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High yield of renewable hexanes by direct hydrolysis–hydrodeoxygenation of cellulose in an aqueous phase catalytic system†

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In aqueous phosphoric acid, cellulose was efficiently converted into hexanes using a Ru/C catalyst combined with layered compounds or silica–alumina materials. In this process, the direct production of hexanes from cellulose can be improved by suppressing the formation of isosorbide, which makes it difficult to yield hexanes by further hydrodeoxygenation. As the co-catalyst, layered compounds showed a significant inhibition effect on the formation of isosorbide from sorbitol due to the steric restrictions of sorbitol dehydration within the interlayers of layered compounds. Typically, layered $LiNbMoO_6$ played a great role in promoting the production of hexanes directly from cellulose and a promising yield (72% carbon mol) of hexanes was obtained. In addition, the protonic acid, H_3PO_4, offered efficient catalysis for the hydrolysis of cellulose and the dehydration of the sorbitol hydroxyl moiety.

Introduction

To compensate for the decline of fossil fuel energy sources, biomass has been developed as a sustainable and renewable alternative of carbon sources for production of chemicals and fuels.[1–13] Cellulose is the most low-cost but substantial raw material of biomass for its annual net yield of over 0.72 trillion tons, which presents it as an attractive carbon source.[14–16] However, cellulose is insoluble in water and other conventional solvents because of its robust structure composed of β-1,4-glycosidic bonds in D-glucose and the abundance of hydrogen bonds between the hydroxyl groups. This feature brings a challenge for researchers to directly convert cellulose into chemicals or fuels, particularly hydrocarbons such as alkanes, which require the process of lowering the high oxygen content. Therefore, direct utilization of cellulose still needs further investigation.[10,17,18]

To transform cellulose into alkanes, hydrodeoxygenation of cellulose-derived water-soluble carbohydrates and sugar alcohols was widely investigated. Recently, significant progress for production of light gasoline alkanes from cellulose-derived sorbitol has been made by Huber and co-workers.[19–21] They developed an aqueous-phase reforming method to transform sorbitol into light alkanes over platinum-based catalysts. For conversion of sorbitol and xylitol into hexanes and pentane in the aqueous phase, respectively, low-cost Ni/HZSM-5 catalysts have been developed by our group.[22–24] Furthermore, the transformation of sugar and sugar polyols into *n*-alkanes over iridium-based catalysts with high yield was also achieved by Tomishige's group.[25] The iridium-catalyzed and the $B(C_6F_5)_3$-catalyzed hydrosilylative reduction of carbohydrates to hexanes has been exploited by the group of Gagné.[26,27]

However, the feedstock of the aforementioned approaches is either carbohydrates or sugars/polyols, which require stepwise reactions from cellulose. The production of alkanes from biomass through a cascade reaction could reduce the energy conversion efficiency of the entire process. Hence, high economic efficiency necessitates direct conversion of cellulose to hexanes. Unfortunately, little focus has been devoted to this direct conversion. However, more recently, some reports on the direct transformation of cellulose into alkanes have been reported. Huber's group,[28] Sekine's group[29] and Takahara's group[30] have reported this direct conversion, but all of them gave a low yield of hexanes. Tomishige used the same catalytic system of $Ir–Re/SiO_2$ + HZSM-5 to convert cellulose into hexanes, which obtained a good yield of hexanes with the addition of a considerable amount of *n*-dodecane.[31] The biphasic system was also used by Sels's group to transform cellulose into straight-chain alkanes over modified Ru/C and $H_4SiW_{12}O_{40}$.[32]

Although, a good yield of alkanes can be achieved from cellulose in a biphasic system or organic phase, the mono-phasic aqueous system is also necessary to explore efficient conversion of cellulose to hydrocarbons from the viewpoint of more economic and more environmentally friendly reaction media.

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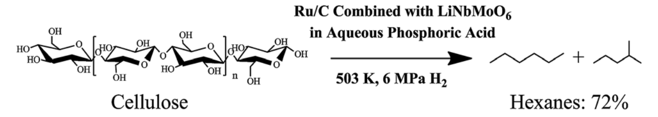


Scheme 1 Direct catalytic conversion of cellulose into hexanes over Ru/C combined with $LiNbMoO_6$ in aqueous phosphoric acid.

Water is the cheapest and most convenient media for the reaction, which suggests that the use of an aqueous phase system for cellulose conversion is attractive. Therefore, it is necessary to develop an efficient and environmentally friendly reaction system to directly convert cellulose into hydrocarbons in aqueous media. In addition, some mild acids have been proposed as environmentally friendly acids for hydrolysis. For example, phosphoric acid can be utilized as a nutrient and fertilizer for microorganisms and plants.[33,34] However, former studies suggested cellulose or cellulose-derived products (glucose or sorbitol) are easily converted into isosorbide.[35–37] Isosorbide is hardly transformed into hexanes, as revealed in this study. Herein, we report a direct selective conversion of cellulose into hexanes by a Ru/C catalyst combined with layered compounds in low concentration phosphoric acid aqueous media. A promising yield (72% C) of hexanes was achieved (Scheme 1), whereas the yield of isosorbide was less than 3%. Hexanes directly produced from cellulose over this catalytic system bring a special environmentally friendly advantage for the development of sustainable and renewable hydrocarbon fuels.

Experimental section

0.2 g Ru/C, 0.8 g substrate, and 40 mL of different concentrations of aqueous phosphoric acid were loaded into a 100 mL stainless autoclave. Different amounts of co-catalyst were added according to different reaction requirements. The reactor was purged with pure H_2 and pressurized with 6 MPa H_2. Then, the reactor was heated to 503 K at a stirring rate of 450 rpm. The starting time of the reaction was when the desired temperature was reached.

The reuse experiments for the aqueous phase catalytic system were carried out without the separation of Ru/C and $LiNbMoO_6$. The process is described below. The conversion was tested for 24 h at 503 K, the autoclave was cooled in ice water and the samples were collected. The next test was carried out by loading 0.8 g fresh cellulose into the autoclave. After the completion of reaction, we used ethanol to separate the solid mixture and the Ru/C catalyst was suspended in the ethanol solution, whereas the used $LiNbMoO_6$ remained at the bottom. The regeneration of $LiNbMoO_6$ was performed by simple calcination of the used catalyst at 903 K for 36 h.

Other details are given in the ESI.†

Results and discussion

Conversion of cellulose

Hydrolysis hydrodeoxygenation of cellulose was investigated by a Ru/C catalyst combined with or without different co-catalysts in aqueous phosphoric acid media at 503 K (Table 1). A commercial Ru/C catalyst was chosen for the conversion of cellulose due to the fact that Ru metal possesses excellent activity for C–O cleavage.[38] However, without the addition of phosphoric acid and the co-catalyst, a single Ru/C catalyst exhibited outstanding hydrogenolysis activity, which broke the C–O bonds and the C–C bonds. As a result, 91% carbon of cellulose was converted to C1–C4 alkanes and the yield of the desired hexanes was only 1.9% with complete conversion of cellulose (entry 1). With the presence of phosphoric acid (0.59 M), the side reaction of C–C cleavage was greatly inhibited. The yield of C1–C4 alkanes was decreased to 6.9% and the yield of desired hexanes was increased to 23.3% (entry 2). In the liquid phase, a large amount (42.1%) of isosorbide was found. In the acidic media, it was easy to yield isosorbide by dehydration from sorbitol, which was formed in the hydrolysis hydrodeoxygenation of cellulose. In the absence of phosphoric acid, the Ru/C catalyst combined with single co-catalyst MCM-41 or $HNbMoO_6$ was tested in aqueous solution. The addition of MCM-41 gave the complete conversion of cellulose (entry 3), whereas the yield of hexanes was very low (7.9%). The main products were C1–C4 alkanes (75.6%). The addition of $HNbMoO_6$ greatly inhibited the conversion of cellulose (entry 11). The main products were small polyols (mainly ethylene glycol and propylene glycol), which indicated the cracking of the C–C bond was still easily performed by Ru/C, whereas the desired reaction of C–O bond cracking was suppressed.

Interestingly, when the Ru/C catalyst combined with MCM-41 in the aqueous phosphoric acid media, the yield of hexanes was remarkably increased (entries 4–7). By increasing the concentration of phosphoric acid, the yield of hexanes could be promoted from 27.6% to 48.6%, whereas the yield of isosorbide was still high (20%–30%). In this catalytic system, C–C cracking reactions such as formation of C1–C4 alkanes from cellulose were promisingly suppressed, and the yield of isosorbide was lower than that of the same reaction conditions without the addition of MCM-41. It is certain that the increased concentration of phosphoric acid promoted the reaction rate of cellulose hydrolysis, as well as favoured the cleavage of C–O bonds with the aid of the protonic acid, which resulted in the dehydration of alcoholic hydroxyls. Moreover, the presence of PO_4^{3-} brought a suppression effect of retroaldol cleavage of glucose to some extent, as suggested in former studies.[39,40] Therefore, the addition of phosphoric acid was necessary in the current study. For the co-catalysts, other silica–alumina materials or solid acids, such as HZSM-5, SBA-15 and γ-Al_2O_3, were also tested (entries 8–10) with the presence of Ru/C and 0.59 M phosphoric acid, and 36.6%, 29.7% and 35.3% yield of hexanes were obtained, respectively. Previous studies suggested the MCM-41 and HZSM-5 were effective for hydrodeoxygenation of carbohydrates and sugar polyols to produce hydrocarbons.[22,25] In the current study, MCM-41 and HZSM-5 also showed higher hexane yields than SBA-15 and γ-Al_2O_3. The effect of HZSM-5 has been suggested by Tomishige's group who found that HZSM-5 was efficient in producing five-membered-ring cycle ethers such as tetrahydrofuran through an internal dehydration reaction.[25] However, in the current catalytic system, a large

Table 1 Hydrolysis hydrodeoxygenation of cellulose to yield hexanes over Ru/C with co-catalyst in aqueous phosphoric acid[a]

					Yield[b] [%]								
Entry	Co-catalyst	$[H_3PO_4]$ [M]	Con. [%]	Carbon balance [%]	Hex	Pent	C1–C4 alkanes	Glu/cel	Sor	Sorb	Iso	Other	Hex/total alkanes[c]
1	—	—	>99.9	95.4	1.9	1.1	91	<0.1	<0.1	<0.1	1.2	<0.1	2.0
2	—	0.59	>99.9	93.6	23.3	12.4	6.9	<0.1	1.6	7.3	42.1	<0.1	54.7
3	MCM-41	—	>99.9	98.3	7.9	13.4	75.6	0.1	<0.1	<0.1	1.3	<0.1	8.2
4	MCM-41	0.21	>99.9	93.5	27.6	12.1	12.8	<0.1	2.0	9.3	29.7	<0.1	52.6
5	MCM-41	0.42	>99.9	91.1	32.8	11.8	11.9	<0.1	1.8	4.5	28.2	<0.1	58.1
6	MCM-41	0.59	>99.9	91.2	40.1	8.9	10.1	<0.1	1.2	2.9	28.0	<0.1	67.9
7	MCM-41	0.85	>99.9	93.9	48.6	9.6	8.6	<0.1	1.1	2.3	23.7	<0.1	72.8
8	HZSM-5	0.59	>99.9	93.4	36.6	16.4	6.0	<0.1	0.8	1.5	32.1	<0.1	62.0
9	γ-Al_2O_3	0.59	>99.9	94.5	35.3	14.4	7.2	<0.1	4.2	1.5	31.9	<0.1	62.0
10	SBA-15	0.59	>99.9	95	29.7	13.8	7.7	<0.1	2.7	10.3	30.8	<0.1	58.0
11	$HNbMoO_6$	—	40	97.3	2.4	1.2	5.1	2.3	0.1	2.4	6.2	19.2	27.6
12	$HNbMoO_6$	0.59	>99.9	86.5	44.7	7.5	10.2	<0.1	1.5	3.6	4.8	14.2	71.6
13	$HNbMoO_6$	0.42	>99.9	88.4	65.9	6.9	4.5	<0.1	0.9	1.0	4.4	4.8	85.3
14	$LiNbMoO_6$	0.42	>99.9	89.2	70.2	5.9	4.6	<0.1	0.2	0.9	3.9	3.5	87.0
15	$LiNbMoO_6$	0.21	>99.9	88.6	72	5.9	4.3	<0.1	0.2	0.7	3.0	2.5	87.6
16	$LiNbMoO_6$	0.12	91.4	85.7	49.6	4.9	3.8	<0.1	1.5	8.9	7.8	1.9	85.1
17	$LiNbWO_6$	0.21	90.5	84.5	47.7	5.5	8.9	<0.1	0.6	0.5	2.1	11.2	76.8
18[d]	$LiNbMoO_6$	0.21	70.5	89.1	41.9	3.1	4.7	0.5	1.1	1.4	5.4	4.7	84.3
19[e]	$LiNbMoO_6$	0.21	94.5	87.3	61.6	3.9	4.4	0.2	1.2	1.6	5.2	4.4	88.1
20[f]	$LiNbMoO_6$	0.21	80.1	88.1	48.2	2.8	5.1	0.6	2.3	1.4	5.1	5.1	85.9

[a] Reaction conditions: 0.8 g microcrystalline cellulose, 0.2 g Ru/C, 0.4 g co-catalyst for entries 3–10 or 0.2 g layered compound for entries 11–17, 40 mL H_2O, 503 K, 6 MPa H_2, 24 h. [b] Hex = *n*-hexane and 2-methylpentane; Pent = *n*-pentane; Glu/cel = glucose and cellobiose; Sor = sorbitol; Sorb = sorbitans, include 1,4-sorbitan and 2,5-sorbitan; Iso = isosorbide; other = 1-hexanol, 1-pentanol, 1,6-hexanediol, ethylene glycol, and propylene glycol. [c] Hex/total alkanes = hexanes/total alkanes. [d] Reaction conditions: 1.6 g microcrystalline cellulose, 0.2 g Ru/C, 0.2 g layered compound, 40 mL H_2O, 503 K, 6 MPa H_2, 24 h. [e] Reaction conditions: 1.6 g microcrystalline cellulose, 0.4 g Ru/C, 0.4 g layered compound, 40 mL H_2O, 503 K, 6 MPa H_2, 24 h. [f] Reaction conditions: 4 g microcrystalline cellulose, 0.5 g Ru/C, 0.5 g layered compound, 40 mL H_2O, 503 K, 6 MPa H_2, 24 h.

amount of by-product isosorbide was formed through the dehydration of sorbitol. Compared with sorbitol, we assume that isosorbide is difficult to undergo ring-open reaction to yield hexanes by further hydrodeoxygenation. Therefore, the inhibition of formation of isosorbide from sorbitol is crucial for improving the production of hexanes. Surprisingly, the promising yield of hexanes was obtained by the combination of the Ru/C catalyst and $HNbMoO_6$ in aqueous phosphoric acid media (entries 12 and 13). Specifically, a 44.7% yield of hexanes was obtained in 0.59 M phosphoric acid. By decreasing the phosphoric acid concentration to 0.42 M, the yield of hexanes was significantly promoted to 65.9%. More importantly, the yield of the by-product isosorbide was considerably lower (less than 5% C) than that of MCM-41 or HZSM-5. It is clear that the formation of isosorbide is greatly inhibited due to the presence of $HNbMoO_6$. Moreover, the total yield of C–C cracking products in the gas phase was approximately 11.4%, which was lower than that of 0.59 M phosphoric acid. In the liquid phase, the side reactions to produce small polyols through C–C cracking were suppressed with only 4.8% carbon in the form of small polyols. This result indicates that high concentration of phosphoric acid catalyses the C–C cracking reaction in the presence of layered compounds. $LiNbMoO_6$ is the precursor of the tested $HNbMoO_6$, which is also a layered compound.[41–47] Interestingly, using $LiNbMoO_6$ as the co-catalyst, higher yields of hexanes were observed (entries 14–16). When the concentration of phosphoric acid was optimized to 0.21 M, the highest yield of hexanes was obtained (72%). With lowering the concentration of phosphoric acid to 0.12 M, the yield of hexanes decreased to 49.6%. This suggests that phosphoric acid is indispensable for conversion of cellulose because the C–O cleavage reaction was catalyzed by the protonic acid. However, the amount of phosphoric acid also affects the hydrodeoxygenation ability of Ru/C and the dehydration of sorbitol, which results in the formation of small polyols and isosorbide. Therefore, a certain balance between the co-catalyst and phosphoric acid concentration should be maintained. Furthermore, the layered compound, $LiNbWO_6$, also possesses activity for the conversion of cellulose to hexanes (47.7%, entry 17). However, tungsten species are also effective in producing ethylene glycol from oligosaccharides or glucose.[48–50] In this catalytic system with the $LiNbWO_6$, 11.2% C yield of small polyols (10.1% C in ethylene glycol and 1.1%C in propylene glycol) was obtained from cellulose as the main by-product in the aqueous phase.

In addition, the amount of substrate cellulose was enlarged over the same catalytic system. Although the conversion of cellulose decreased to 70.5% (entry 18), the 41.9% yield of hexanes was still obtained. When increasing the amount of Ru/C catalyst and layered compound, the yield of hexanes reached 61.6% (entry 19). Entry 20 suggested that the concentrated cellulose could be efficiently converted into hexanes with a yield of 48.2%.

Table 2 Evolution of species in the process of cellulose conversion over Ru/C with MCM-41 or LiNbMoO$_6$ in aqueous phosphoric acid[a]

					Yield [%]								
Entry	Co-catalyst	t [h]	Con. [%]	Carbon balance [%]	Hex	Pent	C1–C4 alkanes	Glu/cel	Sor	Sorb	Iso	Other	Hex/total alkanes
1	MCM-41	0.5	52	95.4	1.2	2.9	3.0	0.5	3.4	13.9	24.7	<0.1	16.9
2	MCM-41	1	75.8	93.3	18.8	3.6	3.5	0.3	2.5	16.5	25.5	<0.1	72.6
3	MCM-41	3	90.2	93.8	29.9	5.3	4.1	0.1	2.7	10.2	32.3	<0.1	76.1
4	MCM-41	6	94.1	87.9	31.8	6.5	5.4	<0.1	3.1	7.7	28.2	<0.1	72.8
5	MCM-41	12	>99.9	83.1	34.4	8.2	7.6	<0.1	2.9	3.8	26.1	<0.1	68.5
6	MCM-41	18	>99.9	89.1	41.6	9.1	8.2	<0.1	1.9	2.9	25.4	<0.1	70.6
7	MCM-41	24	>99.9	93.9	48.6	9.6	8.6	<0.1	1.1	2.3	23.7	<0.1	72.8
8	LiNbMoO$_6$	0.5	20.0	90.0	5.7	0.6	0.5	1.1	4.1	2.8	3.2	<0.1	83.8
9	LiNbMoO$_6$	1	41.1	90.1	24.8	1.1	1.8	0.2	4.2	2.1	3.1	<0.1	89.5
10	LiNbMoO$_6$	3	60.1	85.2	39.1	1.8	2.2	<0.1	3.2	1.8	3.1	<0.1	90.7
11	LiNbMoO$_6$	6	71.8	81.5	45.5	2.3	2.7	<0.1	2.5	1.4	3.0	1.1	90.1
12	LiNbMoO$_6$	12	85.1	90.7	63.4	3.8	2.9	<0.1	1.5	1.2	2.9	1.5	90.4
13	LiNbMoO$_6$	18	95.2	89.8	70.8	4.3	3.5	<0.1	0.9	1.0	3.3	1.7	90.1
14	LiNbMoO$_6$	24	>99.9	88.6	72	5.9	4.3	<0.1	0.2	0.7	3.0	2.5	87.6

[a] Reaction conditions: 0.8 g microcrystalline cellulose, 0.2 g Ru/C, 0.4 gMCM-41 or 0.2 g LiNbMoO$_6$, 40 mL H$_2$O, 503 K, 6 MPa H$_2$. For MCM-41, $[H_3PO_4] = 0.59$ M; for LiNbMoO$_6$, $[H_3PO_4] = 0.21$ M.

As shown in Table 2, further studies were focused on the evolution of other species in the process of cellulose conversion. In the case of MCM-41, the formation of glucose/cellobiose and sorbitol were detected initially, and a considerable amount of dehydration product (sorbitans and isosorbide) was formed from sorbitol (entry 1). However, 5-hydroxymethylfurfural (HMF) was not detected in the process. It might be caused by the fast hydrogenation of HMF or negligible yield.[32] By increasing the reaction time (entries 1–7), hexanes were gradually formed as the main products with the complete conversion of cellulose. After 24 h, a promising hexanes yield of 48.6% was obtained (entry 7), although the yields of C–C cracking products and pentane gradually increased to 9.6% and 8.6%, respectively. The sorbitans were drastically decreased from 16.5% to 3.8% (entries 2–7), whereas isosorbide remained at approximately the same amount (about 26% C). For the dehydration products of sorbitol, isosorbide was robust to be transformed into hexanes. Even after 24 h, a high isosorbide yield (23.7%) was detected in the aqueous phase (entry 7). What intrigued us was that LiNbMoO$_6$ showed excellent activity for conversion of cellulose to hexanes (entries 8–14). In this catalytic system, the yield of isosorbide was maintained at a low level (below 3.5%) along with the conversion process of cellulose. It is evident that the LiNbMoO$_6$ has an excellent suppression effect on the formation of isosorbide compared with MCM-41, although cellulose was not readily converted with the LiNbMoO$_6$ as the co-catalyst (entry 14). When the reaction time was 24 h, the yield of hexanes reached 72%. In gaseous phase, a smaller amount of C1–C4 alkanes and pentane and 2.5% yield of small polyols were obtained.

Reuse experiments of aqueous phase catalytic system were carried out to investigate the durability of the catalyst. As listed in Table 3, the second run also gave a promising result. With the increase of reuse number, the yield of hexanes gradually decreased, and the amount of sorbitol and isosorbide slightly increased. In the fifth run, a hexane yield of 52.8% was obtained. This result was comparable to the result of HNbMoO$_6$ (Table 1, entries 12 and 13). In this catalytic system, HNbMoO$_6$ might be formed by the proton-exchange reaction of LiNbMoO$_6$ in the presence of phosphoric acid (Fig. S12†). More importantly, detectable Ru leaching after the fifth run was the reason for the decreased performance. Furthermore, the catalytic performance of fifth reused LiNbMoO$_6$ could be recovered to that of the fresh LiNbMoO$_6$ by calcination, and a high hexanes yield of 71.5% was also obtained. Those results suggested that the LiNbMoO$_6$ and Ru/C are essentially reusable, and LiNbMoO$_6$ can be regenerated by simple calcination.

Hydrodeoxygenation of glucose, sorbitol, and isosorbide

We did not find the existence of HMF or its derived products (such as 2,5-dihydroxymethylfuran or 2,5-dihydroxymethyltetrahydrofuran) in the liquid phase (Fig. S8 and S9†), and this might be a result of negligible yield or the fast hydrogenation of HMF. On the contrary, large amounts of glucose, sorbitol and isosorbide were detected in the liquid phase when the yield of hexanes was relatively low. It might suggest that these intermediates, particularly isosorbide, had a significant influence on the yield of hexanes. Hence, in the following tests, we deliberately used glucose, sorbitol, and isosorbide to perform extended tests over the Ru/C and co-catalyst LiNbMoO$_6$ in aqueous phosphoric acid.

Glucose can be formed by the hydrolysis of cellulose and cellobiose.[46,51,52] Sorbitol can be obtained from the hydrogenation of glucose[53] and the hydrolysis–hydrogenation of cellulose over noble-metal catalysts.[54–56] With the addition of acid, the ether bonds of cellulose are susceptible to hydrolysis and form oligosaccharides or glucose. In addition, sorbitans (monomolecular dehydration) and isosorbide (bimolecular

Table 3 Reuse of Ru/C and $LiNbMoO_6$ in the cellulose conversion[a]

					Yield [%]								
Usage times	Co-catalyst	$[H_3PO_4]$ [M]	Con. [%]	Carbon balance [%]	Hex	Pent	C1–C4 alkanes	Glu/cel	Sor	Sorb	Iso	Other	Hex/total alkanes
1	$LiNbMoO_6$	0.21	>99.9	88.6	72	5.9	4.3	<0.1	0.2	0.7	3.0	2.5	87.6
2	$LiNbMoO_6$	0.21	>99.9	91.1	71.1	6.8	8.2	<0.1	0.1	0.8	3.5	0.6	82.6
3	$LiNbMoO_6$	0.21	>99.9	85.4	63.4	6.9	8.4	<0.1	0.2	0.9	4.8	0.8	80.6
4	$LiNbMoO_6$	0.21	>99.9	86.3	61.3	9.5	8.2	<0.1	0.5	0.4	4.9	1.5	77.6
5	$LiNbMoO_6$	0.21	90.1	89.1	52.8	9.9	8.5	0.2	0.8	1.3	5.2	1.6	74.2
6[b]	$LiNbMoO_6$	0.21	>99.9	88.7	71.5	5.9	4.5	<0.1	0.3	0.8	3.1	2.6	87.3

[a] Reaction conditions: 0.8 g microcrystalline cellulose, 0.2 g Ru/C, 0.2 g $LiNbMoO_6$, $[H_3PO_4] = 0.21$ M, 40 mL H_2O, 503 K, 6 MPa H_2, 24 h. The yields of aqueous products were calculated by subtracting the yields of former test. [b] Layered compound was calcined at 903 K for 36 h. Fresh Ru/C and phosphoric acid solution were added.

dehydration) can be formed from sorbitol under acidic conditions. It is possible that some reversible reactions can be performed in these three tested feedstocks.

As listed in Table 4, the results of the glucose conversion showed the evolution of reaction species at various times. Within 24 h reaction time, the yields of the cyclic ethers (sorbitans and isosorbide) were high in the absence of $LiNbMoO_6$ (entries 8). Not only does it suggest that glucose is easily hydrogenated into sorbitol over Ru/C, but it also reveals that the formed sorbitol is readily transformed into dehydration products. After 24 h, the yield of desired hexanes was only 14.9% due to the formation of large amount of stable isosorbide. In the case of $LiNbMoO_6$ (entries 1–7), the formation of isosorbide was greatly suppressed within 24 h, and the yield of isosorbide decreased to below 14.5%. The initial formed sorbitans decreased from 13.1% to 0.7%. The results suggest that the addition of co-catalyst $LiNbMoO_6$ shows an excellent suppression effect on the formation of isosorbide. Therefore, a higher yield of hexanes (54.2%) can be obtained (entry 7).

As listed in Table 5, using sorbitol as the substrate, large amounts of sorbitans and isosorbide were detected initially. Their yields reached 48.9% and 40.2%, respectively (entry 1). After 24 h, the high isosorbide yield of 40.2% over the $LiNbMoO_6$ was still obtained (entry 7). This might be caused by the fact that sorbitol can undergo stepwise dehydration to produce sorbitans and isosorbide in the aqueous phase at high reaction temperature.[37] Typically, when protonic acid was added to the reaction system, the isosorbide yield could be improved to a higher level.[36] Without adding $LiNbMoO_6$, only 17.2% C yield of hexanes was obtained (entry 8). Although, the yield of hexanes was increased by adding $LiNbMoO_6$, the yield of 26.7% C was still very low. However, the yield of isosorbide was kept at a high level with/without $LiNbMoO_6$. This might be a result of the fact that isosorbide is a more stable intermediate that is readily formed from dehydration of sorbitol catalysed by protonic acid in the aqueous phase. For the production of desired hexanes from sorbitol hydrogenolysis, it showed that sorbitol could not be efficiently converted into hexanes over the tested catalytic system.

To demonstrate the intrinsically robust feature of isosorbide, it was used as the substrate in the same catalytic system. As listed in Table 6, the yield of hexanes obtained from isosorbide was very low after 24 h. It should be noted that the isosorbide could not be efficiently converted into hexanes with or without the presence of $LiNbMoO_6$. Furthermore, the isosorbide conversion was very low, particularly when $LiNbMoO_6$ was used (only 14.1% isosorbide conversion). This indicates the high yield of hexanes obtained from cellulose over $LiNbMoO_6$ does not result from the fact that $LiNbMoO_6$ has high reactivity for isosorbide conversion to produce hexanes. We assume

Table 4 Evolution of species in the process of glucose conversion over Ru/C with $LiNbMoO_6$ in aqueous phosphoric acid[a]

					Yield [%]							
Entry	Co-catalyst	t [h]	Con. [%]	Carbon balance [%]	Hex	Pent	C1–C4 alkanes	Sor	Sorb	Iso	Other	Hex/total alkanes
1	$LiNbMoO_6$	0.5	45.1	85.5	10.2	0.3	0.5	3.9	13.1	10.1	0.4	92.7
2	$LiNbMoO_6$	1	57.1	87.6	17.1	0.9	1.2	3.7	12.2	14.2	0.7	89.1
3	$LiNbMoO_6$	3	60.5	98.5	32.8	1.4	1.5	2.3	7.7	13.8	0.1	91.9
4	$LiNbMoO_6$	6	72.5	90.1	35.9	3.3	4.9	2.1	3.9	14.1	<0.1	81.4
5	$LiNbMoO_6$	12	91.1	90.1	50.8	5.5	6.1	1.8	2.5	13.9	<0.1	81.4
6	$LiNbMoO_6$	18	98.3	88.1	53.8	7.6	7.8	0.9	1.0	13.8	<0.1	77.7
7	$LiNbMoO_6$	24	99.2	89.9	54.2	8.4	9.1	0.2	0.7	14.1	<0.1	75.6
8	—	24	92.9	90.6	14.9	14.1	11.9	4.2	5.2	39.1	<0.1	36.4

[a] Reaction conditions: 0.8 g glucose, 0.2 g Ru/C, 0.2 g $LiNbMoO_6$, 40 mL H_2O, 503 K, 6 MPa H_2, $[H_3PO_4] = 0.21$ M.

Table 5 Evolution of species in the process of sorbitol hydrogenolysis over Ru/C with $LiNbMoO_6$ in aqueous phosphoric acid[a]

					Yield [%]							
Entry	Co-catalyst	t [h]	Con. [%]	Carbon balance [%]	Hex	Pent	C1–C4 alkanes	Glu	Sorb	Iso	Other	Hex/total alkanes
1	$LiNbMoO_6$	0.5	94.1	99.5	3.7	0.1	0.2	<0.1	48.9	40.2	0.5	92.5
2	$LiNbMoO_6$	1	97.7	>99.9	6.8	0.4	0.4	<0.1	40.7	49.1	0.3	89.5
3	$LiNbMoO_6$	3	98.1	95.2	7.6	0.5	0.5	<0.1	38.9	45.8	0.1	88.4
4	$LiNbMoO_6$	6	98.5	91.1	13.5	1.6	1.1	<0.1	30.6	42.9	<0.1	83.3
5	$LiNbMoO_6$	12	98.9	93.9	22.9	1.9	1.8	<0.1	25.1	41.2	<0.1	86.1
6	$LiNbMoO_6$	18	99.3	89.1	24.8	2.1	2.5	<0.1	18.1	40.9	<0.1	84.4
7	$LiNbMoO_6$	24	99.5	82.8	26.7	2.5	2.8	<0.1	10.2	40.2	<0.1	83.4
8	—	24	93.5	95.8	17.2	9.8	7.8	<0.1	1.4	54.8	<0.1	49.4

[a] Reaction conditions: 0.8 g sorbitol, 0.2 g Ru/C, 0.2 g $LiNbMoO_6$, 40 mL H_2O, 503 K, 6 MPa H_2, $[H_3PO_4] = 0.21$ M.

isosorbide is difficult to deoxygenate due to its two tetrahydrofuranic moieties, which enhance steric hindrance. Hence, it limits the interaction of isosorbide and the catalysts. Moreover, isosorbide is widely and successfully applied as a monomer for medical applications and polymers for its high stability, which in turn enhances the products' stability.[57–59] This also suggests isosorbide is robust to hydrodeoxygenation. Therefore, the formation of isosorbide should be suppressed in the direct conversion of cellulose to alkanes under the current catalytic system.

In the current catalytic system, the presence of $LiNbMoO_6$ plays a critical role in determining the rate of the dehydration reaction of sorbitol. Table 6 shows that the formation of isosorbide is the key barrier for increasing the hexane yield. The results from Table 1,4 and 5 indicate that the formation of isosorbide could be significantly inhibited by the addition of $LiNbMoO_6$, regardless of whether cellulose, glucose or sorbitol was used as the substrate. With the decrease of isosorbide yield, the yield of hexanes sharply increased. Moreover, it should be noted that the suppression effect of isosorbide formation also depended on the substrates with a descending order of cellulose > glucose > sorbitol. This can be explained by the fact that sorbitol can be gradually released from the hydrogenation of glucose. Similarly, sorbitol yield from cellulose required hydrolysis and hydrogenation processes. Compared with sorbitol as the substrate, the sorbitol gradually released from cellulose or glucose might be efficiently intercalated into the space of the layered $LiNbMoO_6$, which actually reduces the chance of isosorbide forming. In contrast, a large amount of sorbitol in the solution would be easily transformed into isosorbide rather than intercalated into the interlayers of $LiNbMoO_6$. Therefore, cellulose as the substrate had a higher yield of hexanes than glucose and sorbitol.

The effect of layered compound $LiNbMoO_6$

Because the addition of $LiNbMoO_6$ gave the highest yield of hexanes with negligible isosorbide in the conversion of cellulose for the current catalytic system, further investigation was focused on the effect of this co-catalyst. Textural properties of MCM-41 and layered compounds $LiNbMoO_6$, $HNbMoO_6$, and $LiNbWO_6$ are given in the ESI (Table S1 and Fig. S1†). The morphologies of layered compounds were characterized by scanning electron microscope (SEM), in which the layered structures of the compounds were clearly observed. FT-IR and NH_3-TPD of the layered compounds are given in the ESI (Fig. S10 and S11†). $HNbMoO_6$ gave a peak around 1033 K which was attributed to very strong acid sites, confirmed by peaks at 3386 cm^{-1} and 1618 cm^{-1}, which were ascribed to O–H and H–

Table 6 Evolution of species in the process of isosorbide hydrogenolysis over Ru/C with $LiNbMoO_6$in aqueous phosphoric acid[a]

					Yield [%]							
Entry	Co-catalyst	t [h]	Con. [%]	Carbon balance [%]	Hex	Pent	C1–C4 alkanes	Glu	Sor	Sorb	Other	Hex/total alkanes
1	$LiNbMoO_6$	0.5	8.9	86.5	1.5	0.1	0.1	1.1	2.1	2.8	<0.1	88.2
2	$LiNbMoO_6$	1	9.1	85.7	3.0	0.2	0.1	0.2	2.2	2.1	<0.1	90.9
3	$LiNbMoO_6$	3	10.2	94.1	4.1	0.3	0.2	<0.1	3.2	1.8	<0.1	89.1
4	$LiNbMoO_6$	6	11.5	97.4	5.5	0.3	0.4	<0.1	2.5	1.4	1.1	88.7
5	$LiNbMoO_6$	12	12.3	95.1	5.8	0.4	0.5	<0.1	1.5	1.2	1.5	86.6
6	$LiNbMoO_6$	18	13.4	91.0	6.9	0.8	0.9	<0.1	0.9	1.0	1.7	80.2
7	$LiNbMoO_6$	24	14.1	95.7	7.4	1.4	1.3	<0.1	0.2	0.7	2.5	73.3

[a] Reaction conditions: 0.8 g isosorbide, 0.2 g Ru/C, 0.2 g $LiNbMoO_6$, 40 mL H_2O, 503 K, 6 MPa H_2, $[H_3PO_4] = 0.21$ M.

O–H, respectively, of adsorbed water molecules on acid sites, whereas other compounds did not have these indications. This suggests that the acidity of the co-catalyst shows no responsibility for the difference of performance in cellulose conversion because the acidity of acidic media plays the dominant role. Therefore, the intercalation effect of layered compounds should be considered. It has been reported that the layered compounds possessed the intercalation effect of substrates within the interlayers.[41–47] Based on the abovementioned results, we assume that the substrate like cellulose-derived glucose and sorbitol could be intercalated into the layered compounds, but isosorbide as the substrate could not be effectively intercalated. To confirm the role of intercalation of substrates, the confinement of glucose, sorbitol, and isosorbide into the narrow spaces between the layers was investigated by immersing $LiNbMoO_6$ in these substrate solutions (0.1 M) for 24 h at room temperature.

X-ray diffraction (XRD) has already been used as an approach to confirm the intercalation of substrates within the interlayers of layered compounds in previous studies.[41–47] In the current study, XRD experiments were also performed to analyse the layered materials after filtrating and drying in air at 353 K (Fig. 1). The results suggested that glucose and sorbitol rather than isosorbide could be intercalated into the interlayers of $LiNbMoO_6$, which was also supported by previous research.[41–47] The peaks of $LiNbMoO_6$ were shifted to lower angles after immersion in glucose and sorbitol solution. Those distinct peaks shifted to lower angles were observed in the case of immersion in glucose solution. It indicated that the basal spacing of $LiNbMoO_6$ was expanded after immersion in glucose or sorbitol. In contrast, the peak did not shift in the case of $LiNbMoO_6$ after immersion in isosorbide solution, which indicated isosorbide could not be intercalated. It should be noted that the dehydration of sorbitol to isosorbide must undergo consecutive 1,4- and 2,6-cyclodehydration. Because sorbitol was intercalated within the interlayers of $LiNbMoO_6$, the terminal OH moieties of sorbitol molecules formed tetrahydrofuranic moieties with difficulty by dehydration due to steric restrictions. However, for the sorbitol in the bulk solution, the formation of isosorbide is readily achieved. Therefore, the great decrease of isosorbide yield after the addition of layered compounds is probably attributed to the steric restrictions of sorbitol dehydration within interlayers of layered compounds. The fascinating ability of layered $LiNbMoO_6$ to inhibit the formation of isosorbide is responsible for the production of hexanes with high yield from cellulose conversion in the current catalytic system.

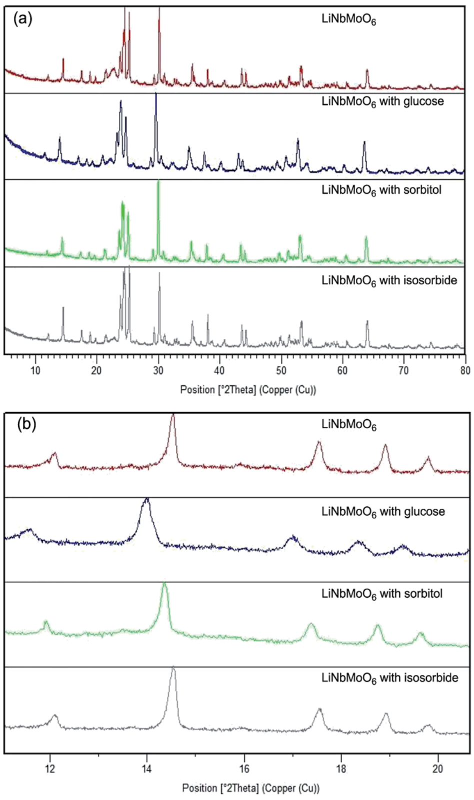
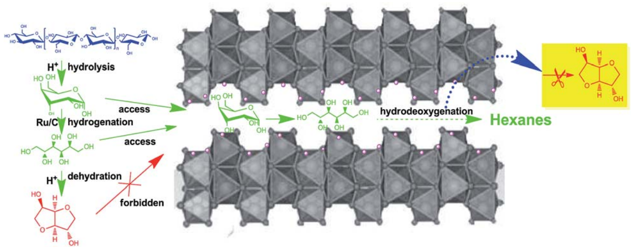


Fig. 1 XRD patterns of $LiNbMoO_6$, and $LiNbMoO_6$ after immersion in aqueous solutions of glucose, sorbitol, or isosorbide.



Scheme 2 The efficient conversion of cellulose to hexanes over $LiNbMoO_6$ and Ru/C in aqueous phosphoric acid.

Based on the abovementioned results, the following route of cellulose conversion is proposed for the influence of glucose, sorbitol and isosorbide. As shown in Scheme 2, with the catalysis of phosphoric acid, cellulose is hydrolysed to yield glucose or other oligomers, which could be adsorbed by layered compounds. Moreover, glucose could be transformed into sorbitol over Ru/C by hydrogenation. For the glucose and/or sorbitol gradually released from the substrate, they can readily, successfully intercalate into the interlayers of the layered compounds. In the active interlayer sites, consecutive C–O cleavage reaction of glucose and/or sorbitol could be performed for the production of hexanes. It is clear that some intermediates are reduced over Ru/C in the bulk solution. In addition, the reduction of intermediates might occur between the interlayers of layered compounds by hydrogen spillover from Ru/C onto the layered compounds.[60–62] For the consecutive dehydration of sorbitol within interlayers, the dehydration of terminal OH moieties of sorbitol molecules to form isosorbide must undergo the formation of tetrahydrofuranic moieties, which was hardly performed within the interlayers. Therefore, the formation of isosorbide within the interlayers hardly occurred. In the case of cellulose conversion, the formation of negligible isosorbide was achieved.

Conclusions

The Ru/C catalyst combined with $LiNbMoO_6$ was efficient in converting cellulose into hexanes through sorbitol in environment-friendly aqueous phosphoric acid. A promising yield of hexanes (72% C) could be directly obtained by the one-pot hydrolysis hydrodeoxygenation of cellulose. The catalytic system shows a good stability, which could be used for several runs without any treatment. Gradually released intermediates from cellulose conversion can be efficiently intercalated into the interlayer of layered compounds. In addition, the layered compounds possessed the excellent inhibition of the formation of isosorbide from cellulose. Hence, the yield of hexanes was promoted.

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