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Hydrogenolysis of glycerol over Pt/C catalyst in combination with alkali metal hydroxides

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Abstract: The hydrogenolysis of glycerol was performed over a Pt/C catalyst in combination with several alkali metal hydroxides and their salts. LiOH was found to be an effective promoter for the selective hydrogenolysis of glycerol to 1,2-propanediol. Hydroxyl ions are the main factor to promote the reaction process by dehydration of the glyceraldehyde intermediate. Lithium ions play a role in assisting the dehydrogenation of glycerol to glyceraldehyde, because they have the right size to coordinate with the alkoxide species. A possible surface reaction mechanism involving the participation of lithium ions was proposed to account for the results obtained in the study.

Keywords: Glycerol, hydrogenolysis, platinum, 1,2-propanediol, lithium cation

1 Introduction

The production of commodity chemicals from biomass-derived molecules is a promising and sustainable alternative to the current industrial practice. In particular, glycerol has been identified by the U.S. Department of Energy as one of the top-12 platform molecules that can be obtained from biomass [1]. Traditionally, glycerol is produced as a byproduct in the process of soap manufacture or fatty acid production. In recent years, owing to the rapid development of the biodiesel industry, large amounts of glycerol are available as a low-cost byproduct. As a consequence, the conversion of glycerol to other high value-added products has drawn widespread attention [2]. One attractive route for the utilization of glycerol involves catalytic hydrogenolysis to 1,2-propanediol (1,2-PDO) and 1,3-propanediol [3-5]. Both of the diol products are important chemicals for the production of polyesters, resins and polyurethanes, but the current production methods of the two propanediols are based on petrochemical feedstocks. Therefore, the hydrogenolysis of biomass-derived glycerol to propanediols is a promising green method. Considering the possibility of industrialization in the near future, the hydrogenolysis of glycerol to 1,2-PDO has much potential and practical use [6].

The hydrogenolysis of glycerol has been investigated over various heterogeneous catalysts [3-5]. Among the catalysts studied, Pt-based catalysts have been found to be relatively efficient for the production of propanediols due to their high selectivity for the cleavage of C–O bond [5,7]. To further improve the catalytic performance, Pt catalysts are usually used in the presence of some additives [7,8]. For example, tungsten containing compounds such as WO_3, H_2WO_4, and $H_4SiW_{12}O_{40}$ were reported as effective additives for the promotion of 1,3-propanediol selectivity over Pt-based catalysts [8-12]. Furthermore, the addition of a certain base like NaOH or CaO to the Pt catalytic system was found to be an efficient method to increase the reactivity and 1,2-PDO selectivity [13-16]. Maris et al. [13,14] reported that the addition of NaOH enhanced the reactivity of Pt to a greater extent. In fact, not only the catalytic performance of Pt, but also that of Cu [17,18], Ru [19-22], and Ni [18] can be improved by basic additives in the glycerol hydrogenolysis reaction. In our previous works [19-21], we have revealed that alkali metal hydroxides are suitable additives for the hydrogenolysis of glycerol to 1,2-PDO over Ru catalysts. As shown in Scheme 1, under basic conditions, the hydrogenolysis reaction firstly occurs via a reversible dehydrogenation of glycerol to glyceraldehyde on the metal sites (step 1). Then, glyceraldehyde undergoes base-catalyzed dehydration to 2-hydroxyacrolein (step 2), which is finally hydrogenated to 1,2-PDO (step 3). The hydroxyl ion (OH^-) can promote the dehydration of glyceraldehyde, thereby increasing the glycerol conversion and 1,2-PDO selectivity. This inspired us to develop a catalytic system for Pt catalysts in combination with basic promoters.

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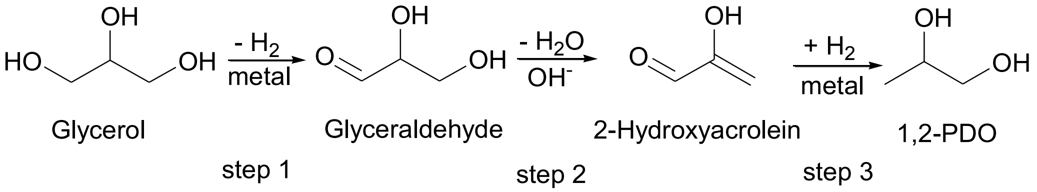


Scheme 1: Hydrogenolysis of glycerol to 1,2-PDO under basic conditions.

Although the importance of basic promoters to the catalytic performance of Pt has been demonstrated in some works, little research has focused on the effect of the base type, and very limited details are known about the role of the metal cation in the reaction process. Therefore, in this study, the hydrogenolysis of glycerol was performed over a Pt/C catalyst in combination with several inorganic bases, with the aim of selecting a good basic promoter for the Pt catalytic system. The role of the alkali metal cation and OH^- in the reaction process was discussed with a proposed surface reaction mechanism.

2 Experimental Procedure

The active carbon-supported Pt catalyst with a metal loading of 5 wt% was obtained from the Institute of Homogenous Catalysis, Sichuan University. The catalyst was prepared by an impregnation technique. Weighed amounts of the active carbon were impregnated with the aqueous solution of chloroplatinic acid hexahydrate (Aladdin). The slurry was stirred overnight at room temperature. Then, the solvent was removed under reduced pressure. Subsequently, the resulting powder was reduced in an autoclave with a hydrogen atmosphere (3 MPa) in ethylene glycol at 200 °C. The reduced catalysts were washed repeatedly with deionized water and acetone, and then dried at 60 °C in vacuum for 4 h prior to the reaction. Glycerol, alkali metal hydroxides and their salts, and other reagents were commercially obtained as AR samples and used as received.

The BET surface area of Pt/C was measured on an auto adsorption/desorption analyzer (ZXF-6, Northwest Chemical Industry) using nitrogen as the adsorbate. Powder X-ray diffraction (XRD) measurements were performed on an X'Pert Pro MPD diffractometer (Philips) equipped with a Cu Kα radiation source (40 kV, 25 mA, λ = 0.15406 nm). About 50 mg of catalyst samples were pressed in the sample holder. The XRD patterns were obtained with a scan rate of 2s/step and a step size of 0.05° (2θ). Transmission electron microscopy (TEM) images were obtained by JEM-1200EX at 100 kV. Scanning transmission electron microscopy (STEM), high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray (EDX) measurements were recorded on a JEOL-2100F electron microscope operated at 200 kV. The sample was ultrasonically suspended in ethanol and deposited on a Cu grid recovered with a thin layer of carbon.

Hydrogenolysis of glycerol was performed in a 20 mL stainless steel autoclave equipped with a magnetic stirrer and an electric temperature controller. The Pt/C catalyst was pre-reduced in the same autoclave. The catalyst, alkali metal hydroxides or salts, and glycerol aqueous solution were charged into the autoclave in desired amounts. The reactor was sealed and purged repeatedly with hydrogen to eliminate air, pressurized to the necessary hydrogen pressure, and then heated to the desired temperature. The detailed reaction conditions are described in Table 1. After the reaction, the products in the liquid phase were analyzed by GC (Agilent 6890N, Agilent Technologies) equipped with a flame ionization detector and a capillary column (Supelco WAXTM, 30 m × 0.53 mm × 1 μm). The gas products were qualitatively checked by GC (9790, Shanghai HaiXin) equipped with a molecular sieve packed column and a thermal conductivity detector.

The conversion of glycerol and the selectivity in liquid products were calculated on a carbon basis according to the following equations:

- Conversion of glycerol (%) = (moles of glycerol consumed/moles of glycerol initially charged) × 100.
- Selectivity (%) = (moles of carbon in specific product/moles of carbon in all detected products) × 100.
- For details, refer to the method described in previous works [23,24].

3 Results and Discussion

The BET surface area of the Pt/C catalyst was determined to be 341 m^2/g. The XRD pattern of Pt/C is given in Figure 1. The major phase presented in the diffractogram is amorphous carbon, with a broad diffraction peak at 2θ = 24.5° [16]. The sharp peak at 2θ = 26.4° indicates that

Table 1: Catalytic performance of Pt/C in the presence of alkali metal hydroxides and salts.[a]

Entry	Base or salt	Conversion (%)	Selectivity (%)[b]				
			1,2-PDO	EG	PO	EO	MO
1	–	11.5	78.8	12.3	5.5	1.5	0.8
2	LiOH	42.8	90.2	4.2	3.6	0.9	0.4
3	NaOH	36.4	87.7	5.5	3.8	1.2	0.3
4	KOH	33.4	86.9	5.3	4.3	1.8	1.0
5	LiOH[c]	<1.0	Trace	–	–	–	–
6	LiOH[d]	53.9	57.7	3.8	7.1	2.5	1.4
7	Li_2CO_3	18.5	88.2	5.1	3.2	1.3	1.6
8	LiCl	7.8	77.1	9.4	8.9	0.7	0.4
9	KOH + LiOH[e]	42.3	87.1	3.9	5.0	1.2	0.9

[a] Reaction conditions: 180 °C, 3 MPa, 12 h, 5 mL 20 wt% glycerol aqueous solution, 195 mg Pt/C, 1mmol base or salt.

[b] 1,2-PDO: 1,2-Propanediol; EG: ethylene glycol; PO: 1-propanol and 2-propanol; EO: ethanol; MO: methanol.

[c] Without Pt/C.

[d] 3 mmol LiOH.

[e] 0.5mmol KOH and 0.5mmol LiOH.

a small amount of graphite (JCPDS Card #41-1487) coexists in the active carbon support. This probably accounts for the relatively low surface area of the Pt/C catalyst. No obvious diffraction peaks can be assigned to Pt crystalline phase (2θ = 39.8°, 46.2° and 67.5°; JCPDS Card #04-0802), suggesting that Pt is well dispersed as small particles on the active carbon.

A representative TEM image of the Pt/C catalyst is shown in Figure 2. As it can be seen in the micrograph, the dispersion of Pt nanoparticles is fairly good, which is in accordance with the XRD result. The average particle size of Pt is around 4.5 nm. The bright field STEM image of the Pt/C catalyst is shown in Figure 3a. To further confirm that those dark spots in the STEM are Pt nanoparticles, we used EDX analysis to measure the elemental distribution of a selected area with (area 1 in Figure 3a) and without (area 2 in Figure 3a) a dark spot. The EDX spectrum of area 1 (Figure 3b) shows obvious Pt signals at 2.1 keV, 9.4 keV and 11.2 keV, whereas no obvious Pt signal can be observed in area 2 (Figure 3c). This indicates that the dark spots in the STEM are mainly Pt nanoparticles. The unmarked peaks in the EDX spectra are attributed to the background Cu signals resulting from the grid used to hold the sample. Figure 4 shows a HRTEM image of the Pt nanoparticles and the corresponding intensity profile. As presented in Figure 4a, the Pt nanoparticles exhibit good crystallinity. According to the intensity profile in Figure 4b, the interplanar distance is 0.19 nm, corresponding to the (200) planes of platinum.

According to the reaction pathway shown in Scheme 1, we envisaged using some basic additives to improve the catalytic performance of Pt/C. Alkali metal hydroxides were used as promoters because they are inexpensive and easily available. As presented in Table 1 (Entries 1 to 4), the addition of alkali metal hydroxides significantly increased the conversion of glycerol and the selectivity to 1,2-PDO. The highest conversion of glycerol and the highest selectivity to 1,2-PDO were obtained in the presence of LiOH. As far as the production of 1,2-PDO is concerned, Pt/C is far superior to Ru catalysts under similar reaction conditions [20]. Moreover, the selectivity to ethylene glycol (a main undesired degradation product) decreased no matter which basic additive was added. This is because

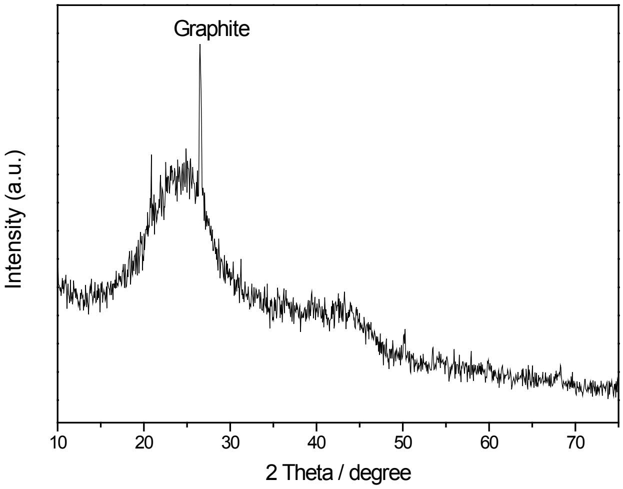


Figure 1: XRD pattern of the Pt/C catalyst.

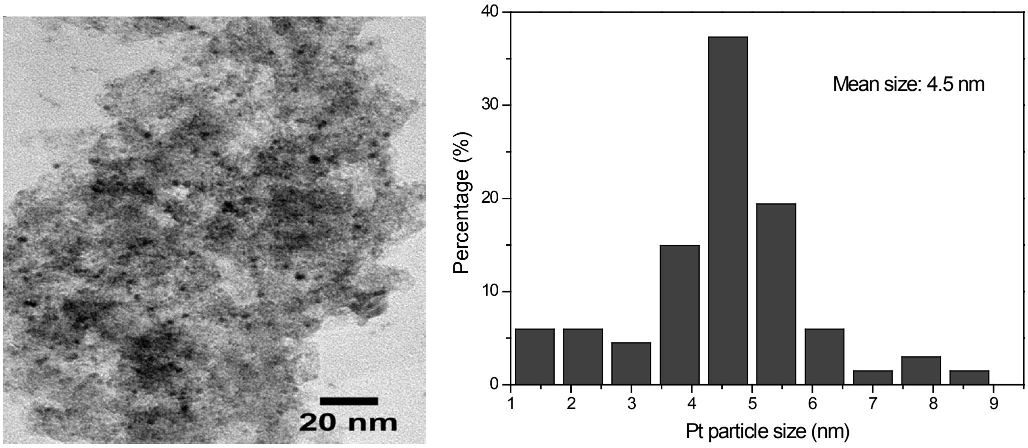


Figure 2: TEM image and particle size distribution of the Pt/C catalyst.

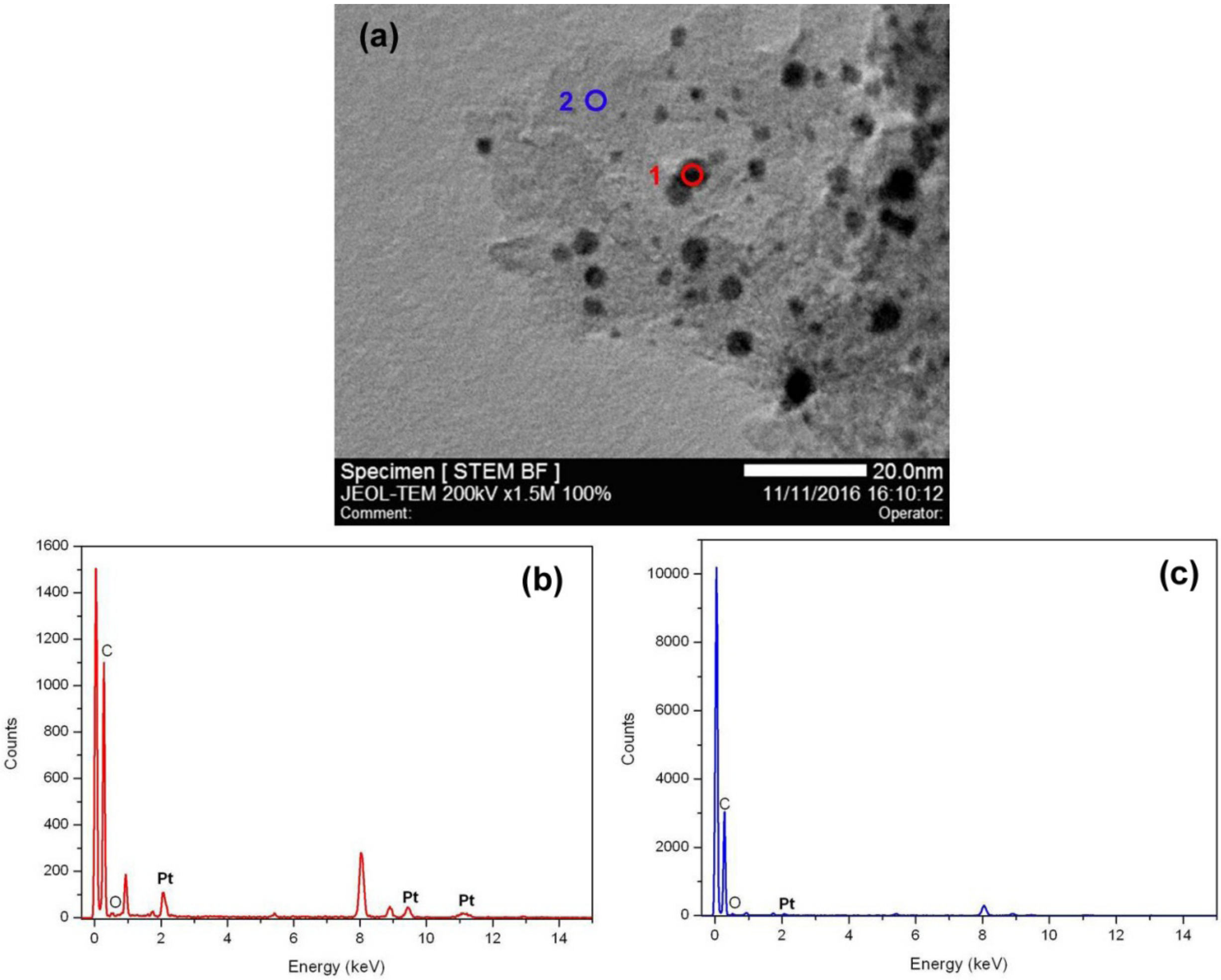


Figure 3: (a) Bright field STEM image of the Pt/C catalyst; (b) Corresponding EDX elemental analysis from area 1 (red circle) in the STEM image; (c) Corresponding EDX elemental analysis from area 2 (blue circle) in the STEM image.

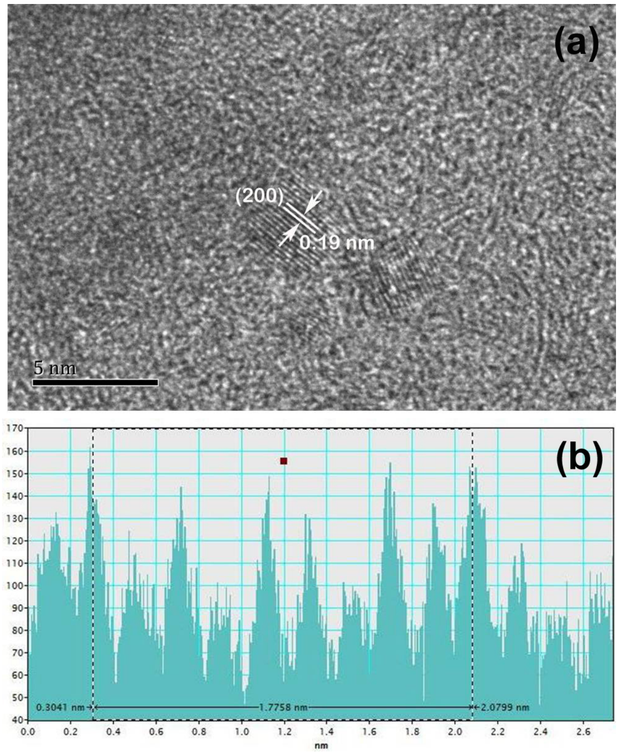


Figure 4: (a) HRTEM image of Pt nanoparticles; (b) Intensity profile created by Digital Micrograph on the marked Pt nanoparticle in the HRTEM image.

OH^- in the aqueous solution can suppress the scission of C–C bonds [5,25]. A blank reaction was performed with LiOH in the absence of a Pt/C catalyst (Entry 5, Table 1); however, almost no reaction occurred. Similar phenomena was observed in the blank reactions of NaOH and KOH, indicating that basic additives are unable to catalyze the hydrogenolysis of glycerol independently, and the metal catalyst is necessary for the reaction. In fact, the metal sites serve both as dehydrogenating and hydrogenating functions in the overall reaction process (step 1 and step 3 in Scheme 1).

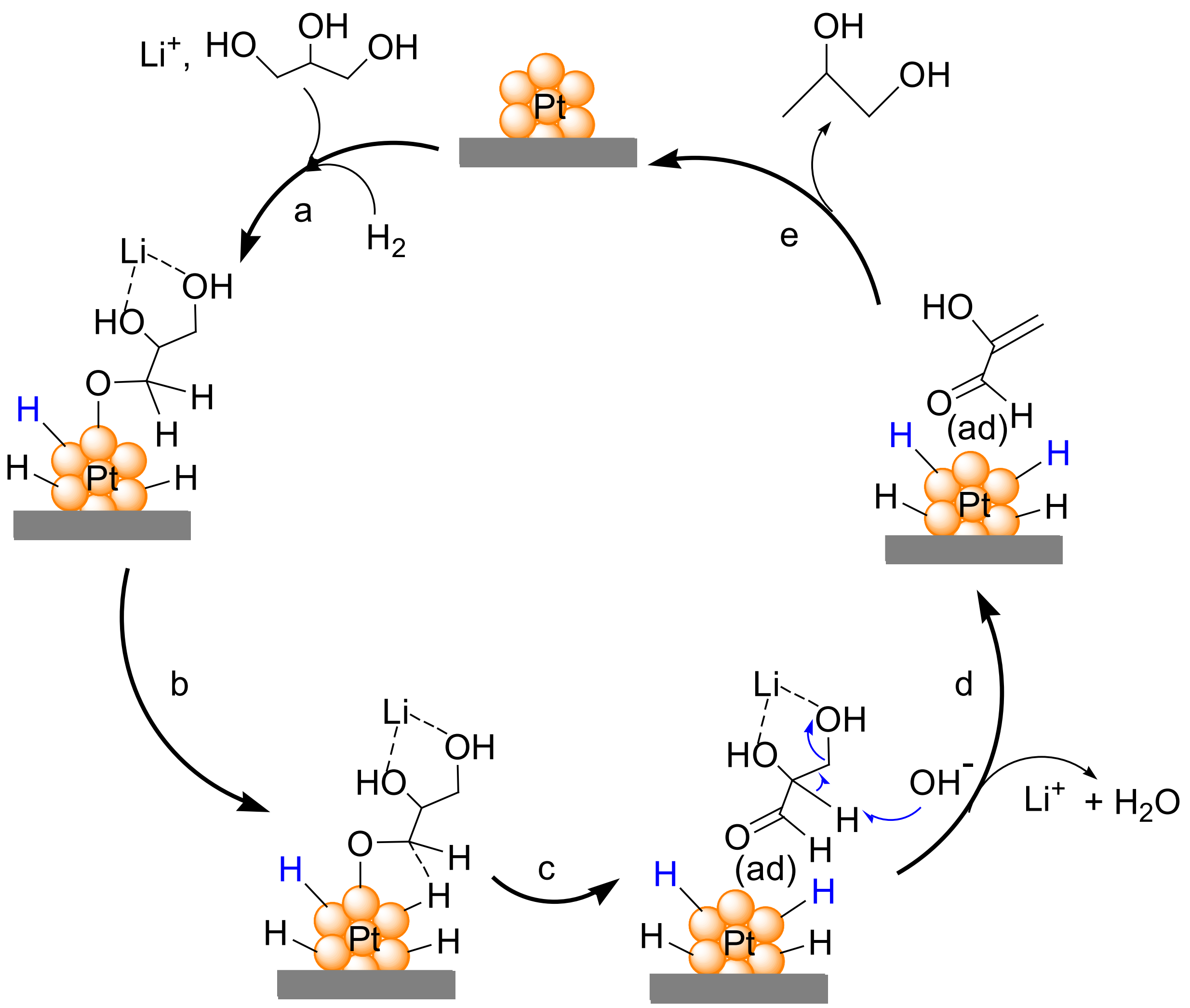
It should be pointed out that the dosage of alkali metal hydroxides can influence the product selectivity. We have studied the effect of the amount of base on the catalytic performance of Ru/TiO_2, and have found that an excess of LiOH will reduce the formation of 1,2-PDO [19]. In this work, experiments with an excess of LiOH, NaOH or KOH were also tested for promotion of the Pt/C catalyst 2. The selectivity of 1,2-PDO significantly decreased when the amount of the base exceeded 3 mmol (Entry 6, Table 1). The work of Maris et al. [13] shows that lactic acid is formed at higher pH. Actually, lactic acid can be produced by a Cannizzaro reaction from the 2-hydroxyacrolein intermediate [22,26]. In addition, there is scarcely any 1,3-propanediol in the liquid products, because the elimination of the secondary hydroxyl group in the glyceraldehyde molecule is very difficult under basic conditions [19]. In order to avoid the formation of undesired side products, optimized reaction conditions were used, as given in Table 1. Using LiOH as a basic promoter for Pt/C, the 1,2-PDO selectivity can be comparable to Cu catalysts [4], whereas the reaction conditions are much milder.

Comparison of Entries 2, 3 and 4 in Table 1 shows that different basic promoters have different effects on the catalytic activity. The alkali metal hydroxides influenced the Pt/C activity in the order of LiOH > NaOH > KOH. Because all of the three bases are strong bases and can fully dissociate in the water solvent, this behavior is not attributed to the concentration of OH^-. A previous study has reported that the metal cation may have a role in the complexation of the hydroxyl group in the reaction of glycerose with alkali [27]. Therefore, the different effect on the catalytic activity is more likely to be associated with the size of the metal cation.

On the basis of the above experimental results and discussions, we believe that lithium ions (Li^+) have the right size to take part in the glycerol hydrogenolysis reaction in basic aqueous solution. The verifying experiments were carried out in which some lithium salts or mixed alkali metal hydroxides were added to the catalytic system. As listed in Entry 7 of Table 1, Li_2CO_3 can also promote the hydrogenolysis of glycerol to 1,2-PDO in high selectivity, but the reaction activity only slightly increased. This result may not be very informative since the solubility of Li_2CO_3 in water is low. It may not completely dissolve in the aqueous solution. More valuable information can be obtained from the addition of LiOH mixed with KOH (Entry 9, Table 1). The concentration of OH^- in this mixed system is the same as that of the neat KOH system (Entry 4, Table 1), but the catalytic activity was much higher, and can even be comparable to that of the neat LiOH system (Entry 2, Table 1). When LiCl was added (Entry 8, Table 1), the reaction occurred more slowly, which maybe due to the poisonous effect of the chloride ion. This experiment also suggests that, without enough OH^-, Li^+ cannot obviously promote the glycerol hydrogenolysis reaction (Entries 7 and 8, Table 1).

Taken together, we can reasonably conclude that: (1) OH^- is the main factor to promote the dehydration of glyceraldehyde; (2) Li^+ can aid the hydrogenolysis reaction, but it needs the presence of adequate OH^-. These conclusions can be explained as follows according to the reaction mechanism shown in Scheme 2.

Although some previous studies have proposed reaction pathways for the hydrogenolysis of glycerol to 1,2-PDO, few works have concerned the possible surface



Scheme 2: A possible mechanism for hydrogenolysis of glycerol to 1,2-PDO over Pt/C in the presence of LiOH. Steps a-c: dehydrogenation of glycerol to glyceraldehyde; step d: dehydration of glyceraldehyde to 2-hydroxyacrolein; step e: hydrogenation of 2-hydroxyacrolein to 1,2-PDO.

reactions. The mechanism illustrated in Scheme 1 cannot show the detailed heterogeneous reaction process. Based on the results and discussions above, it is proposed that Li^+ is involved in the dehydrogenation of glycerol to glyceraldehyde (steps a–c in Scheme 2). Initially, the dissociative adsorption of glycerol on the surface of Pt nanocluster forms alkoxide and hydride species. Simultaneously, Li^+ interacts with the two hydroxyl groups of alkoxide, thereby stabilizing the reactive alkoxide species. Hydrogen is also dissociated and adsorbed on the Pt surface. Then, the α-H of an alkoxide undergoes hydride abstraction to yield a hydride species and adsorbed glyceraldehyde on Pt. Successively, OH^- attacks the hydrogen at the middle carbon atom of glyceraldehyde, which makes the primary hydroxyl group readily removed by dehydration to form 2-hydroxyacrolein (step d in Scheme 2). Water and free Li^+ are also formed in this step. Finally, hydrogenation of 2-hydroxyacrolein gives 1,2-PDO (step e in Scheme 2). It is worth mentioning that the step d must be much faster than the dehydrogenation of glycerol, so that the reversible dehydrogenation-hydrogenation equilibrium between glycerol and glyceraldehyde can proceed forward [3-5]. Otherwise, glyceraldehyde will be hydrogenated back to glycerol over the metal sites. In addition, although the hydride species can be generated from the glycerol (H in blue in Scheme 2), external hydrogen gas is necessary to ensure that the hydrogenation of 2-hydroxyacrolein works smoothly.

Our proposed reaction mechanism can reasonably explain the results in this study, and it may give some valuable insights for further investigation. However, we should point out that the mechanism depicted in

Scheme 2 is not very specific. Although the coordination interaction between Li^+ and oxygenated compounds has been observed in the hydrogenation of glycerose [27] and ketones [28], the exact path for this interaction is not clear and needs further study. Further work is under progress to gain some direct evidence for the surface reaction process.

4 Conclusions

Alkali metal hydroxides are good promoters for the hydrogenolysis of glycerol to 1,2-PDO over Pt/C catalyst. LiOH exhibited the best promotion effect in terms of glycerol conversion and 1,2-PDO selectivity. Li^+ plays a role in assisting the glycerol hydrogenolysis reaction when adequate OH^- is present. A coordination interaction between Li^+ and the alkoxide species probably exists in the process of dehydrogenation of glycerol to glyceraldehyde.

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