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Pt/Solid-Base: A Predominant Catalyst for Glycerol Hydrogenolysis in a Base-Free Aqueous Solution

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Abstract A series of HBeta, HZSM-5, Al_2O_3, MgO and hydrotalcite precursor supported Pt catalysts were prepared and used for glycerol hydrogenolysis to 1,2-propanediol (1,2-TPD) in a base-free aqueous solution. XRD, TEM, CO_2-TPD and H_2-TPD characterizations concluded that the activity for glycerol hydrogenolysis of the tested catalysts depends mainly on their alkalinity and particle size of Pt. A hydrotalcite precursor supported Pt catalyst with strong alkalinity and highly dispersed Pt particles exhibited the predominant performance for the desired reaction (with a 93.0% selectivity of 1,2-PDO at a conversion of 92.1%) in a base-free aqueous solution at lower pressure, and can be recycled simply by filtration.

Keywords Glycerol · Hydrogenolysis · 1,2-Propanediol · Solid base

1 Introduction

1,2-Propanediol (1,2-PDO) is an important chemical as biodegradable functional fluid such as antifreeze, aircraft deicer and lubricant, and as precursor in the synthesis of unsaturated polyester resins and pharmaceuticals [1–3]. Currently, 1,2-PDO is produced from petroleum-derived propylene via selective oxidation to propylene oxide and subsequent hydrolysis [1, 2]. This process is restricted due to the dwindling of the petroleum resource.

Recently, a major surplus of glycerol has resulted from increasing expansion of biodiesel production, and currently disposal of surplus glycerol is by incineration. Searching value-added routes of glycerol conversion would assist with environmental benefits and economic viability of biodiesel manufacture. The catalytic hydrogenolysis of glycerol to 1,2-PDO has attracted much attention in the recent years [2–15] and well summarized in recent published works [16–19]. In published papers, the hydrogenolysis of glycerol to 1,2-PDO is suggested to proceed via either dehydration of glycerol to acetol over acid catalyst followed by catalytic hydrogenation on metal catalyst [2–9] or dehydrogenation of glycerol to glyceraldehydes in alkaline solution followed by dehydration to 2-hydroxyacrolein and hydrogenation [10–14]. According to mechanism of the first possible routine, Chaminand et al. found that a combined Rh/C and H_2WO_4 is effective for the hydrogenolysis of glycerol to 1,2-PDO at a low conversion level [2]. Tomishige and co-workers reported that hybrid Ru/C (or Rh/SiO_2) + Amberlyst catalysts exhibit good performance in the hydrogenolysis of glycerol [4–7]. Recently, Kozhevnikov et al. found a ruthenium-doped (5 wt%) acidic heteropoly salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is an active bifunctional catalyst for the one-pot hydrogenolysis of glycerol to 1,2-PDO (with a 96% selectivity at 21% glycerol conversion) [8].

Cu-ZnO catalyst was also reported for glycerol hydrogenolysis to 1,2-PDO, while its activity is lower and the reaction might be carried out at higher H_2 pressure and longer time [2, 9, 15]. And it was suggested that addition of NaOH is favorable for increasing the formation of 1,2-PDO. Maris and Davis reported that addition of base (NaOH) enhanced the reactivity of Pt to a greater extent, but the

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added base would catalyze the cleavage of C–C bonds leading to the formation of ethylene glycol (E.G.) and the formation of lactate was significant at high PH [10, 11].

Raney Ni, Pt/C, Pd/C, Ru/C and Ni/C were also reported for the hydrogenolysis of glycerol to 1,2-PDO, but their activity and the selectivity of 1,2-PDO are lower [2, 15].

In the bio-diesel based glycerol, most of unreacted catalysts for bio-diesel production (such as NaOH or other alkali metal hydroxides) and soaps (base-neutralized fatty acids) are preferentially distributed into the glycerol phase. And these contaminants typically act as catalyst poisons (to solid acid and supported metal), causing deactivation [18–20]. Due to influence of these impurities, the hybrid metal + NaOH is a promising candidate than the hybrid metal + acid and solid acid supported metal catalyst for the potential application. However, main drawbacks of NaOH addition are the cleavage of C–C bond, the formation of lactate, the reaction mixture needs further neutralization and environmental pollution.

To the best of our knowledge, few studies focus on the application of solid base supported metal catalyst in the hydrogenolysis of glycerol. In this communication, we want to report an efficient solid-base supported Pt catalyst for glycerol hydrogenolysis to 1,2-PDO. A hydrotalcite precursor supported Pt catalysts (Pt/HLT) exhibited the predominant activity and selectivity among the test catalysts (Pt/HBeta, Pt/HZSM-5, Pt/C, Pt/Al_2O_3, Pt/MgO and Pt/HLT) in a base-free aqueous solution under lower pressure and can be recycled simply by filtration.

2 Experimental

2.1 Catalyst Preparation and Characterizations

Hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), MgO, H-ZSM-5 ($SiO_2/Al_2O_3 = 50$), H-Beta ($SiO_2/Al_2O_3 = 50$), tetraammineplatinum (II) chloride hydrate ($PtCl_2\ (NH_3)_4{\cdot}H_2O$) and glycerol were purchased from Shanghai Chemical Reagent Co. (China). All supports were firstly pretreated at 400 °C in air for 4 h, impregnated into an aqueous solution of $PtCl_2\ (NH_3)_4{\cdot}H_2O$, dried at 80 °C in vacuum overnight, and calcined at 550 °C for 5 h. The loading amount of Pt was controlled to 2.0 wt% of the support and was confirmed by inductively coupled plasma (ICP). These catalysts were further reduced in H_2 at 250 °C before catalytic reaction. At the same time, a commercial Pt/C (2 wt%) catalyst was purchased from Johnson-Mathey (Shanghai branch, China) and used as a reference sample.

The structure of the supported Pt catalysts was characterized by X-ray diffraction patterns (XRD) and transmission electronic microscopy (TEM). XRD spectra were detected on a RIGAKU D/MAX 2550/PC diffractometer using Cu$K\alpha$ radiation at 40 kV and 100 mA. Diffraction data were recorded using a continuous scanning at a rate of 0.02°/s, and a step of 0.02°. TEM images of the fresh catalyst were obtained using an accelerating voltage of 200 kV (JEOL-2020F).

The alkalinity and H_2 activation activity of these supported catalysts were carried out via temperature-programmed desorption of CO_2 and H_2 (CO_2-TPD and H_2-TPD). Sample was first reduced at 250 °C in H_2 flow of 30 mL min^{-1} for 2 h, and then cooled to room temperature in purified Ar, exposed to 50% CO_2/Ar (or 50% H_2/Ar) for 30 min, purged by Ar for 5 h in order to eliminate the physical adsorbed CO_2 (or H_2). Temperature-programmed desorption was conducted by ramping to 450 °C at 10 °C min^{-1} and CO_2 ($m/e = 44$ or H_2 $m/e = 2$) in effluent was detected and recorded as a function of temperature by a quadrupole mass spectrometer (OmniStarTM, GSD301, Switzerland).

2.2 Catalytic Reactions

The hydrogenolysis of glycerol was carried out in a custom-designed 50-mL stainless steel autoclave equipped with a thermoelectric couple. The reaction mixture contained 20 mL aqueous solution of glycerol (0.2 g-glycerol/mL) and 0.5 g reduced catalyst. The autoclave was purged with H_2, pressurized with H_2 to 3.0 MPa and placed in an oil bath preheated to the required temperature and vigorously stirred with a magnetic stirrer (MAG-NEO, RV-06 M, Japan). The reactant solution was cooled to room temperature after a reaction time of 20 h. The vapor phase was analyzed using a TCD gas chromatograph (Shimadzu, 8A) equipped with an active carbon column. The liquid phase was directly analyzed using an FID gas chromatograph (Shimadzu, 14B) equipped with a 30 m capillary column (DB-WAX 52 CB, USA).

The five successive reactions of recycled Pt/HLT are carried out in the same procedure described above. The initial catalyst weighted in 0.5 g was firstly reduced H_2 at 250 °C and put into 5 mL aqueous solution of glycerol (0.8 g-glycerol/mL). The autoclave was purged with H_2, pressurized with H_2 to 3.0 MPa and placed in an oil bath preheated to the required temperature and vigorously stirred. After each run, the used Pt/HLT catalyst was recovered simply by filtration and dried at room temperature in vacuum for 12 h.

3 Results and Discussion

XRD spectra of the prepared catalysts are shown in Fig. 1. The crystalline size of Pt detected in XRD (calculated via

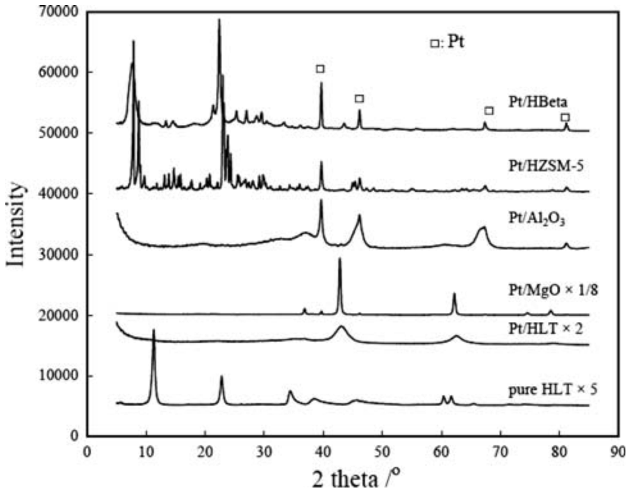


Fig. 1 XRD spectra of supported Pt catalysts

Scherrer–Warren equation on the basis of Pt (111) plane) is summarized in Table 1.

As shown in Fig. 1, the crystalline structure of HBeta and HZSM-5 remains stable in the prepared Pt/HBeta (JCPDS card No.48-0074) and Pt/HZSM-5 (JCPDS card No. 04-0003), which infers that the acidity of the parent zeolite is reserved. While the layered structure of hydrotalcite (JCPDs, card No. 041-1428) collapsed in the prepared Pt/HLT catalyst and MgO is detected. Beside the diffraction peaks of support materials, Pt is detected in Pt/HBeta, Pt/HZSM-5, Pt/Al_2O_3 and Pt/MgO. The calculated particle sizes of Pt in these catalysts are 32.4, 34.1, 21.0 and 49.0 nm, respectively.

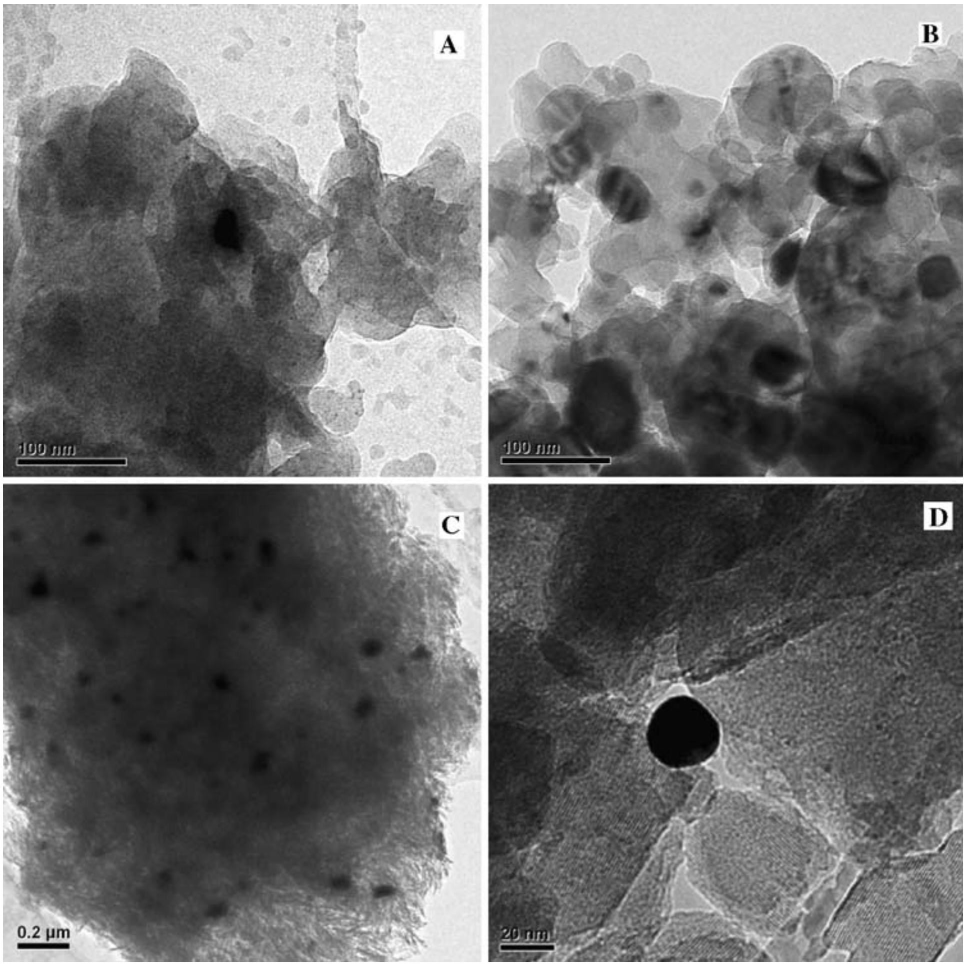
Table 1 The crystalline size of Pt on different supports

Catalyst	Particle size (nm)	
	XRD	TEM
Pt/HLT	ND	12.9
Pt/MgO	49.0	31.1
Pt/Al_2O_3	21.0	27.0
Pt/H-Beta	32.4	20.9
Pt/H-ZSM5	34.1	ND

ND Cannot be detected via XRD or TEM

Figure 2 shows the typical TEM images of Pt/HLT, Pt/MgO, Pt/Al_2O_3 and Pt/H-Beta. The average particles

Fig. 2 TEM images of **a** Pt/HLT, **b** Pt/MgO, **c** Pt/Al2O3 and **d** Pt/H-Beta



size of Pt detected in TEM (summarized in Table 1) was calculated as:

$$d_{\mathrm{TEM}} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where, n_i is the number of particles having a characteristic diameter d_i. It can be found that Pt particles dispersed unevenly in Pt/HLT, Pt/MgO and Pt/H-Beta. Large amount of highly dispersed Pt particles (2–3 nm) were detected in Pt/HLT (Fig. 2a) and Pt/H-Beta (Fig. 2d), while large Pt particles (>20 nm) also appeared in the same image. Mainly bigger sized Pt particles appeared in Pt/MgO (Fig. 2b) and Pt/Al_2O_3 (Fig. 2c), and the calculated average Pt particle size according to above equation are 31.1 and 27.0 nm, respectively. The lower dispersed of Pt in Pt/MgO and Pt/Al_2O_3 would be contributed to the lower surface area of MgO (38.7 m^2/g) and Al_2O_3 (87.3 m^2/g).

Alkalinity of the prepared Pt catalysts detected via CO_2-TPD is shown in Fig. 3. Beside the weakly surface adsorbed CO_2 (with a desorption temperature at 108 °C), two kinds of basic sites are detected in Pt/HLT (with the CO_2 desorption temperature at 184 and 256 °C, respectively). And the total amount of desorbed CO_2 of Pt/HLT is the highest among the prepared catalysts. Only the weakly surface adsorbed CO_2 is detected in Pt/HBeta, Pt/HZSM-5 and Pt/Al_2O_3.

H_2 adsorption and activation on the prepared catalysts was shown in Fig. 4. It can be found that H_2 desorbed easily on the prepared catalyst. Three desorption peaks were detected at 50, 75 and 120 °C. Only one desorption peak (at 50 °C) is detected in Pt/HLT and Pt/MgO. Two desorption peaks at 50 and 75 °C were detected in Pt/Al_2O_3. Beside the desorption peaks at lower temperature, the third desorption peak in Pt/H-Beta and Pt/H-ZSM-5 was detected at 120 and 140 °C, respectively.

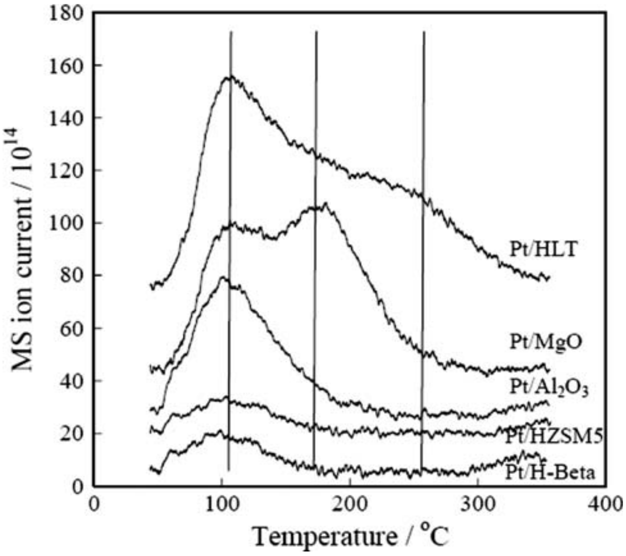


Fig. 3 CO2-TPD of Pt catalyst on different supports

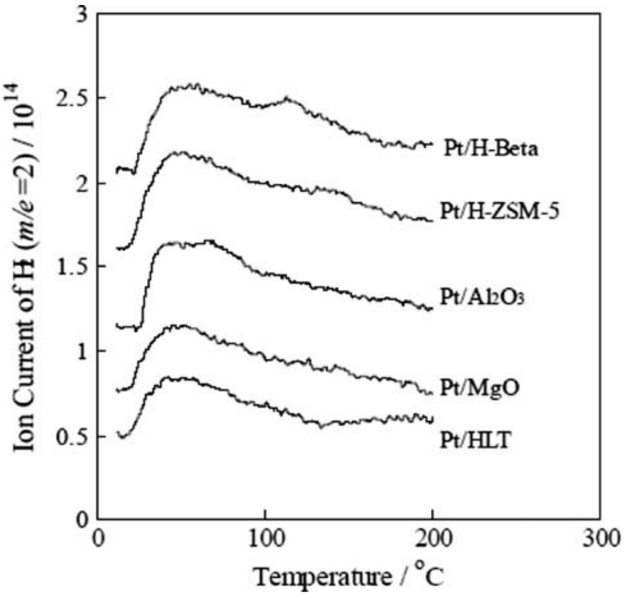


Fig. 4 H2-TPD of Pt catalyst on different supports

Pt/HLT exhibits a predominant activity and selectivity for glycerol hydrogenolysis to 1,2-PDO among the test catalysts (Pt/HBeta, Pt/HZSM-5, Pt/C, Pt/Al_2O_3 and Pt/MgO) in a base-free aqueous solution under lower pressure (3.0 MPa) (Table 2). The detected conversion of glycerol reached 92.1% with a 93.0% selectivity of 1,2-PDO. Pt/MgO also exhibits higher activity for the hydrogenation of glycerol. However, the activity of solid acids supported Pt catalysts is quite low (the detected conversion of glycerol was less than 10%).

These results indicated that the hydrogenolysis of glycerol to 1,2-PDO could be performed over a solid base

Table 2 Hydrogenolysis of glycerol over supported Pt catalysts

Catalyst	Conv (%)	Selectivity (%)				
		1,2-PDO	1,3-PDO	E.G.	PO	Others
MgO	<1	–	–	–	–	–
Hydrotalcite	<1	–	–	–	–	–
Pt/MgO	50.0	81.2	1.6	6.4	5.8	5.0
Pt/HLT	92.1	93.0	0.0	3.9	3.0	0.0
Pt/Al_2O_3	39.0	81.2	1.5	6.3	8.0	3.0
Pt/HZSM-5	4.0	19.5	0.0	0.0	45.5	35.0
Pt/HBeta	7.0	9.5	0.0	5.5	6.0	79.0
Pt/C	1.8	43.6	44.3	0.9	11.0	0.2
Pt/C + NaOH[a]	7.3	81.9	11.1	3.4	3.4	0.2

Reaction conditions: 3.0 MPa H_2, 0.5 g catalyst, 20.0 mL aqueous solution of glycerol (0.2 g-glycerol/mL), 20 h, 220 °C

[a] The initial pH was controlled at 12

Table 3 Recyled Pt/HLT for hydrogenolysis of glycerol

Recycling times	Conv (%)	Selectivity (%)				
		1,2-PDO	1,3-PDO	E.G.	PO	Others
1	98.3	91.7	0.2	3.9	3.8	0.4
2	97.9	91.8	0.4	5.6	1.9	0.3
3	93.5	92.4	0.3	5.5	0.8	1.0
4	85.6	93.4	0.5	5.0	0.5	0.6
5	70.5	94.0	0.4	3.0	2.0	0.6

Reaction conditions: 3.0 MPa H_2, 0.5 g catalyst in the first run, 5.0 mL aqueous solution of glycerol (0.8 g-glycerol/mL), 20 h, 220 °C

supported catalyst. And the detected activity for glycerol hydrogenolysis of the tested catalysts depended mainly on their alkalinity and Pt particles size (see Table 2; Fig. 3). Although the detected Pt particles sizes in Pt/HZSM-5 and Pt/HBeta are smaller than that in Pt/MgO, their activities are very low because of the poor alkalinity. On basic supports, the predominant activity of Pt/HLT than that of Pt/MgO could be contributed partially to its highly dispersed Pt particles (Table 1; Fig. 2). At the same time, H_2-TPD experiment also showed that there is no clear relation between the hydrogen activation ability of these catalysts and the Pt particle size (Fig. 4). These characterizations results could be concluded that the activity of the supported Pt catalysts for glycerol hydrogenolysis to 1,2-PDO in a base-free aqueous solution depends mainly on the alkalinity of the catalysts and the particles size of Pt.

As the reference experiments, neither individual commercial Pt/C catalyst nor MgO or hydrotalcite is active for the hydrogenolysis of glycerol. But the activity of Pt/C was enhanced by the assistance of added base (NaOH), and the conversion of glycerol increased to 7.3% with a 1,2-PDO selectivity of 81.9%. These results are similar with that of reported in literatures [10, 11], which confirmed that catalytic hydrogenolysis of glycerol must be performed by a bifunctional catalyst system. Pt/solid-base is a predominant catalyst for glycerol hydrogenolysis in a base-free aqueous solution.

The results of five successive reactions are summarized in Table 3, where the used Pt/HLT was recovered simply by filtration. The recovered Pt/HLT is found to be active in the repeated runs, although the conversion of glycerol and yield of 1,2-PDO decreased somewhat.

4 Conclusions

In conclusion, we found that Pt/solid-base is a predominant catalyst for glycerol hydrogenolysis in a base-free aqueous solution. A hydrotalcite precursor supported Pt catalyst (Pt/HLT) exhibited the predominant activity and higher 1,2-PDO selectivity among the test catalysts (Pt/H-Beta, Pt/H-ZSM5, Pt/C, Pt/Al_2O_3, Pt/MgO and Pt/HLT) under lower pressure. XRD, TEM and CO_2-TPD characterizations concluded that the basic properties of the catalyst contributed obviously to its activity for glycerol hydrogenolysis, while smaller sized Pt particles of on the base support is more active.

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