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# Highly Selective Sorbitol Hydrogenolysis to Liquid Alkanes over Ni/HZSM-5 Catalysts Modified with Pure Silica MCM-41

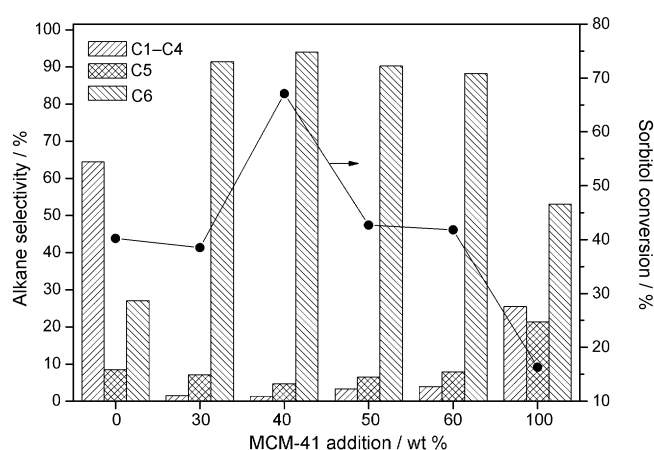
Qing Zhang,<sup>[a]</sup> Ting Jiang,<sup>[a]</sup> Bing Li,<sup>[b]</sup> Tiejun Wang,<sup>\*,[a]</sup> Xinghua Zhang,<sup>[a]</sup> Qi Zhang,<sup>[a]</sup> and Longlong Ma<sup>\*,[a]</sup>

The research of liquid fuels derived from renewable biomass has attracted increasing concern, owing to its potential as a substitute for fossil fuels.<sup>[1]</sup> Lignocellulosic plants are the cheapest and most abundant source of biomass on the earth, which can be efficiently transformed into sugar monomers (e.g., xylose and glucose) by means of acid or enzymatic hydrolysis and, therefore, they have been broadly selected as raw materials for the production of liquid fuels.<sup>[2]</sup> However, there is a key challenge for the deoxygenation of sugars or sugar polyols, such as sorbitol, to produce higher energy liquid hydrocarbons. Inspiringly, the group of Dumesic developed a new and effective strategy for sorbitol conversion to liquid fuels by aqueous phase reforming in 2004.<sup>[2a]</sup> In this process, a bifunctional Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, containing acidic and metal centers, was used to fulfill the dehydration of the hydroxyl groups of sorbitol and was followed by successive hydrogenation and reforming into lighter alkanes (C<sub>1</sub>-C<sub>6</sub>). Thereafter, the development of this process involved in the catalytic processing of biomass was propelled rapidly.<sup>[1d,f,3]</sup> For instance, Li and Huber<sup>[3a]</sup> identified the reaction chemistry for aqueous phase reforming of sorbitol into liquid alkanes over the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Kirilin et al.<sup>[3b]</sup> demonstrated that the aqueous phase reforming of sorbitol was quite complicated, and about 250 compounds were detected in the transformation intermediates of sorbitol by using gas chromatography combined with mass spectrometry. However, the active components of the aforementioned catalysts are expensive noble metals, wherein the cleavage of C-C bond occurred readily and, thereby, caused a decrease in the formation of liquid alkanes.

In this regard, a low-cost supported Ni/HZSM-5 catalyst has been developed for the replacement of precious metal catalysts. HZSM-5 zeolite shows a comparable catalytic performance, however it also shows a stronger Brønsted acidity, which leads to the formation of coke and poor stability under the severe hydrothermal conditions of aqueous phase reforming.<sup>[3c,4]</sup> Fortunately, the MCM-41 mesoporous material, first reported in 1992, has been confirmed to exhibit high hydro-

thermal stability, a large surface area, and a controllable mesoporous diameter, which has motivated broad application in catalysis.<sup>[5]</sup> Moreover, MCM-41 contains a certain number of Lewis acidic sites and thus can be used to adjust the amount of Brønsted acidity of other zeolites, such as MCM-22.<sup>[6]</sup> In this communication, we discuss the enhanced catalytic performance of the Ni/HZSM-5 catalysts modified with pure silica MCM-41 for sorbitol hydrogenation to liquid hydrocarbons. To the best of our knowledge, this is the first study being concerned in the field so far. The structural properties of the catalysts containing different amounts of MCM-41 were investigated by using N<sub>2</sub> physical adsorption and infrared spectroscopy, and the variety in the acidity distribution was also characterized by infrared spectroscopy using pyridine as a probe molecule.

Shown in Figure 1 is the catalytic performance of 2% Ni/HZSM-5 added with different amounts of MCM-41 for sorbitol hydrogenation. The results of the liquid residues analyzed by HPLC are summarized in Table S1 (See the Supporting Information). A low activity with sorbitol conversion of 40% and the liquid alkanes (pentane and hexane) selectivity of 35.6% was obtained over 2%Ni/HZSM-5, wherein a larger amount of lighter alkanes (C<sub>1</sub>-C<sub>4</sub>) in the gas phase and methanol in the liquid phase were formed, indicating that C-C hydrogenolysis was easily performed by HZSM-5, owing to its strong acidity, which was demonstrated in our previous study.<sup>[3c]</sup> Meanwhile, a lower conversion of sorbitol was found for 2% Ni/MCM-41 (16.3%) with less methanol production, which implies that C-O or C-C hydrogenolysis was relatively difficult to accomplish on pure



**Figure 1.** Catalytic performance of 2% Ni/HZSM-5 catalysts added with different amounts of MCM-41 for sorbitol hydrogenation. Prior to activity test, the catalyst was reduced by a flow of H<sub>2</sub> (30 mL min<sup>-1</sup>) at 500 °C for 3 h. The reaction was performed at 240 °C and 4.0 MPa for 1 h under the stirring speed of 200 r min<sup>-1</sup>.

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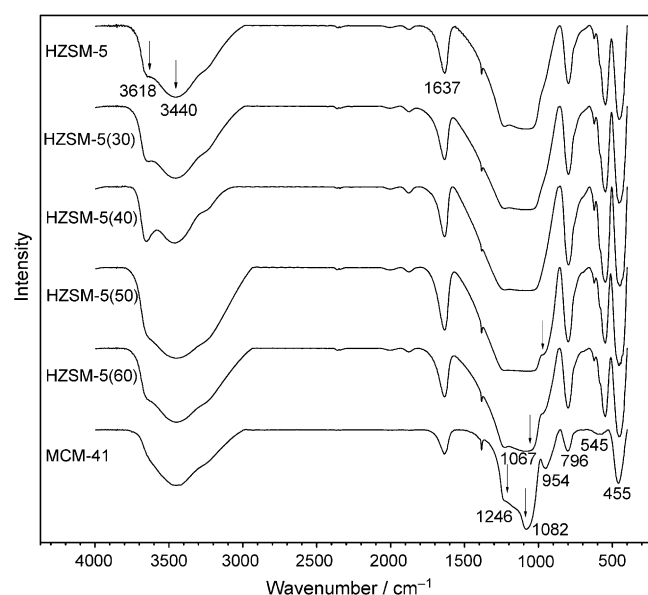
silica MCM-41 most likely because it only contains weak acidic sites. The selectivity of pentane and hexane, however, was both higher than that of over 2% Ni/HZSM-5, and was accompanied by a clear decrease in the selectivity of lighter alkanes. Interestingly, the gaseous product of sorbitol hydrogenation was completely dominated by hexane with the selectivity of 91.4% over 2% Ni/HZSM-5(30), although the sorbitol conversion was relatively unchanged in the process. In addition, the maximum activity of sorbitol conversion (67.1%) and liquid alkanes selectivity (98.7%) was found over 2% Ni/HZSM-5(40), which then decreased as the amount of added MCM-41 was increased over the range 40–60 wt%, wherein the selectivity of hexane maintained at 90–94%, which is higher than those obtained on the Pt-based catalysts.<sup>[2a]</sup> This means that by using the correct amount of MCM-41 additive, the conversion of sorbitol into liquid alkanes can be significantly enhanced. Therefore, it may be deduced that the positive effect of MCM-41 on the product selectivity may be attributed to the interaction between HZSM-5 and MCM-41.

BET surface areas and structural properties of 2% Ni/HZSM-5 with different amounts of MCM-41 added are shown in Table 1. It is clear that the surface area of the 2% Ni/HZSM-5 composite increased distinctly with increasing amounts of MCM-41 added. The surface area was sharply enhanced from 332 m<sup>2</sup> g<sup>−1</sup> to 441 m<sup>2</sup> g<sup>−1</sup> when 30 wt% of MCM-41 was added to the catalyst and then gradually increased as the amount of MCM-41 increased from 40 wt% to 50 wt%. Interestingly, further increases in MCM-41 up to 60 wt% gave a marked increase in the surface area (630 m<sup>2</sup> g<sup>−1</sup>), which is a bit less than that of 2% Ni/MCM-41, wherein larger pore volumes can also be detected in the process of MCM-41 addition. Notably, the same pore volume occurred in 2% Ni/HZSM-5 catalysts containing 40 wt% and 50 wt% of MCM-41, whereas the average pore diameter in the former was slightly larger than in the latter, indicating that the change of structural property in HZSM-5 may exist when 40 wt% MCM-41 was added, but this proposal has yet to be validated.

As the adsorption capacity of the catalyst was increased by the addition of certain amounts of MCM-41, the collision of sorbitol molecules and hydrogen in the resultant mesopores favors the diffusion and desorption of the products, which,

therefore, improves the efficiency of sorbitol hydrogenation. This can be expressed clearly by the activity results of the catalyst for the reaction (Figure 1). However, even though the size of Ni particles on 2% Ni/HZSM-5 changed a little after the addition of MCM-41, these Ni particles seem to be relatively insensitive to the MCM-41 added.

To investigate the functional group characteristics of the HZSM-5 composites with different amounts of MCM-41, FTIR spectroscopy was used and the spectra collected at room temperature are presented in Figure 2. The bands at  $\tilde{\nu}$  = 455, 545



**Figure 2.** IR spectra of the HZSM-5 composites with different amounts of MCM-41.

and 796 cm<sup>−1</sup> were observed over HZSM-5, which can be associated with the stretching vibration of [AlO<sub>4</sub>] or [SiO<sub>4</sub>] groups in the HZSM-5 framework. The two bands at  $\tilde{\nu}$  = 1637 and 3440 cm<sup>−1</sup> were also detected and are attributed to HZSM-5, for which the former can be assigned to the bending vibration of water molecules adsorbed, while the latter can be attributed to hydrogen-bonded silanol groups and water molecules adsorbed in the zeolite.<sup>[7]</sup> As for the MCM-41 sample, two bands at  $\tilde{\nu}$  = 455 and 796 cm<sup>−1</sup> that arise from the vibration of [SiO<sub>4</sub>] groups were also found, and the intensities of both bands were much lower than those of HZSM-5, owing to the absence of [AlO<sub>4</sub>] groups in the framework of pure silica MCM-41. Moreover, one band at  $\tilde{\nu}$  = 1082 cm<sup>−1</sup>, accompanied by two shoulders at  $\tilde{\nu}$  = 954 and 1232 cm<sup>−1</sup>, can be confirmed to be the characteristic asymmetric stretching band of Si-O-Si bridges.<sup>[7,8]</sup> When the percentage of MCM-41 in the HZSM-5 composite was as high as 60%, the band at  $\tilde{\nu}$  = 1082 cm<sup>−1</sup> was found to shift to  $\tilde{\nu}$  = 1067 cm<sup>−1</sup>. This shift can be elucidated by the strengthening of coulombic interactions within the amorphous silica network in the Si-O-Si bridges, which were mainly generated by the in-

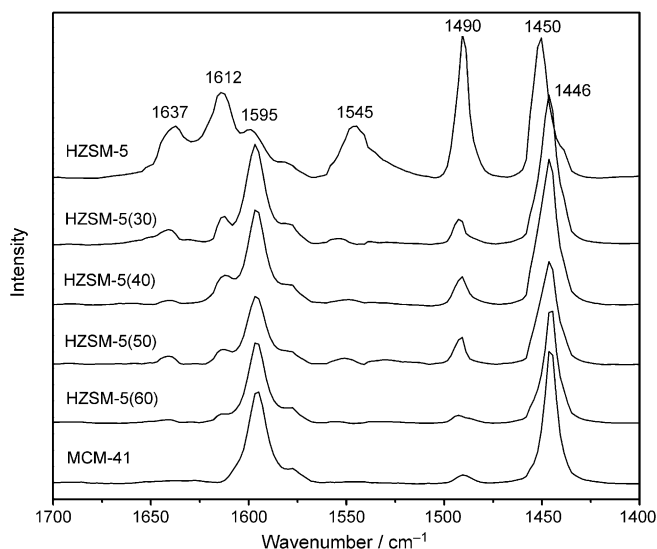
**Table 1.** Surface areas, structural properties and average Ni particle diameter (*d*) of 2%Ni/HZSM-5 added with different amounts of MCM-41.

Samples <sup>[a]</sup>	BET surface area [m <sup>2</sup> g <sup>−1</sup> ]	Pore volume [cm <sup>3</sup> g <sup>−1</sup> ]	Average pore diameter [nm]	Adsorption capacity [cm <sup>3</sup> g <sup>−1</sup> ]	<i>d</i> <sup>[b]</sup> [nm]
2% Ni/HZSM-5	332	0.18	2.14	73.57	31.7
2% Ni/HZSM-5(30)	441	0.25	2.25	101.21	28.2
2% Ni/HZSM-5(40)	487	0.29	2.41	117.22	32.6
2% Ni/HZSM-5(50)	510	0.29	2.33	111.81	34.1
2% Ni/HZSM-5(60)	630	0.41	2.58	144.75	32.6
2% Ni/MCM-41	693	0.82	4.73	159.25	51.5

[a] The numerical value in bracket is referred to the weight percentage of MCM-41 added in the corresponding HZSM-5 composite. [b] Calculated from Ni(111) by using the Scherrer equation (Figure S1).

creased condensation of silanol groups.<sup>[9]</sup> In addition, the intensity of the shifted band decreased sharply with increasing the amount of HZSM-5, owing to the shrinkage of the pore structure. This conclusion is supported by the work of Koh et al.<sup>[7]</sup> who used an in situ EDXRD technique. Additionally, the data collected by N<sub>2</sub> physical adsorption analysis also confirm this finding. Notably, a weak band at  $\tilde{\nu}=3618\text{ cm}^{-1}$  was observed for HZSM-5, which can be associated with hydroxyl groups of framework Al.<sup>[10]</sup> The relative intensity of this peak was found to slightly increase when the amount of MCM-41 was increased to 40% and then decreased, suggesting that Si species in the MCM-41 framework could partially extract the framework Al to form Si-OH-Al groups after calcined at 500 °C, which can thereby modulate the acidity and framework of HZSM-5 composites.

The acidity of the HZSM-5 composites with different amounts of MCM-41 was measured by Py-IR spectroscopy and the results are shown in Figure 3. IR bands at  $\tilde{\nu}=1450, 1595$



**Figure 3.** Infrared spectra of pyridine on the HZSM-5 composites with different amounts of MCM-41 at the desorption temperature of 100 °C.

and  $1612\text{ cm}^{-1}$  were observed for HZSM-5, which can be attributed to the adsorption of pyridine coordinated on Lewis acid sites.<sup>[11]</sup> IR bands near  $\tilde{\nu}=1545$  and  $1637\text{ cm}^{-1}$  are associated with pyridine adsorption on Brønsted-acid sites, which are generally assigned to the framework Al. In addition, the band at  $\tilde{\nu}=1490\text{ cm}^{-1}$  is ascribed to the vibration of the pyridine ring on Brønsted and Lewis acid sites.<sup>[12]</sup> However, MCM-41 exhibits only two strong bands at  $\tilde{\nu}=1446$  and  $1595\text{ cm}^{-1}$  and a weak band at  $\tilde{\nu}=1490\text{ cm}^{-1}$  after pyridine chemisorption, indicating that the effect of Brønsted acid sites is negligible and that Lewis acid sites are the dominant acid centers in MCM-41, owing to the absence of the framework Al. Interestingly, the intensity of Brønsted acid sites in HZSM-5 decreased sharply when a small amount of MCM-41 was added to HZSM-5, such as 30 wt%, while that of Lewis acid sites increased distinctly. Meanwhile, the band arising from Lewis acid sites at  $\tilde{\nu}=$

$1450\text{ cm}^{-1}$  shifted to  $\tilde{\nu}=1446\text{ cm}^{-1}$ , indicating that pyridine molecules adsorbed on weak Lewis acid sites can be easily removed and the amount of pyridine adsorbed increased, owing to the increase in the intensity of these sites. Also, this means that the number of Si-O-Si groups or silanol increased because of the strengthening of the interaction between HZSM-5 and MCM-41, which is in accordance with that the IR analysis. Generally, dehydration by C–O hydrogenolysis in the sorbitol molecule was mostly performed on the weak-acid sites, whereas the strong-acid sites were used for C–C hydrogenolysis to generate lighter alkanes by successive hydrogenation. Thus, the appropriate amount of total acid sites and Lewis acid sites can easily result in the production of liquid alkanes from sorbitol hydrogenation on the Ni/HZSM-5 composites. This is testified by the results of activity tests and Py-IR over the 2% Ni/HZSM-5(40) catalyst. Moreover, the intensity of Lewis acid sites decreased gradually with the amount of MCM-41 added beyond 40 wt%, implying that an optimum proportion between HZSM-5 and MCM-41 may exist in the framework of the HZSM-5 composites.

In summary, we have demonstrated that the catalytic activity of Ni/HZSM-5 for sorbitol hydrogenation to liquid alkanes can be significantly enhanced by the appropriate addition of MCM-41. The catalyst containing 40 wt% MCM-41, exhibits a maximal sorbitol conversion of 67.1% and a liquid alkanes selectivity of 98.7%. The enhanced surface area and adsorption capacity of the catalyst by added MCM-41 can promote sorbitol interacted with hydrogen. In addition, the silicon species in the framework of MCM-41 could extract the framework Al in HZSM-5 and thus modulate the amount and distribution of acidic sites, which favors C–O hydrogenolysis in the sorbitol molecule into liquid alkanes. These findings are of great significance for designing and improving the catalysts applied in the biorefinery industry.

## Experimental Section

Full experimental details, including the preparation, characterization, and catalytic activity test of the catalysts, are provided in the Supporting Information section.

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**Keywords:** alkanes • hydrogenation • MCM-41 • Ni/HZSM-5 catalyst • sorbitol

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