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Hydrogenolysis of glucose into propylene glycol over Pt/SiO2@Mg(OH)2 catalyst

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Abstract: One-pot selective conversion of glucose is a green approach compared with petroleum-based processes to produce 1,2-propylene glycol (1,2-PG), but its realization is hindered by various side reactions. Here we demonstrate a feasible strategy of Pt/SiO2@Mg(OH)2 core-shell catalyst to achieve the 1,2-PG yield of 53.8% by a three-pronged promotion, including enhancement of the glucose-fructose isomerization and retro-aldol condensation (RAC), as well as re-conversion of by-product hexitol into 1,2-PG. We creatively realized the *in situ* synthesis of the core-shell structure using a self-existent Mg(OH)2 base instead of extraneous base in hydrothermal process and it achieved a stable performance during reuse by protecting Pt from leaching.

1,2-Propylene glycol (1,2-PG) is a key raw material in the synthesis of many useful chemical intermediates, such as unsaturated polyester, plasticizer and surfactant. It is also a final product applied in refrigeration, foods, pharmaceuticals and other industries.[1] Typical manufacturing ways of 1,2-PG are the petroleum products transformation and direct biomass hydrogenolysis.[1c, 2]. Comparatively, the latter approach is considered green, renewable and sufficient with bio-feeds, such as polysaccharide (e.g. stalk and cellulose)[1b, 3], monosaccharide (e.g. glucose and fructose)[4] or sugar alcohol (e.g. hexitol and glycerol)[5]. Among them, conquering glucose conversion pathway is of great significance because glucose is not only a start material for 1,2-PG production, but also a necessary intermediate for conversion of polysaccharide biomass into 1,2-PG.

The hydrogenolysis of glucose is a complex reaction network comprising isomerization, retro-aldol condensation (RAC), hydrogenation, dehydrogenation, dehydration, etc.[2] During these processes, in addition to 1,2-PG, a variety of by-products can be coproduced, such as ethylene glycol, sorbitol, mannitol, butanediol and hexanediol. Thus, in order to make 1,2-PG generation route the dominant and consequently increase the yield of 1,2-PG, two feasible strategies can be adopted: direct promotion of the key steps in 1,2-PG routes and inhibition of by-products routes. In the former strategy, glucose-fructose isomerization and carbon bond cleavage via RAC are regarded as the key steps to promote the 1,2-PG generation according to the previous studies[6]. The isomerization of glucose to fructose (aldose to ketose) always occurred on Lewis sites via 1,2-hydrogen shift[7], on Brønsted sites via HMF intermediate[8] and on basic sites via enediol anion[9]. While the RAC reaction

occurred on base sites[3b, 10] or transition-metal sites [6d, 11], which could catalyze C_6 sugars (with β-hydroxyl carbonyl) into small intermediates. Because the RAC and isomerization steps always take place on different active sites, it is difficult to realize the synchronous promotion of them on a same catalyst. In order to overcome this problem, researchers tried to develop catalysts act on both RAC and isomerization, such as Pt-SnOx/Al2O3 for cellulose conversion into polyols[6b], Ni-SnOx/Al2O3 for cellulose conversion into acetol[6c], ZnO modified Ru/C for glucose conversion into propylene glycol[4d], M-Sn/Beta (M=Zn, In, Pb) for glucose or biomass conversion into lactic acid[11b, 12], and Ca(OH)2 modified CuCr catalysts for cellulose conversion into ethylene glycol. Although these catalysts can enhance both the RAC and isomerization steps in the specific reaction system, it is still faces with challenges to get a high yield for glucose selective conversion into 1,2-PG because they may not balance with other reaction steps perfectly, such as hydrogenation and dehydration. So there are still a lot of by-products generated. Thus, besides the promotion of RAC and isomerization, a direct inhibition of by-products in glucose hydrogenolysis is also a required strategy to obtain a satisfied 1,2-PG yield. Furthermore, it will be welcomed if the by-products can be re-converted into 1,2-PG, although it is seldom studied. Therefore, we will focus on the development of catalyst which act both on isomerization and RAC promotion and by-products inhibition.

On the basis of a summary of predecessor's research results (Table S1), we were inspired by them that base catalysts have potential to act on both isomerization of aldose to ketose and C-C cleavage via RAC, although some of the catalysts were not applied in hydrogenolysis of glucose into 1,2-PG. Thus, a series of base modified Pt catalysts were employed to investigate the feasibility of combination of base sites and hydrogenation sites to realize the hydrogenolysis of glucose into 1,2-PG in this study. As Figure S1 shown, by screening a series of metal oxide and base co-catalysts, MgO and Mg(OH)2 were discovered beneficial for 1,2-PG promotion when combined with Pt/SiO2 catalyst. Furthermore, when combined with Pt/K-10, Pt/Al2O3 and Pt/Beta, MgO and Mg(OH)2 also showed an obvious 1,2-PG promotion effect (Figure S2). Thus, based on this effective strategy, the Mg(OH)2 modified Pt/SiO2 catalysts were synthesized. The optimum core-shell catalyst (Pt/SiO2@Mg(OH)2), its *in situ* hydrothermal synthesis process and the promotion mechanism on hydrogenolysis of glucose into 1,2-PG were focused on in this paper.
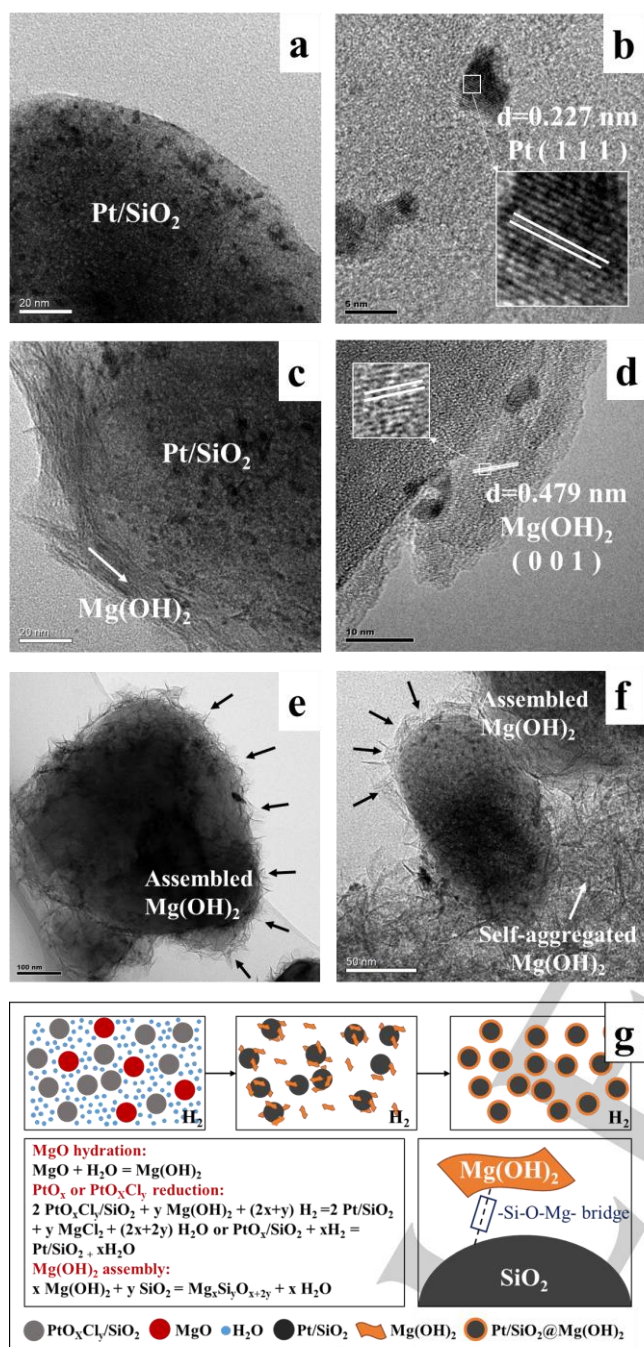
Figure 1. The core-shell structure of $Pt/SiO_2@Mg(OH)_2$. (a) The TEM image of Pt/SiO_2 (5 wt% Pt). (b) The HRTEM image of Pt/SiO_2. (c) The TEM image of $Pt/SiO_2@5Mg(OH)_2$. (d) The HRTEM image of $Pt/SiO_2@5Mg(OH)_2$. (e) The TEM image of $Pt/SiO_2@5Mg(OH)_2$. (f) The TEM image of $Pt/SiO_2@50Mg(OH)_2$. (g) The *in situ* hydrothermal synthesis process of core-shell $Pt/SiO_2@Mg(OH)_2$ catalyst. Hydrothermal condition: 200 °C, 6 MPa initial pressure of H_2, 4 h.

The TEM images of Pt/SiO_2 and $Pt/SiO_2@Mg(OH)_2$ catalysts were displayed in Figure 1. The Pt/SiO_2 could be observed in Figure 1 (a) and the lattice spacing of Pt (0.227 nm) was in accord with the (111) plane (Figure 1 (b)). After hydrothermal treatment of Pt/SiO_2 with MgO precursor, the magnesium species were mainly assembled on the surface of Pt/SiO_2 as a shell with the thickness in the range of 10-20 nm (Figure 1 (c) and (e)). The species were confirmed as magnesium hydroxide

by HRTEM (Figure 1 (d)), and the measured lattice spacing (0.479 nm) was in accord with the (001) plane of magnesium hydroxide. The magnesium hydroxide can also be confirmed by XRD patterns (Figure S3 (b)) and TGA spectra (Figure S4). In the hydrothermal process, the conversion of the MgO precursor into $Mg(OH)_2$ could be attributed to the plenty of hydroxyl groups presented in hydrothermal condition[13]. In addition, the morphology of a complete particle could be observed clearly observed in TEM images (Figure 1 (e) and (f)) and SEM images (Figure S5), where it could be that $Mg(OH)_2$ shell was completely coated on Pt/SiO_2 particle in the form of laminate structure. The formation of laminated $Mg(OH)_2$ might be attributed to the preferred orientation of (001) plane in the hydrothermal condition and the high temperature condition favoured the formation of Mg-OH ionic bond by providing more energy and subsequently promoted the growth of (001) plane[13b, 14]. And the possible formation mechanism of the core-shell structure was shown in Figure 1 (g). Firstly, the MgO precursor hydrated into $Mg(OH)_2$ in hydrothermal condition. Secondly, also because of hydrothermal condition, $Mg(OH)_2$ disassociated into Mg^{2+} and OH^- and they then were rearranged to form laminate $Mg(OH)_2$. Thirdly, the laminate $Mg(OH)_2$ as a base could corroded the surface of SiO_2 to form $Mg_xSi_yO_{x+2y}$ bridge on the interface of $Mg(OH)_2$ and SiO_2. Therefore, the whole process is temperature dependent. As shown in Figure S6, the core-shell structure could not generated at too low temperature (100 °C) or too high temperature (300 °C) because Mg-O-Si bridge could not generated at 100 °C and the SiO_2 particles were destroyed by base under 300 °C. Some previous studies[15] achieved a similar core-shell structure by adding additional base into hydrothermal system. In this work, we realized the synthesis of core-shell structure using a self-existent $Mg(OH)_2$ base instead of extraneous base. In the meanwhile, the Pt species in $[PtO_xCl_y]$ [16] or PtO_x form on SiO_2 could also be reduced into Pt(0) nanoparticles, so that a separate reduction process was not needed. Thus, because of the intensive method, the catalytic reaction could take place *in situ* without any normal operation such as washing, drying or calcination after the synthesis of $Pt/SiO_2@Mg(OH)_2$.

Since this study aimed at the base modified catalysts for hydrogenolysis of glucose into propylene glycol, the basicity of the Pt/SiO_2 containing 0-100 wt % of $Mg(OH)_2$ was analyzed by CO_2-TPD, as shown in Figure S7. As curves 1 and 9 showed, both Pt/SiO_2 with and without hydrothermal treatment displayed no obvious desorption peak. In contrast, Pt/SiO_2 containing 2.5-100% $Mg(OH)_2$ (curves 2 to 7) had two desorption peaks appeared at about 100 °C and 700-750 °C, which suggested weak basic sites and strong basic sites, respectively. The CO_2 desorption peak at lower temperature could be assigned to the CO_2 adsorption as bicarbonate species on $Mg(OH)_2$ surface hydroxyl groups, while that at higher temperature is more commonly attributed to bidentate and mon-dentate carbonates on the MgO surface[13b]. Based on the CO_2-TPD curves, the basic sites quantities of the catalysts were displayed in Table 1. It could be observed that the actual quantities of basic sites of all $Pt/SiO_2@Mg(OH)_2$ catalysts (column 3) were obviously larger than the theoretical value calculated by simply stacking $Mg(OH)_2$ and Pt/SiO_2 (column 4), indicating that the combination of $Mg(OH)_2$ and Pt/SiO_2 provided more basic sites than separated ones. Thus, the basic sites within $Pt/SiO_2@Mg(OH)_2$ could be

Table 1. The basicity of catalysts tested by CO_2-TPD.

Entry	Catalyst	The quantity of basic sites (mmol/g)		Gain (mmol/ g) [d]	Gain ratio (%) [e]
		Actual	Theoretical [c]		
1	Pt/SiO$_2$[a]	0.000	-	-	-
2	Pt/SiO$_2$[b]	0.003	-	-	-
3	MgO[a]	0.065	-	-	-
4	MgO[b] (Mg(OH)$_2$)	0.365	-	-	-
5	Pt/SiO$_2$@2.5Mg(OH)$_2$[b]	0.028	0.012	0.016	133.3
6	Pt/SiO$_2$@5Mg(OH)$_2$[b]	0.050	0.020	0.030	150.0
7	Pt/SiO$_2$@7.5Mg(OH)$_2$[b]	0.072	0.028	0.044	157.1
8	Pt/SiO$_2$@10Mg(OH)$_2$[b]	0.079	0.036	0.043	119.4
9	Pt/SiO$_2$@50Mg(OH)$_2$[b]	0.171	0.124	0.047	37.9
10	Pt/SiO$_2$@100Mg(OH)$_2$[b]	0.232	0.184	0.048	26.1

[a] without hydrothermal treatment; [b] with hydrothermal treatment under the condition of 200 °C, 6 MPa of H_2, 4 h, 400 r/min; [c] Theoretical value of basic sites quantity (mmol/g) = The mass of Mg(OH)$_2$ in the catalysts×0.365 + the mass of Pt/SiO$_2$×0.003; [d] The combination gain (mmol/g) = The quantity of basic sites (mmol/g) - Theoretical value of basic sites quantity (mmol/g); [e] The combination gain ratio (%) = The coordinate enhancement (mmol/g) / Theoretical value of basic sites quantity (mmol/g).

Figure 2. The catalytic reaction performance of Pt/SiO$_2$ and Pt/SiO$_2$@Mg(OH)$_2$ with different Mg(OH)$_2$ loadings: (a) The effect of Mg(OH)$_2$ loading on 1,2-PG yield; (b) The effect of Mg(OH)$_2$ loading on product distribution. Reaction condition: catalyst (200 mg), glucose (11.25 mg/ml, 10 ml) and H_2 (initial 6 MPa) at 180°C for 4 h. 1,2-HDO = 1,2-hexanediol; 1,2-BDO = 1,2-butanediol; 1,2-PG = 1,2-propylene glycol; EG = ethylene glycol

divided into two main parts, namely separated Mg(OH)$_2$ part (regarded as ordinary sites) and Mg(OH)$_2$ assembled Pt/SiO$_2$ part (regarded as enhanced sites). The combination gains provided by enhanced sites were listed in Column 5. With the increasing of Mg(OH)$_2$ content, the combination gain increased firstly because more Mg(OH)$_2$ assembled onto SiO$_2$ led to more enhanced basic sites and then remained at about 0.044 mmol/g, which could be attributed to the saturation of Mg(OH)$_2$ and Pt/SiO$_2$ assembly sites. The saturation of Mg(OH)$_2$ and Pt/SiO$_2$ assembly sites could also be observed in TEM images (Figure 1 (f)). When magnesium hydroxide was excess (50 wt%), they prefer to self-aggregate rather than assemble on Pt/SiO$_2$ as a thicker shell because of the limitation of SiO$_2$ surface sites.

Then the catalytic performance of the above Pt/SiO$_2$@Mg(OH)$_2$ for hydrogenolysis of glucose into 1,2-PG were investigated (Figure 2). As shown in Figure 2 (a), the optimal 1,2-PG yield (53.8%) was achieved over Pt/SiO$_2$ assembled by 5 wt% of Mg(OH)$_2$. Actually, 2.5 to 10 wt% could be regarded as the efficient range, which might be attributed to a suitable amount of base sites. Beyond this range, the poor performances were gained over excessive or insufficient Mg(OH)$_2$ loading. In order to illuminate the reason, the product distributions were displayed in Figure 2 (b). In the absence of Mg(OH)$_2$, the yield of 1,2-PG was lower than 20%, and it could be attributed to the generation of the main by-product 1,2-hexanediol (1,2-HDO). While in present of Mg(OH)$_2$, the yield of 1,2-HDO sharply decreased, suggesting the significantly inhibiting effect of Mg(OH)$_2$ on the generation of 1, 2-HDO.
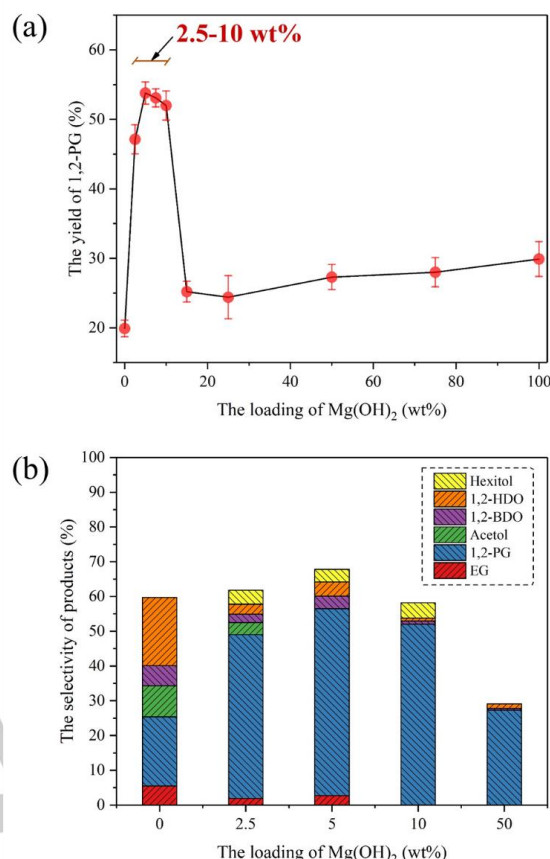
The GC-MS results (Figure S8) showed that in the absence of Mg(OH)$_2$, 1,2-HDO covered 22.97% of the peak area and 1,2-PG covered 12.38%, while in the presence of 5 wt% Mg(OH)$_2$, 1,2-HDO decreased to 3.37% and 1,2-PG increased to 85.74%. The above results indicated the significant effect of Mg(OH)$_2$ on products distribution, especially for 1,2-HDO and 1,2-PG. When the Mg(OH)$_2$ loading was higher than 10 wt%, the yield of 1,2-PG sharply decreased, reasoning from the negative effects of excess base sites caused by superfluous Mg(OH)$_2$ on conversion of dihydroxyacetone (DHA) into 1,2-PG (Table S2, Entries 1 to 7). The similar negative effects could be also be observed for other base co-catalysts (Table S2, Entries 8 to 17), which could explain the poor performance on these base displayed in Figure S1.

To further understand the reaction process and to propose the possible reaction pathway, Pt/SiO$_2$ and the above optimum Pt/SiO$_2$@Mg(OH)$_2$ containing 5wt% Mg(OH)$_2$ (abbreviated as Pt/SiO$_2$@Mg(OH)$_2$) were employed to the time course tests, shown in Figure 3. The time -20 to 0 (min) represented the heating process and the temperature changes were displayed in Figure S9. As shown in Figure 3(a), with the conversion of

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Scheme 1. The possible reaction routes for glucose hydrogenolysis.
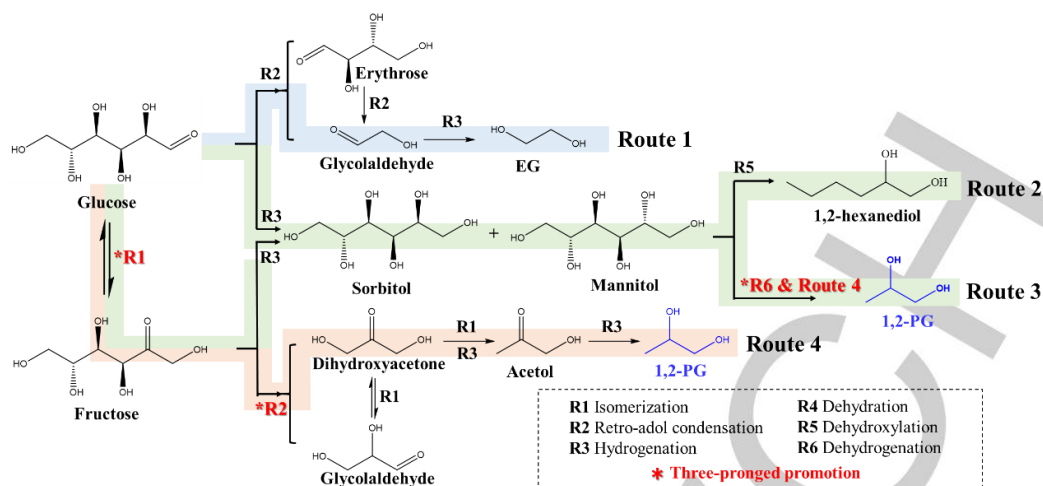
glucose, fructose generated rapidly and soon decreased, which peaks at time -5. It could suggest that the fructose was an intermediate product. And then, as fructose decreased, dihydroxyactone (DHA) increased rapidly and then decreased gradually, which could also suggest an intermediate product property obviously. Finally, glucose as a reactant, fructose and DHA as intermediate products, converted into 1,2-PG with the yield of 53.8%. Thus, the possible pathway of glucose into 1,2-PG was proposed in Scheme 1 (Route 4). The previous studies could also agree with this route that 1,2-PG could generated by isomerization of glucose into fructose, RAC of fructose into DHA and PLA, and subsequent acetol hydrogenation[2]. In addition, as shown in Figure 3(b), the time course of Pt/SiO$_2$ suggested that the 1,2-PG route was consistent with Pt/SiO$_2$@Mg(OH)$_2$, although the route efficiency (1,2-PG yield) was different. In terms of by-products, hexitol as the direct hydrogenation product of glucose or fructose could be converted into final by-products in the reaction systems. In the absence of Mg(OH)$_2$ (Figure 3 (b)), hexitol generated rapidly at time -15 to 0 and then decreased. With the decrease of hexitol, by-product 1,2-HDO generated with the yield higher than 15%, which indicated that hextiol converted into 1,2-HDO by dehydroxylation under the catalysis of Pt/SiO$_2$. In contrast, as Figure 3(a) shown, under the catalysis of Pt/SiO$_2$@Mg(OH)$_2$, hexitol increased slowly and then with its decrease after time 120, the yield of 1, 2-HDO did not increase but the yield of 1,2-PG continuously increased to 53.8%. This time course result could verify the discussion on the significant effect of Mg(OH)$_2$ on 1,2-HDO and 1,2-PG distribution in Figure 2. Thus, we proposed the the Route 2 and Route 3 in Scheme 1.

Based on above proposed reaction pathway, the effect of Mg(OH)$_2$ will be discussed here. One aspect of the Mg(OH)$_2$ effect was that Pt/SiO$_2$@Mg(OH)$_2$ could make the route of hexitol into 1,2-PG (Route 3) become more dominant than the dehydroxylation of hexitol into 1,2-HDO (Route 2). And it was observed in the above mentioned results (products distribution (Figure 2) and time course (Figure 3)). To further demonstrated the effect of Mg(OH)$_2$ on hextiol conversion, the sorbitol and mannitol as reactants were employed into the reaction. As shown in Table S3, entries 5 to 8, the mannitol and sorbitol could not convert to 1,2-PG but gained a 88.9% and 88.3% 1,2-HDO selectivity over Pt/SiO$_2$ without Mg(OH)$_2$. While over
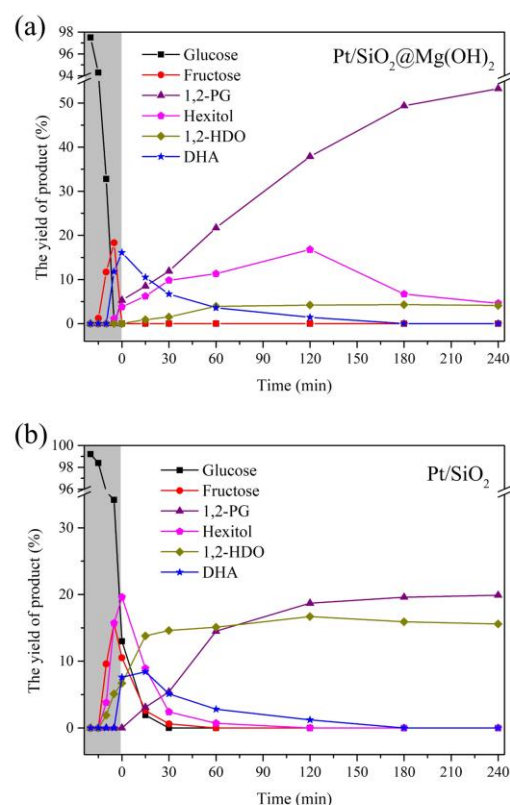

Figure 3. The time course of glucose hydrogenolysis over (a) Pt/SiO$_2$@Mg(OH)$_2$ and (b) Pt/SiO$_2$ catalysts. Reaction condition: catalyst (200 mg), glucose (11.25 mg/ml, 10 ml) and H$_2$ (initial 6 MPa) at 180 °C. 1,2-HDO = 1,2-hexanediol; 1,2-BDO = 1,2-butanediol; 1,2-PG = 1,2-propylene glycol; DHA = dihydroxyactone.

Pt/SiO$_2$@Mg(OH)$_2$, the selectivity of 1,2-PG increased from 0% to 66.4% and 62.9%, respectively. The re-conversion of hexitol might be realized through the promotion of hexitol dehydrogenation into sugar and the repeat of Route 4 into 1,2-PG by Pt/SiO$_2$@Mg(OH)$_2$[5c, 17]. Based on previous studies[5d, 17-18], the reaction temperature of sugar alcohols dehydrogenation and consequent reactions could occur usually above 200 °C, while in this work, it could be achieved at 180 °C over

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Pt/SiO$_2$@Mg(OH)$_2$ catalyst. The lower temperature make it possible to combine Route 3 with Route 4 to together promoted the 1,2-PG generation. However, the contribution of hexitol by-product could not make a so different 1,2-PG yield between Pt/SiO$_2$ (19.9%) and Pt/SiO$_2$@Mg(OH)$_2$ (53.8%). Thus, the other aspect of Mg(OH)$_2$ effect on Route 4 was investigated. The reactions of the possible intermediates over Pt/SiO$_2$@Mg(OH)$_2$ and Pt/SiO$_2$ catalysts were performed and the results were showed in Table S3. As listed in entries 1 and 3, fructose was catalyzed into 1,2-PG with a yield of 43.7% over Pt/SiO$_2$, while glucose could only achieve 19.9% yield of 1,2-PG because of the isomerization barrier between glucose and fructose. While, Pt/SiO$_2$@Mg(OH)$_2$ (entries 2 and 4) broke through the isomerization barrier, leading to the efficient conversion of glucose into 1,2-PG. By synthesizing these data, the pseudo-yield[19] of isomerization reaction over Pt/SiO$_2$ and Pt/SiO$_2$@Mg(OH)$_2$ were 45.5 and 95.7%, respectively, which indicated the promotion effect of Mg(OH)$_2$ on isomerization of glucose into fructose (R1, Scheme 1). In previous studies, a similar effect of Mg/NaY[20] on glucose isomerization in a single glucose-fructose reaction system could support the effect of Mg species. Moreover, the pseudo-yield of RAC reaction was increased to 98.4% over Pt/SiO$_2$@Mg(OH)$_2$ from 50.9%, which could be obtained by calculating the data in Entries 3, 4, 11 and 12. The increased pseudo-yield of RAC was higher than that in existing literature[4a, 6a, 10, 21] (e.g., 90% over InCl$_3$ and 49% over SnCl$_2$[19]). Hence, the promotion of R1 and R2 in Route 4 (Scheme 1) were simultaneously achieved by Pt/SiO$_2$@Mg(OH)$_2$. In conclusion, the effect of Mg(OH)$_2$ on 1,2-PG generation could be attributed to the three reasons, including the promotion of isomerization and RAC, as well as the re-conversion of by-product hexitol.

Besides the reaction performance of Pt/SiO$_2$@Mg(OH)$_2$, catalytic stability in recycling is also an important property for the practical application of catalysts. Therefore, the reusability of Pt/SiO$_2$@Mg(OH)$_2$ and Mg-Pt/SiO$_2$ synthesized by three traditional methods were investigated. As Figure 4 shown, the yield of 1,2-PG obtained by Pt/SiO$_2$@Mg(OH)$_2$ slightly decreased from 53.8% to 49.8% and 44.5% by the second and third runs, respectively. It showed more stable performance than other catalysts. It could be attributed to slighter metal leaching, which was verified by Figure 4 (right y). The Pt loading in Pt/SiO$_2$@Mg(OH)$_2$ decreased from 5.12 to 4.65 and then to 4.45 wt% and the Mg(OH)$_2$ loading was decreased from 5.03 to 4.78 and then to 4.45 during three times of reuse. In contrast, Pt/SiO$_2$ showed a more significant Pt leaching. The difference indicated the Mg(OH)$_2$ shell might suppress the leaching of Pt on SiO$_2$ and rendered them stable under the reaction conditions. A similar effect of solid base on catalytic stability was also reported by Sun, et al.[5b] in Ni/C combined with Ca(OH)$_2$ system. Compared to a series of Mg-Pt/SiO$_2$ catalysts with different structures, the stability of Pt/SiO$_2$@Mg(OH)$_2$ might be attributed to the core-shell structure, where Mg(OH)$_2$ shell prevented the Pt particles from leaching into the reaction media. However, Mg-Pt/SiO$_2$ (PtF) prepared by impregnation method showed poor yields although the Pt could be prevented from leaching by Mg species, reasoning from the coverage of Pt active sites by Mg species. While the core-shell structure of Pt/SiO$_2$@Mg(OH)$_2$ did not cover the Pt active sites when protected the Pt particles. Thus, Pt/SiO$_2$@Mg(OH)$_2$ prepared by *in situ* hydrothermal process showed both excellent yield and stability.
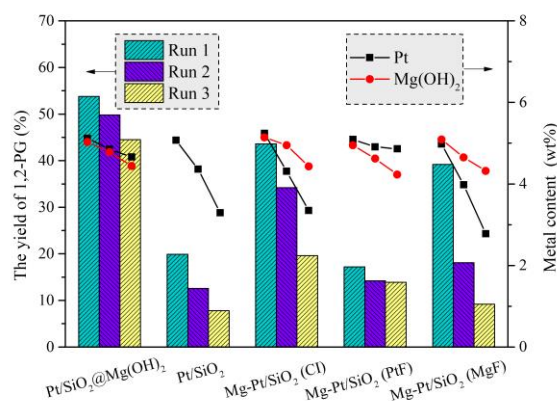

Figure 4. Reusability and metal leaching of catalysts synthesized by different methods. Reaction condition: catalyst (200 mg), glucose (11.25 mg/ml, 10 ml) and H$_2$ (initial 6 MPa) at 180 °C for 4 h.

In summary, we demonstrate a feasible strategy of magnesium hydroxide assembly onto Pt/SiO$_2$ to achieve a three-pronged promotion of 1,2-PG production, including enhancement of isomerization of glucose into fructose and RAC of fructose, as well as re-conversion of by-product hexitol into 1,2-PG. The Pt/SiO$_2$@Mg(OH)$_2$ possessed a core-shell structure by *in situ* hydrothermal process and showed both excellent performance and stability. This work could help facilitate studies on development of high-valued chemicals from biomass derivatives over base modified catalysts.

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6

COMMUNICATION

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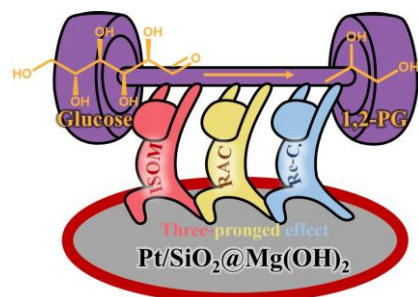
Three-pronged effect: Glucose can be converted into 1,2-PG with a yield of 53.8% via Pt/SiO$_2$@Mg(OH)$_2$ core-shell catalyst, which attributed to three aspects of promotion: isomerization, RAC and re-conversion of hexitol. Moreover, the core-shell structure synthesized by in situ hydrothermal process can protect Pt from leaching, leading to stable reuse performance during reuse.