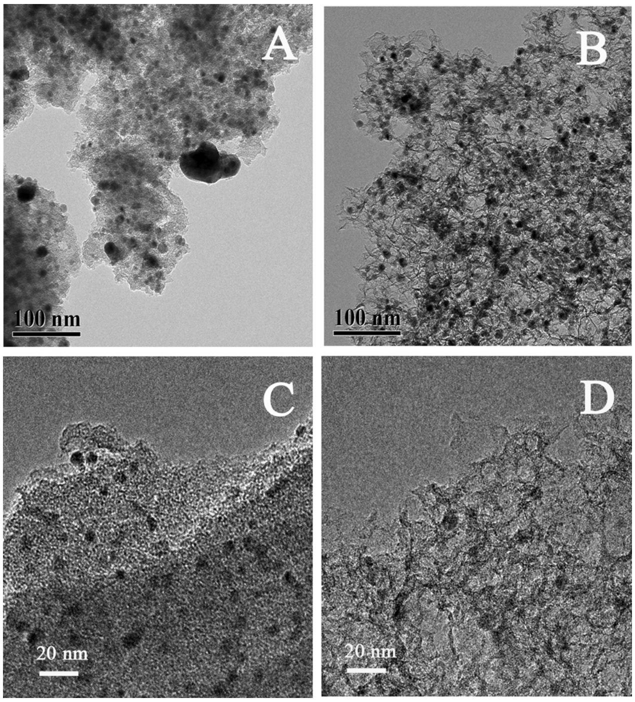

Fig. 1 TEM images of 20%Ni/AC (A), 20%Ni/MC (B), 1%Ir-5%Ni/AC (C), and 1%Ir-5%Ni/MC (D).

particles are ~ 10 nm in size. In contrast, over the 20%Ni/AC, as well as Ni particles of ~10 nm, many large nickel particles are formed in sizes of several tens of nanometres. This is consistent with the XRD result that the Ni on the MC has notably higher dispersion than that on the AC (Fig. S1†). The unique 3-D open structure and the suitable pore size distributions of the MC might contribute to the better metal dispersion. The bimetallic catalysts of 1%Ir-5%Ni/AC and 1%Ir-5%Ni/MC have similar metal particle size distributions in the range 2–10 nm. EDX analysis of many individual particles shows that the molar ratio of Ni to Ir is not uniform from one particle to another, but most of the particles are composed of two metals (Fig. S2†), in agreement with the XRD result (Fig. S1†) that Ni and Ir form alloys in the bimetallic catalyst.

The catalytic performances of catalysts were evaluated for microcrystalline cellulose conversion at 245 °C and 6 MPa H_2 for 30 min. As shown in Table 1, the MC supported nickel catalyst gave very good performance. On the 20%Ni/MC catalyst, the cellulose conversion reached 84.5% and the hexitol yield was up to 42.1% (Entry 2). This result is even better than that over the supported Ru catalyst reported in the literature, where the best yield of hexitols was 39.3% and the cellulose conversion was 85.5%.[8b] In contrast, for 20%Ni/AC catalyst, the cellulose conversion was 61.9% and the hexitol yield was merely 19.7% (Entry 1). Clearly, the MC supported nickel catalyst is much more efficient than the AC supported counterpart for cellulose conversion. Considering the nickel dispersion on the AC is inferior to that on the MC, we supplemented RANEY® Ni catalyst to the 20%Ni/AC to improve the hydrogenation ability. However, the mixed catalyst did not show notable improvement either in the cellulose conversion or in the hexitol yield (Entry 3). Accordingly, one can conclude that the different performance of Ni/MC and Ni/AC mainly originates from the different nature of carbon materials.

The promising activity of the Ni/MC catalyst encouraged us to further investigate its stability during repetitive runs. To facilitate the catalyst recycling after the reaction, ball-milled cellulose was used as the feedstock. As shown in Fig. 2A, the hexitol yield reached 60.8% in the first run with the 20%Ni/MC catalyst. The catalyst became even more active for the formation of hexitols in the second run. However, the hexitol yield began to decline remarkably in the subsequent runs until 22.3% in the fifth run. Therefore, in spite of very good performance of the fresh Ni/MC catalyst, it can not be recycled. The TEM image of the spent catalyst after 5 repetitive runs reveals significant aggregation/

Table 1 The polyols product distribution from the cellulose conversion over different catalysts[a]

		Yield (%)									
Entry	Catalyst	EG	1,2-PG	HA	Gly	Ery	Man	Sor	Hexitol	Gas	Conv. (%)
1	20%Ni/AC	11.9	4.2	4.0	0.9	1.7	4.6	15.1	19.7	10.0	61.9
2	20%Ni/MC	9.9	3.7	3.3	3.8	2.6	2.7	39.4	42.1	6.0	84.5
3	Mixed catalyst[b]	9.9	5.4	4.3	2.4	1.3	6.8	13.5	20.3	13.2	—
4	1%Pt-5%Ni/MC	7.3	3.4	4.2	4.9	2.8	7.5	39.9	47.4	3.4	100
5	1%Pd-5%Ni/MC	5.3	3.0	3.6	5.1	3.0	5.6	47.6	53.2	2.6	100
6	1%Ru-5%Ni/MC	3.3	3.0	7.7	5.2	2.3	12.6	41.6	54.2	13.8	100
7	1%Rh-5%Ni/MC	5.3	3.5	4.8	5.4	3.4	8.3	51.5	59.8	7.7	100
8	1%Ir-5%Ni/MC	4.7	3.4	5.6	6.7	3.0	9.6	47.9	57.5	2.6	100
9	1%Ir/MC	7.6	4.3	11.6	1.4	0.7	1.1	3.6	4.7	1.3	90.4
10	5%Ni/MC	8.1	3.8	7.1	1.6	1.0	2.5	7.9	10.4	2.3	85.7
11	Mixed catalyst[c]	8.3	5.7	1.2	4.4	2.7	4.5	32.5	37.0	1.7	92.3
12	2%Ir-5%Ni/MC	9.5	2.7	2.8	2.6	3.1	6.0	47.5	53.5	1.2	99.5
13	3%Ir-5%Ni/MC	8.9	2.4	0	2.4	2.9	7.0	47.8	54.8	1.3	100
14	4%Ir-4%Ni/MC	8.0	1.9	5.7	2.2	2.4	11.5	46.8	58.3	2.4	100
15	1%Ir/AC	5.5	3.3	15.7	1.1	0.8	1.3	2.2	3.5	4.1	65.6
16	5%Ni/AC	11.8	5.0	2.2	0.7	1.4	1.5	6.0	7.5	7.8	58.6
17	1%Ir-5%Ni/AC	15	7.5	5.4	—	2.7	4.7	8.0	12.7	3.8	78.9

[a] The reactions were conducted at 245 °C and 6 MPa H_2 for 30 min. EG, 1,2-PG, HA, Gly, Ery, Man, Sor represent ethylene glycol, 1,2-propylene glycol, hydroxyacetone, glycerol, erythritol, mannitol, and sorbitol, respectively. [b] 0.15 g RANEY® Ni was mixed with 0.15 g 20%Ni/AC. [c] 0.15 g 1%Ir/MC was mixed with 0.15 g 5%Ni/MC.

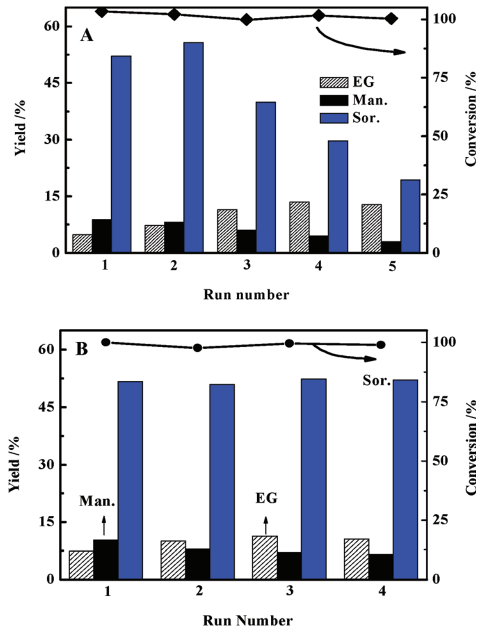

Fig. 2 The reusability of Ni-based catalysts in cellulose conversion. (A) 20%Ni/MC with ball-milled cellulose as the feedstock; (B) 4%Ir-4% Ni/MC with microcrystalline cellulose as the feedstock.

agglomeration of the Ni particles (Fig. S3†), which is probably caused by the leaching of the Ni particles out of the catalyst into hot water and re-deposition on the catalyst surface. On the other hand, we noticed that the conversions of ball-milled cellulose were kept at 100% in the recycling tests, which implies that the activity for hydrolysis of cellulose does not decay by the leaching of Ni. In other words, the MC support may play important roles in promoting the hydrolysis of cellulose, while the Ni component catalyzes the hydrogenation of sugars.

Noble metals have good hydrothermal stability and excellent hydrogenation activities. Furthermore, when they combine with nickel, the bimetallic catalysts usually show distinguished hydrogenation performance thanks to the tunable electronic and chemical properties superior to those of the parent metals.[16] Herein, we introduce the noble metals to Ni catalysts to enhance the catalytic activity and stability.

Table 1 shows the results of cellulose conversion over various Ni-based bimetallic catalysts. All the MC supported bimetallic catalysts gave 100% cellulose conversion (Entries 4–8). Meanwhile, the hexitol yields were from 47% to 60% depending on the noble metals, and following the order of 1%Pt-5%Ni/MC < 1%Pd-5%Ni/MC < 1%Ru-5%Ni/MC < 1%Ir-5%Ni/MC < 1% Rh-5%Ni/MC. The best result was obtained over the 1%Rh-5% Ni/MC catalyst with the hexitol yield as high as 59.8%. This is the highest value obtained so far on heterogeneous catalysts. The 1%Ir-5%Ni/MC catalyst was only slightly less active than the 1%Rh-5%Ni/MC catalyst, but Ir is much cheaper than Rh and will be a more practical choice in industrial applications. Therefore, we made a more detailed study of Ir-Ni/MC catalyst system. Compared with the two monometallic catalysts as well as their mechanical mixture (Entries 9–11), the MC supported Ir-Ni bimetallic catalysts presented strong synergistic effects. We also investigated the effect of the amount of Ir on the performance of the Ir-Ni/MC bimetallic catalysts. Increasing the Ir loading from 1% to 4% (Entries 8, 12–14) did not result in pronounced enhancement in the hexitol yield.

The reusability of the Ir-Ni/MC bimetallic catalyst was tested and the results are shown in Fig. 2B and Fig. S4.†In the four repetitive runs, the 1%Ir-4%Ni/MC gives a much improved stability than monometallic 20%Ni/MC. Further increasing the Ir loading to 4% results in even more stable performance; no sign of any decay is observed on 4%Ir-4%Ni/MC. The XRD patterns (Fig. S5†) and TEM images (Fig. S6†) of the used catalyst show no aggregation of metal particles occurred on the Ir-Ni/MC bimetallic catalyst. This result demonstrates that the noble metal modified nickel catalysts are rather durable in hydrothermal conditions for cellulose conversion.

In contrast to the MC-supported Ir-Ni bimetallic catalysts, the AC-supported Ir-Ni bimetallic catalysts behaved rather poorly in the conversion of cellulose to hexitols, and no synergistic effect occurred (Entries 15–17). This is a surprising result because the particle sizes as well as structures of the bimetallic particles look very similar in AC and MC supports.

To uncover the underlying reason for the different behaviors of AC and MC supported Ir-Ni bimetallic catalysts, we designed some control experiments. Firstly, we compared their catalytic performance for the reaction of glucose hydrogenation, which is an intermediate step in the conversion of cellulose to hexitols. The results show that the addition of a small amount of noble metals to the monometallic nickel catalysts could enhance greatly the activity for glucose hydrogenation, and a strong

Table 2 Cellulose hydrolysis over different carbon materials[a]

		Yield (%)				
Cat.	Feedstock	Cello.	Glu.	Fru.	HMF	Con.[b](%)
Blank	Microcrystalline cellulose	1.5	6.7	0.5	3.8	29.3
AC	Microcrystalline cellulose	—	2.5	0.3	0.2	26.9
MC	Microcrystalline cellulose	0.6	14.7	1.0	0.5	38.9
Blank	Ball-milled cellulose	1.4	8.2	2.1	1.5	35.7
AC	Ball-milled cellulose	1.7	10.1	2.0	1.3	45.3
MC	Ball-milled cellulose	0.9	41.0	2.7	2.0	71.2

[a] The reactions were conducted with a rapid temperature ramp: from room temperature to 245 °C in 45 min and then rapidly cooled to room temperature with water; Cello., Glu. and Fru. represent cellobiose, glucose and fructose, respectively. [b] The cellulose conversion was calculated based on the carbon balance: Con.(%) = (moles of total organic carbon in the liquid phase)/(moles of carbon in the cellulose fed into the reactor)×100%.

synergistic effect was observed between the two metals (Table S2†). The better hydrogenation activity of the MC-supported bimetallic catalysts would decrease sugar degradation under harsh reaction conditions and result in higher hexitol yield in the cellulose conversion. On the AC supported bimetallic catalysts, however, no such synergistic effect was found in the glucose hydrogenation.

Secondly, we conducted the reactions of cellulose hydrolysis with MC and AC supports without metal loading. As shown in Table 2, in the absence of carbon materials, 29.3% microcrystalline cellulose was degraded in the blank experiment and produced glucose in a yield of 6.7%. The presence of the AC support does not bring about any increase either in the cellulose conversion or in the yield of sugars, suggesting the AC acts only as an inert support and does not participate in the hydrolysis of cellulose. In contrast, in the presence of MC, the conversion of microcrystalline cellulose was increased to 38.9% and the glucose yield was up to 14.7%. When the cellulose was ball milled and used as the feedstock, the yield of glucose over MC was further increased to 41.0%. Evidently, the MC support itself presented notable catalytic activity for hydrolysis of cellulose into sugars. This is consistent with the results reported by Fukuoka *et al.*[14]

Thirdly, we conducted adsorption experiments using cellobiose and glucose as the probe molecules, respectively. It is found that the uptake of cellobiose and glucose on the MC are 0.149 and 0.041 g g^{-1}, respectively, which is almost double that over the AC support (0.071 and 0.022 g g^{-1} for cellobiose and glucose respectively). This result indicates that the sugar intermediates produced during the cellulose degradation are more readily adsorbed on the MC surface, which will facilitate the subsequent hydrogenation reaction taking place on the Ni sites thereon and result in a higher yield of hexitols. More importantly, it has more than three times the cellobiose uptake than glucose on the MC support which strongly suggests that the MC support possesses a unique function to adsorb and activate the β-1,4-glycosidic bonds of cellulose, which should account for its higher activity for the hydrolysis of cellulose.[5a]

The above three control experiments provide strong evidence that the MC is not only acting as a support for dispersing active metal components, it also plays important roles in adsorption and activation of both cellulose and glucose, and thereby promotes greatly the hydrolysis of cellulose as well as the hydrogenation of glucose.

In summary, we have developed highly active and robust Ni-based bimetallic catalysts for the selective transformation of cellulose into hexitols. The high activity of MC for cellulose hydrolysis, the mesoporous structure of MC facilitating reactant transportation, and the enhanced hydrogenation activity of bimetallic catalysts are responsible for the excellent performance of MC supported bimetallic catalysts. By efficiently coupling the hydrolysis reaction and "*in situ*" hydrogenation of oligosaccharides, the hexitol yield has reached as high as 59.8%, which is the best yield ever reported on solid catalysts to date. The strategy in the present work to develop efficient catalysts might provide guidance for the cellulosic biomass conversion to polyols.

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