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Natural Celluloses as Catalysts in Dehydrogenation of $NaBH_4$ in Methanol for H_2 Production

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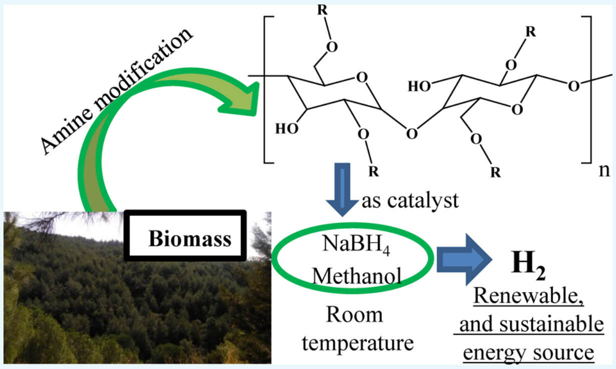

ABSTRACT: Cellulose, the most abundant renewable biopolymer, exists in many forms, such as microgranular cellulose (MGCell), sigmacell cellulose (SCell), cellulose fibers (FCell), and α-cellulose (AlfaCell). Several of these cellulose forms were protonated with an amine-containing agent polyethyleneimine (PEI), and the modified celluloses (XCell-PEI$^+$) were studied as catalysts in methanolysis of $NaBH_4$ for hydrogen (H_2) generation. It was found that the SCell-PEI$^+$-catalyzed reaction is the fastest one among the modified celluloses with a hydrogen generation rate of 5520 ± 119 mL H_2/(g of catalyst × min). The activation energies of MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$ were determined as +21.7, +23.4, +24.8, and + 21.8 kJ/mol, respectively. Reusability of catalysts was investigated, and regeneration of cellulose based catalysts after the fifth cycle could be readily achieved by HCl treatment to completely recover its activity. Therefore, PEI-modified-protonated cellulose forms constitute sustainable, re-generable, and renewable catalysts for production of H_2, an environmentally benign green energy carrier.

INTRODUCTION

Conventional energy sources, mainly coal, oil, and natural gas are major contributors of greenhouse gas emissions and also generate harmful nitrogen oxides, sulfur oxides, and smog, causing serious environmental and health problems.[1−4] Greenhouse gases, in turn, degrade the Earth's ecosystem.[5] Consequently, there are two rational ways to tackle this problem: (1) reduce economic activity around the world, or (2) switch to sustainable sources of energy.[6,7] Hydrogen (H_2), as one of the cleanest fuel sources, has a high specific energy content (142 MJ kg^{-1}) and is expected to have a significant impact in energy production in the future.[8−11] However, storage and transport complications remain challenging tasks to widespread implementation of the "hydrogen economy", as H_2 is a gas under ambient conditions and needs to be liquefied at high pressure (40 g/L at 700 bar) or at low temperature (70 g/L at 20 K).[12,13]

Due to its high hydrogen content of 10.8% by weight, $NaBH_4$ is recognized as an ideal H_2 storage material among other forms of hydrides. From $NaBH_4$, highly pure, CO-free (CO is toxic to fuel cells) H_2 can be readily generated.[14−16] In addition, non-flammability and high stability in the air, controllable H_2 production capability, and even byproduct recycling capabilities are some of the other important advantages that make $NaBH_4$ the most widely available metal hydride amongst all hydrides.[17] Many metal nanoparticles, such as Ru, Pt, Co, and Ni, have been reported as catalysts in dehydrogenation of $NaBH_4$ in water for H_2 production.[18−20] However, new and alternative reaction pathways were needed for fast and controllable dehydrogenation reaction of $NaBH_4$ due to the slow reaction kinetics, low conversion yield at low and ambient temperatures, and the low dissolution of $NaBH_4$ in water at subzero temperatures.[21]

Interestingly, H_2 production from dehydrogenation of $NaBH_4$ in methanol, as shown in eq 1, has faster reaction kinetics than dehydrogenation of $NaBH_4$ in water, even at subzero temperatures.[22]

$$NaBH_4 + 4CH_3OH \rightarrow 4H_2 + NaB(OCH_3)_4 \qquad (1)$$

The production of methanol from renewable sources, such as biomass-based feedstocks and even CO_2, favors the use of methanol as a solvent in the dehydrogenation of $NaBH_4$.[2] In addition, the lower freezing point of methanol in comparison to water is also a great advantage for the dehydrogenation of $NaBH_4$ in methanol that can easily be carried out at temperatures below zero in the presence of a suitable catalyst.

In the literature, metal nanoparticles,[23−25] metal-free polymers,[26−29] carbon-based materials,[30,31] clays,[32,33] and

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even natural polymers[34] have been reported as catalysts in the dehydrogenation of $NaBH_4$ in methanol to produce H_2. Cellulose is a natural renewable polymer found in various biomass species, including trees, grasses, and crops, as the most abundant biopolymer that is widely used in the paper, textile, and biofuel industries, as well as in biomedical applications due to its biocompatible, biodegradable, and low-toxicity nature and its excellent physical, chemical, and mechanical properties.[35] The total production of over 1000 tons/year make cellulose the most copious natural polymer in the world.[36,37] Given its natural origins and abundance, cellulose is considered a green and sustainable resource to produce renewable and biocompatible materials with desired properties by means of chemical modification and preparation of composites.[38,39] In addition, cellulose is applied in drug delivery systems,[40] toxic metal and organic compound removal,[41] sensor applications,[42] and ethanol production.[43] In this study, various forms of natural cellulose were applied as a metal-free catalyst in dehydrogenation of $NaBH_4$ in methanol for H_2 production. Microgranular cellulose (MGCell) was modified with amine group-containing modification agents ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetraamine (TETA), tris(2-amino ethyl) amine (TAEA), and polyethyleneimine (PEI) after pretreatment with epichlorohydrin (ECH) in dimethylformamide at 90 °C. The modified MGCells were then tested as the catalyst in H_2 production from $NaBH_4$ in methanol. The effect of the number of amine groups of the modification agents and the reaction temperature on the H_2 generation rate by MGCells from $NaBH_4$ in methanol was investigated. Moreover, the most effective modification agents were chosen for modification of sigmacell cellulose (SCell), cellulose fibers (FCell), and α-cellulose (AlfaCell). These modified celluloses were also tested as catalysts in dehydrogenation of $NaBH_4$ in methanol to generate H_2. Finally, the effects of cellulose type and activation energy on the hydrogen generation rate were compared.

RESULTS AND DISCUSSION

Modification and Characterization of Cellulose. MGCell was chemically modified with various numbers of amine groups by using the modification agents EDA, DETA, TETA, TAEA, and PEI in a two-step reaction, as illustrated in Figure 1. In the first step, ECH, a coupling agent, reacted with the hydroxyl groups of MGCell. The hydrogen atoms of the primary and secondary amine groups are able to react with the epoxy groups of ECH via nucleophilic addition reaction.[44,45] Hence, the amine groups of the modification agents were covalently bonded to MGCell-ECH through the epoxide groups of ECH.

As can be seen from the digital camera images of bare MGCell and EDA, DETA, TETA, TAEA, and PEI-modified MGCells, the white color of bare MGCell turned to tones of yellow upon modification that increased in intensity with the increasing number of amine groups in the modifying agents with the exception of TAEA that gave a brown color to TAEA-modified MGCell.

The FT-IR spectra of MGCell and its modified forms are shown in Figure S1. The characteristic peaks of cellulose at 1161 and 1048 cm^{-1} were observed in all materials.[46] The peaks at around 1650 and 1450 cm^{-1} were shared by all modification types and are attributed to N−H bending vibrations. As expected, the band intensities increased with an increase in amine content of the modifying agents. Moreover, the surface charges of the native and modified MGCells in bare and protonated forms are summarized in Table 1.

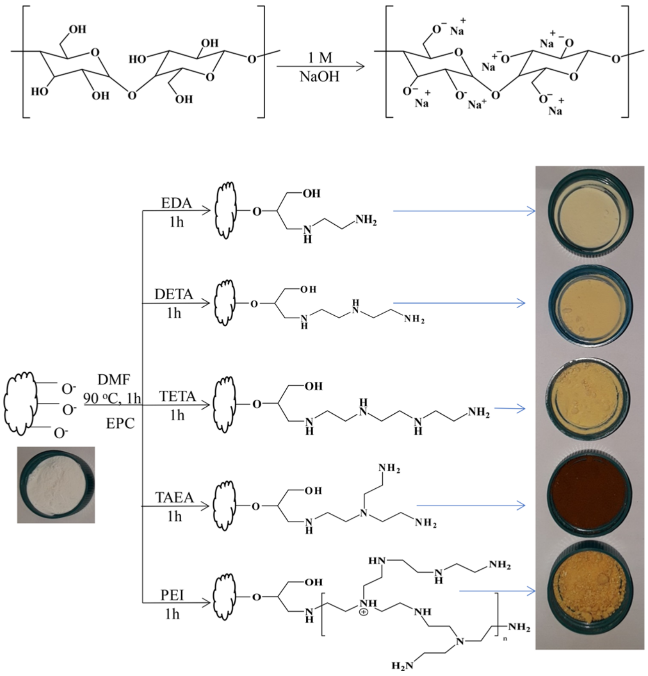

Figure 1. Modification of cellulose by various amine-containing reagents and digital camera images of modified microgranular cellulose (MGCell).

The surface charge of native MGCell was measured as −13.1 ± 1.1 mV and increased to +7.8 ± 1.3, +15.2 ± 2.3, +21.3 ± 1.7, 24.7 ± 2.1, and 27.4 ± 3.3 mV after EDA, DETA, TETA, TAEA, and PEI modification, respectively. Moreover, the modified MGCells demonstrated more positive surface charges as 17.4 ± 1.9, +33.6 ± 3.1, +39.4 ± 2.4, +41.2 ± 2.8, and + 55.4 ± 3.7 mV in the same respective order upon protonation with HCl treatment.

Use of Modified Celluloses as Catalysts. Various amine-containing materials are widely recognized as potential catalysts for H_2 production in methanolysis of $NaBH_4$.[32,46] To that end, the MGCell and amine modified forms, MGCell-EDA, MGCell-DETA, MGCell-TETA, MGCell-TAEA, and MGCell-PEI, were tested as catalysts in methanolysis of $NaBH_4$ and the corresponding graph is illustrated in Figure 2a. The self-dehydrogenation reaction of 0.0965 g $NaBH_4$ in methanol was completed in 32.5 min with 250 ± 2 mL of H_2 generation, whereas 50 mg of native MGCell-catalyzed dehydrogenation reaction lasted 24 min with 251 ± 2 mL of H_2 release. The HGR value of the MGCell-catalyzed reaction was calculated as 408 ± 11 mL H_2/(g of catalyst × min) from half of the H_2-generated curve (approximately 125 mL). On the other hand, the catalytic activity of MGCell was significantly enhanced upon amine modification and was proportional to the increase in the number of amines in the modifying agent. Fifty milligrams of MGCell-EDA-, MGCell-DETA-, MGCell-TETA-, MGCell-TAEA-, and MGCell-PEI-catalyzed methanolysis of $NaBH_4$ were completed in 20, 10, 7, 6, and 6 min with 251 ± 2 mL of H_2 generation, respectively.

The HGR values of the catalysts were calculated from half of the H_2 release curves (approximately 125 mL) as 816 ± 72, 1171 ± 84, 1373 ± 99, 1603 ± 85, and 1628 ± 74 mL H_2/(g

Table 1. Zeta Potential Changes of Various Celluloses after Modification and Protonation

material	zeta Potential (mV)		material	zeta potential (mV)	
	bare	protonated		bare	protonated
MGCell	−13.1 ± 1.1		MGCell-PEI	+27.4 ± 3.3	+55.4 ± 3.7
MGCell-EDA	+7.8 ± 1.3	+17.4 ± 1.9	SCell-PEI	+25.6 ± 1.9	+58.7 ± 4.1
MGCell-DETA	+15.2 ± 2.3	+33.6 ± 3.1	FCell-PEI	+23.1 ± 2.1	+44.3 ± 5.2
MGCell-TETA	+21.3 ± 1.7	+39.4 ± 2.4	AlfaCEll-PEI	+26.7 ± 2.4	+49.7 ± 2.8
MGCell-TAEA	+24.7 ± 2.1	+41.2 ± 2.8			

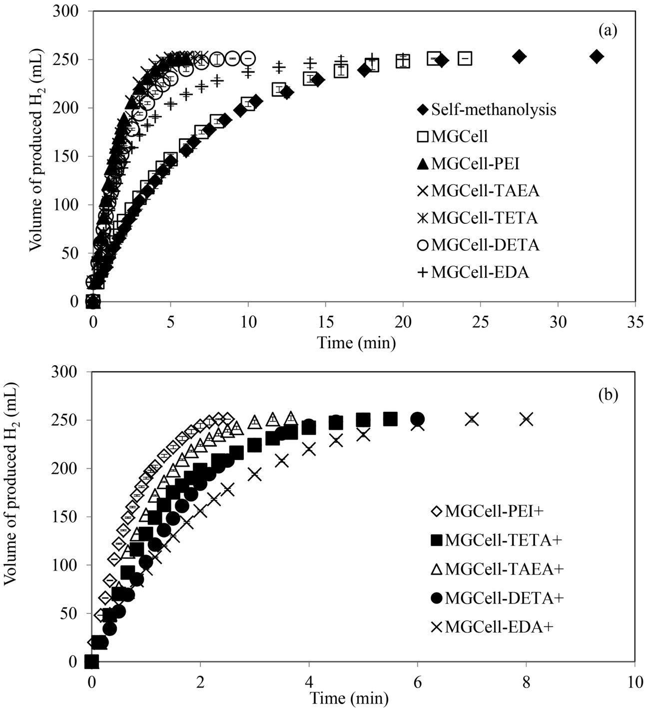

Figure 2. H_2 production from the dehydrogenation reaction of $NaBH_4$ in methanol via (a) self methanolysis and methanolysis catalyzed by various types of amine-modified MGCell and (b) methanolysis catalyzed by protonated forms of amine-modified MGCell [reaction conditions: 50 mg catalyst, 20 mL methanol, 0.0965 g $NaBH_4$, 25 °C, 1000 rpm].

of catalyst × min), respectively. Catalytic potentials of the protonated forms of modified MGCell in methanolysis of $NaBH_4$ are shown in Figure 2b, where volumes of released H_2 were plotted as a function of time. MGCell-EDA$^+$-, MGCell-DETA$^+$-, MGCell-TETA$^+$-, MGCell-TAEA$^+$-, and MGCell-PEI$^+$-catalyzed methanolysis of $NaBH_4$ were completed in 8, 6, 5, 3.6, and 2.5 min with 251 ± 2 mL of H_2 release, respectively. The calculated HGR values of protonated MGCell increased by at least two-fold as compared to unprotonated catalysts generating 1188 ± 49, 1731 ± 71, 1782 ± 57, 2508 ± 74, and 3463 ± 98 mL H_2/(g of catalyst × min), respectively.

As PEI modification appears to provide the best catalytic performance among modification agents, SCell, FCell, and AlfaCell were also modified with PEI to determine the effect of cellulose type on H_2 production and the corresponding FT-IR spectra are shown in Figure S2a. PEI-modified MGCell, SCell, FCell, and AlfaCell showed almost the same peaks as N−H bending and stretching bands between 1640−1650 and 1461 cm^{-1}. Common characteristics of the peaks in FT-IR spectra of all cellulose types were observed between 1140−1160, and 1040−1020 cm^{-1} and are in accordance with the literature.[47]

TGA thermograms of MGCell, SCell, FCell, AlfaCell, and their corresponding PEI-modified forms are presented in Figure S2b. It was observed that thermal decomposition of the bare cellulose occurred between 280−310 and 330−380 °C with approximately 80% weight loss. On the other hand, PEI-modified cellulose types exhibited different thermal stabilities with the first decomposition step observed between 180 and 310 °C with 47 ± 5% weight loss and the second step observed between 410 and 620 °C with a total of 95 ± 4% weight loss.

The SEM images of bare and PEI-modified celluloses are shown in Figure 3. All the native celluloses were shown to be in a rod-like shape with smooth surfaces. Upon PEI modification, the surfaces of all types of cellulose become rough and wrinkled as seen under SEM.

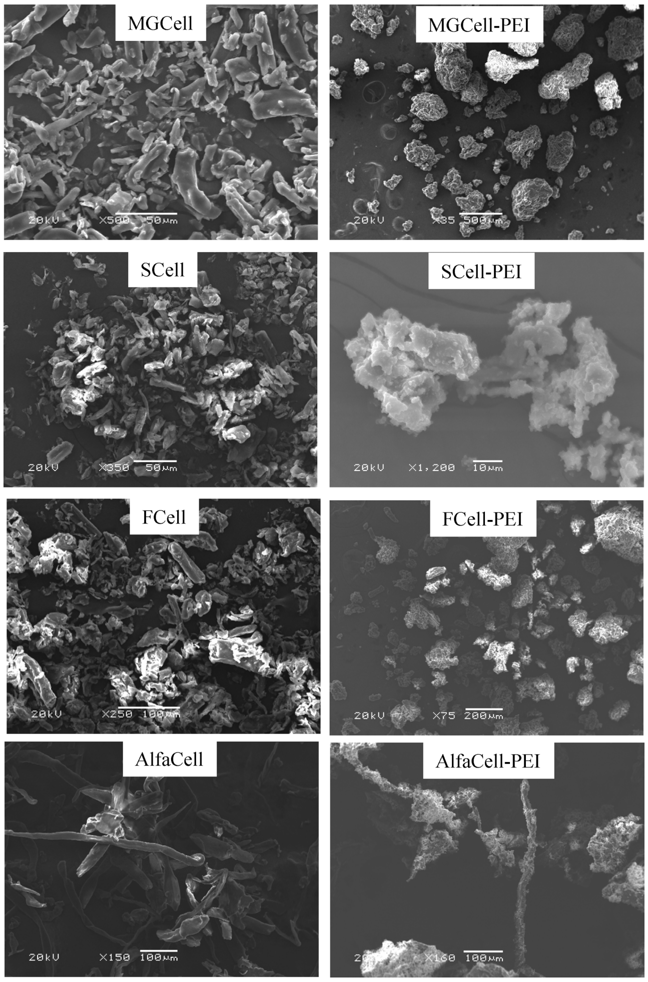

Figure 3. SEM images of native MGCell, SCell, FCell, AlfaCell, and their corresponding PEI modified forms.

Surface charges of the PEI-modified celluloses before and after protonation are presented in Table 1. The surface charge of MGCell at −13.1 ± 1.1 mV increased to +27.4 ± 3.3 mV after PEI modification and further increased up to +55.4 ± 3.7 mV upon protonation. Similarly, the negative surface charges of SCell, FCell, and AlfaCell were measured around −10 mV and increased to +25.6 ± 1.9, +23.1 ± 2.1, and + 26.7 ± 2.4 mV, respectively, after PEI modification and reached +58.7 ± 4.1, +44.3 ± 5.2, and + 49.7 ± 2.8 mV after protonation.

The catalytic activities of MGCell-PEI, SCell-PEI, FCell-PEI, and AlfaCell-PEI in methanolysis of $NaBH_4$ are compared in Figure 4a as 251 ± 2 mL H_2 were generated in 6, 4.5, 7 and 5.5 min, respectively. The HGR values for PEI-modified celluloses were calculated as 1648 ± 86, 2225 ± 81, 1347 ± 67, and 1785 ± 101 mL H_2/(g of catalyst × min).

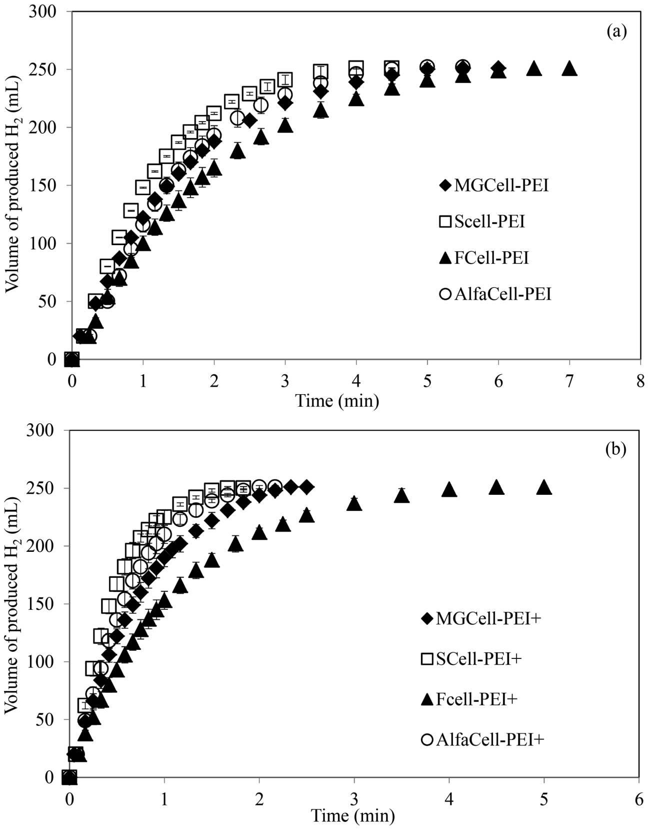

Figure 4. H_2 production curves from the catalytic dehydrogenation reaction of $NaBH_4$ in methanol via (a) PEI-modified types of celluloses and (b) protonated forms of PEI-modified types of cellulose [reaction conditions: 50 mg catalyst, 20 mL methanol, 0.0965 g $NaBH_4$, 25 °C, 1000 rpm].

As seen in Figure 4b, the dehydrogenation reactions catalyzed by protonated celluloses were completed much faster than with unprotonated catalysts (in 2.5, 1.8, 5, and 2.2 min with 251 ± 2 mL H_2 release, respectively). Moreover, the HGR values for MGCell-PEI$^+$-, SCell-PEI$^+$-, FCell-PEI$^+$-, and AlfaCell-PEI$^+$-catalyzed methanolysis were calculated to be 3463 ± 98, 5520 ± 119, 2308 ± 105, and 4407 ± 121 mL H_2/(g of catalyst × min), respectively. The obtained H_2 generation data suggest that the PEI-modified SCell exhibited the best catalytic performance in terms of the reaction rate and HGR values for both protonated and un-protonated forms. The catalytic performances of the other celluloses followed in the decreasing order AlfaCell-PEI, MGCell-PEI, and FCell-PEI, showing the same pattern consistently in both the protonated and unprotonated forms. The surface areas of the MGCell and SCell were determined as 2.7 and 2.8 m^2/g, respectively, and also the surface area of the AlfaCell is reported to be 1.6 m^2/g in the literature.[48] As can be reasoned from these values, no significant differences exist between the surface areas of the used cellulose types. Additionally, from the SEM analysis, the size of the cellulose types were elucidated to range in 25−60 μm for MGCell, 15−35 μm for SCell, 10−100 μm for FCell, and 100−1000 μm for AlfaCell, respectively. The morphological differences between used cellulose types were also clearly seen in SEM images as shown in Figure 3. Collectively, although morphological variations among the cellulose types may arise some degree of differences in their catalytic performances, cellulose itself exhibited a low catalytic activity. On the other hand, amine groups were elucidated to act as primary active sites providing major catalytic active sites for H_2 generation. The catalytic activity of modified cellulose types increased with the increasing number of amine groups on the modification agents. Furthermore, as suggested by Lu et al., the dehydrogenation reaction of $NaBH_4$ proceeds directly to protonated amine groups.[54] Thus, the generated amine groups on the modified cellulose catalysts are the major responsible groups in methanolysis reaction of $NaBH_4$. The hydrolysis reaction of $NaBH_4$ for H_2 generation was explained in the literature[49] that can be readily adopted for the methanolysis of $NaBH_4$ and was as also suggested elsewhere according to equations given below.[50]

$$NaBH_4 \leftrightarrow Na^+ + BH_4^- \tag{2}$$

$$BH_4^- + H^+ \leftrightarrow BH_3 + H_2 \tag{3}$$

$$BH_3 + 3CH_3OH \leftrightarrow B(CH_3O)_3 + 3H_2 \tag{4}$$

$$B(CH_3O)_3 + CH_3OH \leftrightarrow B(CH_3O)_4^- + H^+ \tag{5}$$

Accordingly, as shown in reaction in eq 3, the increase in the number of protons shifts the equilibrium toward the product site (increase H_2 production) according to well-known Le Chatelier's principle. Therefore, the increase in the number of protons that can be accomplished with existence of amine groups in the reaction medium was expected to result in enhanced hydrogen generation rates.[51]

Furthermore, as reported, the acid addition to the H_2 generation medium can retard the formation of hydrated byproducts generated in the BH_4^- hydrolysis reaction.[52,53] In another study, ammonium derivatives, which are essentially conjugated acids, were shown to catalyze the $NaBH_4$ hydrolysis reaction.[54] Therein, the reaction between the catalyst and $NaBH_4$ was catalyzed by means of positively charged catalysts according to the reaction given in eq 6.

$$^{+}NH_xR_{4-x}^{\ +} + BH_4^- \rightarrow NH_{x-1}R_{4-x} + H_2 + BH_3 \tag{6}$$

In eq 6, a proton was provided by the catalyst responsible for the formation of H_2 and BH_3 molecules, and the reaction proceeds according to eq 4. Finally, the H^+ ions produced in eq 5 re-protonates the catalysts and recycles the whole process.

According to the obtained results and in corroboration with the literature, the reaction mechanism for the modified cellulose catalysts was suggested and given in Figure S3 where borohydride anion (BH_4^-) interacts with protonated amine groups of the catalyst, and the resultant borane

Table 2. Activation Parameters and HGRs of PEI-Modified Celluloses

materials	activation parameters			HGR (mL H_2·min^{-1}·g^{-1}) temperature (°C)				
	E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)	−10	0	10	25	40
MGCell-PEI$^+$	+21.7	+28.6	−179	386	714	1255	3463	9552
SCell-PEI$^+$	+23.4	+31.3	−168	796	1413	2436	5520	8160
FCell-PEI$^+$	+24.8	+33.4	−168	257	552	1131	2308	3960
AlfaCell-PEI$^+$	+21.8	+28.8	−178	499	1145	2281	4398	6206

molecules (BH_3) react with the solvent, methanol. Then, the hydrogen atom of borane along with the hydrogen atom of methanol is released as H_2 gas and the reaction continues until all hydrogen in the borane molecule is finished. The three methoxy group remains bonded to the borane molecules, and thus, trimethoxy borate ($B(OCH_3)_3$) is produced as a byproduct of the reaction. Finally, one CH_3OH molecule interacts with $B(OCH_3)_3$ molecules, and the reaction was terminated with the formation of $B(OCH_3)_4$ releasing a H^+ ion. Then, this produced H^+ ion recycles the catalyst by protonating it.

Activation Parameters. The catalytic activities of PEI-modified protonated celluloses were investigated in methanolysis of $NaBH_4$ at five different temperatures: −10, 0, 10, 25, and 40 °C. The H_2 generation volumes in the presence of 50 mg of each catalyst are shown as a function of time in Figure S4. The H_2 generation plot of MGCell is shown in Figure S4a, and 13, 7, 4, 2.5, and 1.1 min of reaction times were recorded at −10, 0, 10, 25, and 40 °C, respectively. HGR values for the catalysts were calculated as 386 ± 44, 714 ± 63, 1255 ± 55, 3463 ± 98, 9552 ± 149 mL H_2/(g of catalyst × min) at −10, 0, 10, 25, and 40 °C, respectively. The effect of temperature on SCell-PEI$^+$-catalyzed reaction is presented in Figure S4b. It was observed that approximately 250 ± 2 mL H_2 was produced in 16, 7, 3.5, 1.8, and 1.1 min at −10, 0, 10, 25, 40 °C, respectively. The calculated HGR values for SCell-PEI$^+$-catalyzed dehydrogenation reactions of $NaBH_4$ in methanol were found to be 796 ± 96, 1413 ± 75, 2436 ± 85, 5520 ± 119, and 8160 ± 196 mL H_2/(g of catalyst × min) at −10, 0, 10, 25, and 40 °C, respectively. The FCell-PEI$^+$ and AlfaCell-PEI$^+$-catalyzed H_2 generation plots are summarized in Figure S4c,d. HGR values for the catalysts increased from 257 ± 111 to 3960 ± 154 mL H_2/(g of catalyst × min) for FCell-PEI$^+$ and from 498 ± 61 to 6206 ± 131 mL H_2/(g of catalyst × min) for AlfaCell-PEI$^+$ catalyzed dehydrogenation reaction of $NaBH_4$ in methanol. As expected, the reaction rate accelerated with increasing reaction temperatures.

The calculated activation parameters of E_a, ΔH, and ΔS for PEI-modified protonated catalysts are summarized in Table 2, and the corresponding Arrhenius and Eyring plots are shown in Figure S5a,b, respectively.

The E_a values of the reactions were calculated as +21.7, +23.4, +24.8, and + 21.8 kJ/mol, respectively, for MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$ catalysts. As evidenced from these values, the MGCell-PEI$^+$-catalyzed reaction realized the lowest activation energy among the modified celluloses with an E_a of +21.7 kJ/mol. Moreover, the ΔH and ΔS values of the reactions were calculated to be +28.6 kJ/mol and − 179 J/mol·K for MGCell-PEI$^+$; +31.3 kJ/mol and − 168 J/mol·K for SCell-PEI$^+$; +33.4 kJ/mol and − 168 J/mol·K for FCell-PEI$^+$; and 28.8 kJ/mol and − 178 J/mol·K for AlfaCell-PEI$^+$. The obtained E_a values of +21.7, +23.4, +24.8, and + 21.8 kJ/mol for MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$-catalyzed reactions, respectively, are comparable to those reported in the literature. The E_a values for PEI-HCl-catalyzed dehydrogenation reaction of $NaBH_4$ in methanol was reported at 23.7 kJ/mol,[26] for carbon spheres (CSs) derived from lactose was reported at 23.8 kJ/mol,[30] and for Cellulose-ECH-DETA-HCl-catalyzed reaction was reported at 23.7 kJ/mol,[34] all of which are quite similar with the E_a values obtained in this study. In contrast, several metal nanoparticles used for methanolysis of $NaBH_4$ are reported to have much higher activation energies: Ru/Al_2O_3 was reported at 51.0 kJ/mol,[21] Ru_5Co/C at 36.8 kJ/mol,[23] and Co-P/CNTs-Ni at 49.9 kJ/mol.[24] Other materials, such as p(TAEA-co-GDE)-HCl, catalyzed the same reaction at 30.4 kJ/mol,[28] carbon black-PEI-HCl at 34.7 kJ/mol,[31] and HNTs-NH_2 at 30.4 kJ/mol.[33] On the other hand, lower E_a values have been reported for catalytic methanolysis of $NaBH_4$ by Fe-B at 7.02 kJ/mol,[25] p(4-VP)$^{++}C_6$ at 13.8 kJ/mol,[27] p(AMPS)-TDA-1 PIL microgels at 14.3 kJ/mol,[29] and Hal-PEI$^+$ at 16.4 kJ/mol.[32] Considering the relatively low E_a values of the PEI-modified and protonated celluloses, such materials have the potential to serve as affordable, environmentally safe, and sustainable catalysts for H_2 generation. Consequently, the E_a values of catalysts presented in this study are comparable and mostly lower than most of the studies reported in the literature.[21,23−31,33,34] Celluloses as the most abundant natural biopolymers in different forms can be easily obtained from biomass, exploiting them as efficient catalysts by means of suitable chemical modifications with facile procedure stands out as more valuable alternatives for H_2 generation studies. Although, there exists reported catalysts with lower activation energy than the values obtained in this study, those are generally metal-based catalysts; thus, regarding the environmentally benign, inexpensive, and laborless production of the catalysts reported in this study, cellulose-based catalysts can be considered as more valuable than most of the reported catalysts in the literature.

Reusability and Regeneration Studies. Catalysts often represent a significant part of the operating cost of a chemical process at the commercial scale. It is therefore essential to ensure catalyst longevity with a minimal loss of activity over several cycles of use for financial and environmental sustainability purposes. Hence, reusability of the MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$ catalysts in H_2 production was investigated and the obtained results are summarized in Table 3. All reactions occurred with 100% conversion with the catalytic activity of MGCell-PEI$^+$ decreasing at the slowest pace (among all cellulose catalysts tested) from 100% to 91 ± 3, 78 ± 4, 78 ± 5, and 78 ± 5% after the second, third, fourth, and fifth cycles, respectively.

The catalytic activity of the SCell-PEI$^+$ catalyst declined from 100% to 98 ± 1, 87 ± 3, 76 ± 5, and 68 ± 6% after five consecutive cycles, respectively. Similarly, the catalytic activity of FCell-PEI$^+$ and AlfaCell-PEI$^+$ catalysts dropped from 100%

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Table 3. Reusability of PEI-Modified Different Types of Cellulose Catalysts in $NaBH_4$ Methanolysis

		number of usage				
materials	%	1st	2nd	3rd	4th	5th
MGCell-PEI$^+$	activity	100	91 ± 3	78 ± 4	78 ± 5	78 ± 5
SCell-PEI$^+$	activity	100	98 ± 1	87 ± 3	76 ± 5	68 ± 6
FCell-PEI$^+$	activity	100	87 ± 4	81 ± 2	72 ± 6	72 ± 4
AlfaCell-PEI$^+$	activity	100	93 ± 2	78 ± 4	66 ± 5	66 ± 8

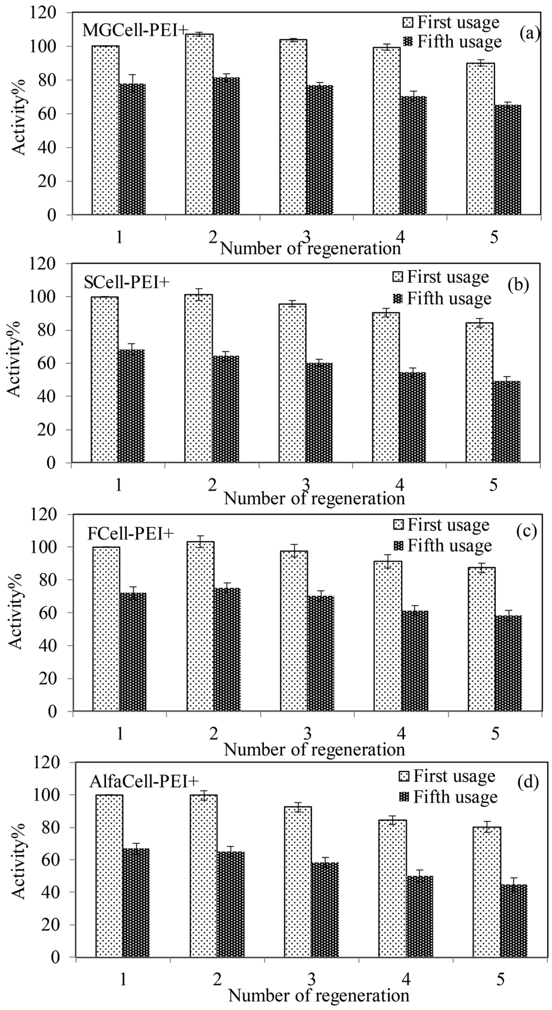

Figure 5. Regeneraton ability of (a) MGCell-PEI$^+$, (b) Scell-PEI$^+$, (c) FCell-PEI$^+$, and (d) AlfaCell-PEI$^+$ catalysts for methanolysis of $NaBH_4$ [reaction conditions: 50 mg catalyst 20 mL methanol, 25 °C, 1000 rpm].

to 72 ± 4, and 66 ± 8%, respectively, after the fifth use in dehydrogenation of $NaBH_4$ in methanol. In summary, 100% conversion was observed in all reactions with approximately a 20% decrease in the catalytic activity for MGCell-PEI$^+$ and a 30% decrease for SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI+ after the fifth use in the methanolysis of $NaBH_4$.

The regeneration capability of catalysts is one of the economically most important aspects for industrial applications. It aims at reversing decreased activity of the catalysts to extend their lifespan. For this purpose, after five cycles of use, PEI-modified protonated catalysts were regenerated with 100 mL of 1 M HCl solution for 1 h and after each of the five regenerations, each catalyst was used for five consecutive catalytic cycles. The activities of the catalysts during the first and last (fifth) use after each regeneration are presented in Figure 5, where panels (a), (b), (c), and (d) of Figure 5 show the catalytic activity of MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$, respectively.

The catalytic activity of MGCell-PEI$^+$ decreased from 100% to 78 ± 5% after the fifth cycle of reuse and increased to 107 ± 1.3% after first regeneration. Then, the activity dropped to 81 ± 2.4% at the end of the fifth cycle after the first regeneration. The catalytic activity of the regenerated MGCell-PEI$^+$ catalyst increased to 104 ± 1.1% from 81 ± 2.4% after the second regeneration and decreased to 76 ± 1.9% during the fifth use. After the first regeneration, the catalytic activity of MGCell-PEI$^+$ increased to 99 ± 1.9% from 76 ± 1.9% and decreased to 70 ± 2.8% after the fifth use. After the fourth regeneration, the activity of MGCell-PEI$^+$, increased from 70 ± 2.8% to 90 ± 1.7% and decreased to 65 ± 1.7% in the fifth cycle of the final regeneration. Similar trends, although with slightly lower activities, were observed with the other tested cellulose catalysts. Overall, the repeated usability test of the PEI-modified-protonated celluloses indicates that these catalysts, irrespective of structure, can be used in five consecutive cycles at a time with more than 66% of their original catalytic activity. Moreover, their activity can be restored to approximately 80% of the original activity with chemical regeneration and thus allow them to be used for a total of 25 methanolysis reaction of $NaBH_4$ with a catalytic activity of at about 50% of the original activity or higher.

■ CONCLUSIONS

Hydrogen is a carbon-free energy carrier with great potential for use in industrial applications. The difficulty of molecular H_2 storage has raised interest in hydrides, like the high hydrogen-content $NaBH_4$, as storage molecules from which H_2 can be generated readily in the presence of a catalyst. In this context, the design of potent low-cost catalysts comes into prominence for commercial hydrogen production. In an effort to identify catalysts made of low-cost, abundant raw materials, various forms of the natural biopolymer cellulose (MGCell, SCell, FCell, and AlfaCell) were tested as metal-free catalysts for H_2 generation in methanolysis of $NaBH_4$. MGCell and the other forms of cellulose were successfully modified with a number of amines, namely, EDA, DETA, TETA, TAEA, and PEI. Moreover, each of the modified forms of cellulose was protonated via HCl treatment to develop higher positive charges on the surface of the catalyst. MGCell-PEI$^+$ exhibited the best overall catalytic performance with a hydrogen generation rate (HGR) of 3463 ± 98 mL H_2/(g of catalyst × min) and an activation energy (E_a) of +21.7 kJ/mol, which is comparably low and hence competitive with established catalysts. Increased surface charges of the protonated MGCells seemed to provide better catalytic performance as expected from the suggested reaction mechanism (Figure S3). Furthermore, reusability and regeneration studies of the cellulose catalysts substantiated their potential for commercial viability as demonstrated by MGCell-PEI$^+$ whose activity decreased to 78 ± 5% after the fifth consecutive use for H_2 production reactions and was fully restored upon HCl treatment, enabling it to complete at least 25 reaction cycles. This study indicates that natural cellulose-based catalysts with high HGR and low E_a values can become a reality in the effort to develop sustainable metal-free catalysts for H_2 production from hydrides.

■ EXPERIMENTAL SECTION

Materials. Microgranular cellulose (MGCell, Microgranular form, Sigma-Aldrich), Sigmacell cellulose (SCell, Type 20, 20 μm size, Sigma-Aldrich), cellulose fibers (FCell, fiber form, medium size, Sigma-Aldrich), and Alfa cellulose (Powder form, Sigma Aldrich) were used as received. The modifying agents ethylenediamine (EDA, 99.5%, Sigma-Aldrich), diethylenetriamine (DETA, 99%, Sigma-Aldrich), triethylenetetramine (TETA, 60%, Sigma-Aldrich), tris(2-aminoethyl)amine (TAEA, 96%, Aldrich), and polyethyleneimine (PEI, 50% solution in water, Mn:1.800, Sigma-Aldrich) with epichlorohydrin (ECH, 99%, Sigma-Aldrich) as coupling agents were also used as received. Sodium hydroxide (NaOH, 98%, Sigma-Aldrich), hydrochloric acid (HCl, 36.5−38%, Sigma-Aldrich), and ethanol (99.8%, Sigma-Aldrich) were used for pH arrangement and protonation and regeneration reactions, whereas methanol (99.8%, Sigma-Aldrich) and dimethylformamide (DMF, 99%, Merck) were used as solvents and sodium borohydride ($NaBH_4$, 98%, Merck) was used as H_2 source. Distilled water (DW, GFL 2108) was used throughout the experiments.

Modification of MGCell with Various Types of Amine. The modification of MGCell with various types of amine, such as EDA, DETA, TETA, TAEA, and PEI were carried out by following the literature with some modifications.[32,34] First, 1.0 g MGCell was treated with 1 M 100 mL NaOH for 2 h for each modification agent separately and washed with DW to remove excess NaOH. Then, these NaOH-treated MGCells were placed into 45 mL of DMF with 1 mL of ECH and were stirred at 800 rpm at 90 °C for 1 h. Then, 3 mol of EDA, DETA, TETA, and TAEA, and 3 mL of PEI in 5 mL DMF were added into the solutions separately, and mixed at 800 rpm at 90 °C for 1 h more. Finally, EDA-, DETA-, TETA-, TAEA-, and PEI-modified MGCells were washed with acetone, ethanol, and water to remove unreacted ECH and modification agents. Then, these washed amine-modified MGCells were placed into 100 mL of 1 M HCl solution to protonate the amine groups on the modified MGCells and were then washed with water and acetone once each and dried in an oven at 50 °C and stored in closed tubes for further usage.

Modification and Protonation of Various Types of Cellulose with PEI. MGCell, SCell, FCell, and AlfaCell weighing 1.0 g each were treated with 100 mL of 1 M NaOH for 2 h and washed with water to remove excess NaOH from cellulose. Then, each cellulose was placed into a flask with 45 mL of DMF and 1 mL of ECH at 90 °C for 1 h. Next, 3 mL of PEI solution mixed with 5 mL of DMF were added into this solution and stirred at 90 °C for 1 h more. The PEI-modified various types of cellulose, denoted as MGCell-PEI, SCell-PEI, FCell-PEI, and AlfaCell-PEI, were washed with ethanol, water, and acetone and dried in an oven at 50 °C. Then, all of these PEI-modified celluloses were treated with 100 mL of 1 M HCl to protonate the amine groups and were washed with DW and acetone. The obtained PEI-modified protonated celluloses, denoted as MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$, were dried in an oven at 50 °C and stored in closed tubes for further use.

Characterization. The size and morphology of the various celluloses and their modified protonated forms were visualized by scanning electron microscopy (SEM, Jeol JSM-5600 LV). The SEM images of the samples were acquired at an operating voltage of 20 kV upon placing them on carbon tape-attached aluminum SEM stubs and sputter-coating with gold to a few nanometers of thickness in vacuum.

The FT-IR spectrum of MGCell, MGCell-EDA, MGCell-DETA, MGCell-TETA, MGCell-TAEA, MGCell-PEI, SCell-PEI, FCell-PEI, and AlfaCell-PEI were recorded by using an FT-IR spectrometer (Thermo Nicolet iS10) with the attenuated total reflection (ATR) method within the range of 4000 and 650 cm^{-1}.

Thermal stabilities of the used various cellulose types and their amine-modified protonated forms were compared via thermal gravimetric analysis (SII TG/DTA 6300, EXSTAR) under a continuous nitrogen atmosphere with a flow rate of 200 mL/min and 10 °C/min heating rate from 90 to 800 °C.

Zeta potential measurements of MGCell, MGCell-EDA, MGCell-DETA, MGCell-TETA, MGCell-TAEA, MGCell-PEI, and the other PEI-modified celluloses and their corresponding protonated forms were conducted at 25 °C using a zeta potential analyzer (ZetaPlus, Brookhaven Inst. Corp., BIC) by suspending the samples in DW. Average results were collected by 10 consecutive measurements in a run and presented with the corresponding standard deviations.

Modified Celluloses as Catalysts in H_2 Production from $NaBH_4$. MGCell, MGCell-EDA, MGCell-DETA, MGCell-TETA, MGCell-TAEA, and MGCell-PEI were used as catalysts in dehydrogenation of $NaBH_4$ in methanol (methanolysis) following published procedures.[31,32,34] Similarly, the setup used for H_2 generation studies was as reported in the literature.[31,32,34] Specifically, 20 mL of methanol, 50 mg of catalyst, and 125 mM of $NaBH_4$ were dissolved in a round bottom flask at 25 °C at 1000 rpm stirring. The flask was then attached to the setup, where a concentrated H_2SO_4-containing trap was used to capture the evaporated methanol from the reaction. Then, H_2 generation was pursued in a water-filled cylinder that was inverted to record the gradual decrease in the water level during H_2 generation from NaH_4 methanolysis.

The catalytic H_2 generation performance of MGCell, MGCell-EDA, MGCell-DETA, MGCell-TETA, MGCell-TAEA, and MGCell-PEI and their corresponding protonated forms in the methanolysis of $NaBH_4$ were investigated, and the hydrogen generation rates (HGRs), expressed in mL H_2/(g of catalyst × min), were determined for each catalyst. Moreover, the PEI-modified forms of cellulose and their protonated forms were also assessed as metal free catalysts in methanolysis of $NaBH_4$.

Activation Parameters. The effect of temperature on MGCell-PEI$^+$-, SCell-PEI$^+$-, FCell-PEI$^+$-, and AlfaCell-PEI$^+$-mediated dehydrogenation of $NaBH_4$ in methanol were investigated at −10, 0, 10, 25, and 40 °C, and the activation parameters activation energy (E_a), enthalpy (ΔH), and entropy (ΔS) values were calculated by using the Arrhenius (eq 7) and Eyring (eq 8) equations.

$$\ln(k) = \ln(A) - E_a/RT \tag{7}$$

$$\ln(k/t) = -(\Delta H/R)(1/T) + \ln(k_B/h) + \Delta S/R \tag{8}$$

where k is the rate constant of the reaction, E_a is the activation energy, T is the absolute temperature, k_B is the Boltzmann constant at $1.381 \times 10{-}23$ J·K^{-1}, and h is Planck's constant at 6.626×10^{-34} J·s, while ΔH is the activation enthalpy, ΔS is the activation entropy, and R is the gas constant at 8.314 JK^{-1}·mol^{-1}.

Reuse and Regeneration of Catalysts. The reuse studies of PEI-modified protonated celluloses MGCell-PEI$^+$, SCell-PEI$^+$, FCell-PEI$^+$, and AlfaCell-PEI$^+$ were conducted according to the previously reported literature.[31,32,34] Briefly, 0.0965 g of $NaBH_4$ and the catalysts weighing 50 mg each were placed in individual flaks of 20 mL methanol and the activity % of each catalyst was calculated by quantifying the half-point of total generated H_2 gas. Additionally, the conversion % of the reactions was also determined from total H_2 production in methanolysis of $NaBH_4$. Then, 0.0965 g of $NaBH_4$ was added to the same media of each catalyst four additional times (cycles) upon completion of each reaction. The changes in the activity % of each catalyst and the conversion % of the reactions were calculated.

Furthermore, after five consecutive cycles of catalyst reuse in methanolysis of $NaBH_4$, 50 mg of the catalysts were retreated with 100 mL of 1 M HCl for 1 h and subjected to an additional set of five consecutive reactions (cycles) after each catalyst regeneration. The H_2 generation activities of the regenerated catalysts were determined, and their catalytic performances were compared.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01653.

> FT-IR spectra of EDA, DETA, TETA, TAEA, and PEI modified MGCell; FTIR spectra and TGA thermograms of PEI-modified types of celluloses; suggested mechanism of amine-catalyzed dehydrogenation reaction of $NaBH_4$ in methanol; PEI$^+$ (protonated) modified cellulose-catalyzed methanolysis reaction of $NaBH_4$ at various temperatures; and Arrhenius and Eyring plots of the catalysts in methanolysis of $NaHBH_4$ (PDF)

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Notes

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■ ABBREVIATIONS

MGCell, microgranular cellulose; SCell, sigmacell cellulose; FCell, cellulose fibrillated; AlfaCell, Alfa cellulose; ECH, epichlorohydrin; DMF, dimethylformamide; EDA, ethylenediamine; DETA, diethylenetriamine; TETA, triethylenetetraamine; TAEA, tris(2-aminoethyl)amine; PEI, polyethyleneimine; $NaBH_4$, sodium borohydride; H_2, hydrogen gas; HGR, hydrogen generation rate; E_a, activation energy; ΔH, activation enthalpy; ΔS, activation entropy; SEM, scanning electron microscopy; FT-IR, Fourier transform infrared spectroscopy; TGA, thermogravimetric analysis.

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