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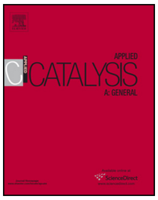

Influence of Pd precursors and Cl addition on performance of Pd-Re catalysts in glycerol hydrogenolysis to propanediols

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ABSTRACT

Pd-Re/SBA-15 catalysts with different Pd precursors were prepared by the impregnation method. N_2 adsorption-desorption, XRD, H_2-TPR, TEM and NH_3-TPD were used to characterize the physical and chemical properties of the catalysts. Pd-Re catalysts with different precursors showed different activities in the reaction of glycerol hydrogenolysis. 5Pd-5Re/SBA-15 with $PdCl_2$ as Pd precursor had higher activity than those with $Pd(NO_3)_2$ and $Pd(OAc)_2$ as precursors. The existence of Cl could affect the particle sizes, reduction behaviors and the acid properties of Pd-Re catalysts.

1. Introduction

Glycerol is produced as a by-product during the production of biodiesel by the transesterification of vegetable oils or animal fats with methanol. During this process, 1 kg of glycerol would be produced as a by-product from 10 kg of raw materials [1–3]. Converting this over-produced glycerol into more value-added downstream products can not only decrease the price of biodiesel, but also use biomass efficiently. The catalytic hydrogenolysis of glycerol can produce 1,2-propanediols (1,2-PD), 1,3-propanediols (1,3-PD) and other chemicals, including propanols and glycol. Among these chemicals, 1,2-PD can be used to produce cosmetics, antifreeze, epoxy resin and so on. For 1,3-PD, which is much more valuable than others, it could be used in the pharmaceuticals industry [4,5].

For glycerol hydrogenolysis, non-noble metals including Cu, Ni and noble metals including Ru, Pd and Pt have been often used as the active components of catalysts. For the most of Cu and Ni catalysts, 1,2-PD was the main product. Xia et al. [6] prepared a multiwall carbon nanotube-pillared layered $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ catalyst and used in glycerol hydrogenolysis, and the conversion of glycerol and selectivity to 1,2-PD were 64.8% and 99.3%, respectively. Zhu et al. [7] used CuCe-SBA catalysts in hydrogenolysis of biomass-derived glycerol and sugar alcohols, and got about 97% yield of 1,2-PD from glycerol hydrogenolysis at 180 °C. Yu et al. [8] employed Ni/AC treated with KBH_4 in this reaction, and the conversion of glycerol over Ni/AC reached 63.2% after 24 h reaction and the selectivity to 1,2-PD was 77.4%. Jiang et al. [9] prepared bimetallic Ni-Co catalysts and found that with the promoting effect of ceria, the total glycol selectivity over Ni-Co-Ce catalysts could reach about 81%. For noble metal based catalysts, most of them could convert glycerol to 1,3-PD and 1,2-PD, but the selectivity to 1,3-PD was low. Vanama et al. [10] found that Ru/MCM-41 could convert 62% of glycerol in the reaction under 230 °C, while the selectivities to 1,2-PD and 1,3-PD were 38% and 20%, respectively. Liu et al. [11] texted Pt/WO_3 catalysts, and the ratio of 1,3-PD to 1,2-PD was 9.6. $Pt/WOx/Al_2O_3$ catalysts were studied by García-Fernández et al. [12], and 1,3-PD selectivity reached 52% in the glycerol hydrogenolysis. Zhu et al. [13] also studied the $Pt\text{-}WOx/Al_2O_3$ bifunctional catalysts in glycerol hydrogenolysis with a fixed-bed reactor, and the selectivity to 1,3-PD could reach 66% at 160 °C. Pd-based supported catalysts also showed activity in the glycerol hydrogenolysis. Musoline et al. [14] prepared different supported PdCo catalysts with co-precipitation method. Using PdCo catalysts got about 70% glycerol conversion and selectivity to 1,2-PD was 86.5% when *n*-propanol (1-PO) was used as the solvent. Jiang et al. [15] tested a Pd-Ni bimetallic catalyst in glycerol hydrogenolysis, and after 4 times recycle, the catalyst could still maintain its activity and selectivity to 1,2-PD, compared with the fresh one. Recently, Re also gains much attention as a co-active component, and Ru-Re [16,17], Pt-Re [18], Rh-Re [19] and Ir-Re [20] all showed relatively good activities.

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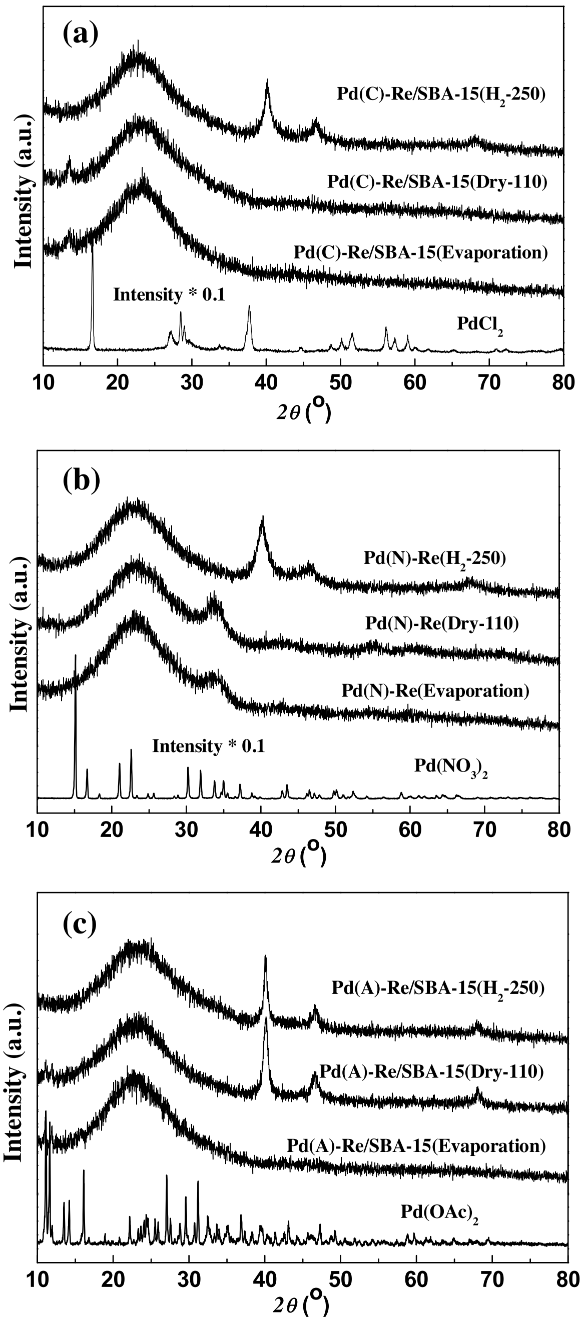

Fig. 1. Wide angle XRD patterns of Pd-Re catalyst prepared with different treatments. (a) Pd(C)-Re/SBA-15 (b) Pd(N)-Re/SBA-15 and (c) Pd(A)-Re/SBA-15.

In our previous study [21], the addition of Re into the Pd catalyst greatly increased the conversion of glycerol. But the influences of Pd precursors and Cl component on the properties of the Pd-Re catalysts and the catalytic performance in glycerol hydrogenolysis were rarely investigated. To further study the behaviors of Pd-Re bi-component catalysts, different Pd precursors and Cl component addition into Pd-Re catalysts were studied in this work. The effects of Pd nitrate, Pd chloride and Pd acetate as the precursors of Pd on the activities of Pd-Re catalysts were investigated. On the other hand, the influence of Cl addition into the Pd-Re catalyst during impregnation process, when Pd nitrate and Pd acetate were used as precursors, on the properties and performance of Pd-Re catalysts were also studied.

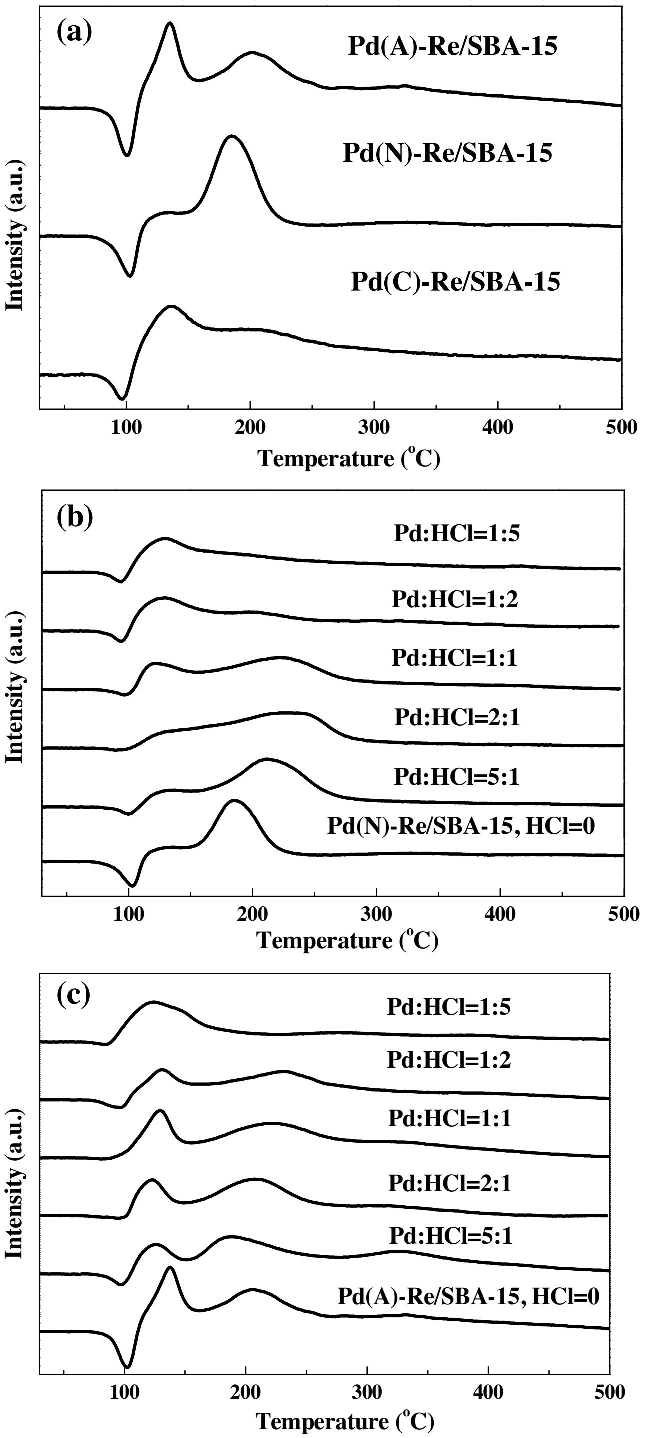

Fig. 2. H_2-TPR profiles of catalysts. (a) Pd-Re/SBA-15 prepared with different Pd precursors, (b) Pd(N)-Re/SBA-15 prepared with different amounts of HCl addition, (c) Pd(A)-Re/SBA-15 prepared with different amounts of HCl addition.

2. Experiments

2.1. Catalysts preparation

SBA-15 (a kind of ordered mesoporous silica) was used as the support of Pd-Re catalysts and prepared by the method mentioned in a literature [22]. The brief preparation process was as follows: P123 ($EO_{20}PO_{70}EO_{20}$, $M_w = 5800$) was dissolved in an aqueous solution of HCl (2 mol/L) and stirred at 35 °C for 4 h until the solution

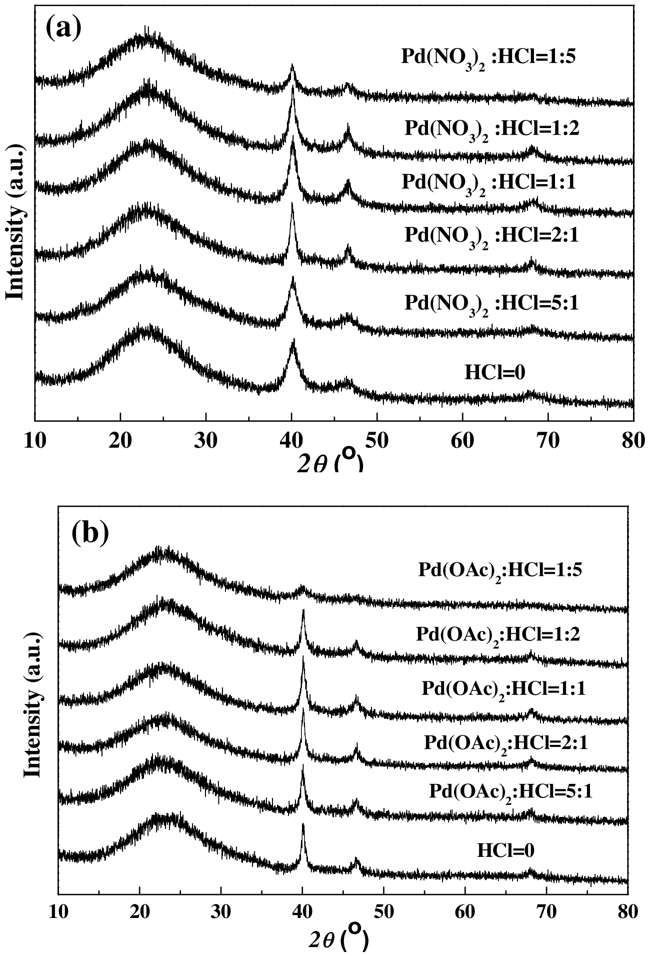

Fig. 3. Wide angle XRD patterns of Pd-Re catalysts prepared with different amounts of HCl addition and treated with H_2 at 250 °C. (a) Pd(N)-Re/SBA-15, (b) Pd(A)-Re/SBA-15.

became transparent. Tetraethoxysilane (TEOS) was then added into the solution and hydrolyzed at 35 °C for 20 h, and then formed gel was aged at 80 °C for 24 h. After cooled down, the precipitation was filtered and washed until the filtrate was neutral, the obtained paste was dried at 40 °C for 48 h and calcinated in flowing air at 500 °C for 5 h.

All bi-component Pd-Re/SBA-15 catalysts were all prepared by the co-impregnation method. A typical procedure was as below. $PdCl_2$ was dissolved in HCl aqueous solution (0.03 mol/L HCl, 0.06 mol/L $PdCl_2$), then the $PdCl_2$-HCl aqueous solution was mixed with $HReO_4$ aqueous solution, and SBA-15 powder was added into this mixed solution for impregnation with stirring at room temperature for 10 h. After the water was evaporated by rotary evaporation, the obtained solid sample was dried at 110 °C overnight. The theoretical contents of Pd and Re were all 5 wt%, while the actual contents of Pd and Re in the catalysts measured by ICP analysis were all near to the theoretical ones. Before using in the reaction, all Pd-Re/SBA-15 catalysts were reduced with flowing H_2/N_2 at 250 °C or 500 °C for 2 h. The Pd-Re/SBA-15 catalysts prepared using $PdCl_2$ and $HReO_4$ were denoted as Pd(C)-Re/SBA-15. When $Pd(NO_3)_2$ or $Pd(OAc)_2$ was used as Pd precursor and $HReO_4$ as Re precursor, the catalysts were denoted as Pd(N)-Re/SBA-15 or Pd(A)-Re/SBA-15.

For investigating the effect of Cl addition on Pd-Re catalysts, Cl component using HCl or NaCl as Cl precursor was introduced into Pd(N)-Re/SBA-15 or Pd(A)-5Re/SBA-15.

2.2. Catalysts characterization

The specific surface areas, pore volumes and pore size distributions of Pd-Re/SBA-15 catalysts were measured by N_2 adsorption-desorption at −196 °C, using a Micromeritics ASAP 2010C analyzer.

The crystal structures of all 5Pd-5Re/SBA-15 catalysts were characterized by powder X-ray diffraction (XRD). The experiments were carried out in a Rigaku D/max 2500 powered at 40 kV, 200 mA and Cu*Ka* radiation. For small angle XRD from 0.6° to 3°, the scan step was 1°/min. For wide angle XRD from 10° to 80°, the scan step was 10°/min.

H_2-TPR was used to characterize the reduction behaviors of Pd-Re catalysts. The characterizations were carried out on Quantachrome CHEM-3000. For a typical measurement, 0.1 g of the catalyst was firstly pretreated in flowing Ar at 250 °C for 2 h and then cooled down to room temperature. As part of Pd oxide was reduced when contacted with H_2 immediately even at room temperature [23], two steps of H_2-TPR process were employed for the characterizations. For step I, the catalyst was maintained at 30 °C under flowing Ar, then the Ar gas was changed from sample tube path into bypass, while 5%H_2/Ar flowing gas was introduced into the sample tube path and kept in 5%H_2/Ar at 30 °C until the baseline was stabilized. Immediately, changing H_2/Ar gas from bypass to sample path would result in a pulse signal and this was recorded. During this step I process, the residual Ar in the sample path would also cause signals after introducing 5%H_2/Ar into sample path. For this reason, SBA-15 was also used as a blank for characterizing the residual Ar. After maintaining the sample in 5%H_2/Ar for 20 min, the step I was end, and the step II was started. For step II of the TPR, the temperature was increased from 30 °C to 500 °C with the rate of 15 °C/min.

NH_3-TPD was used to characterize the acid properties of Pd-Re catalysts with Quantachrome CHEM-3000. In a typical procedure, 0.1 g of the sample was pretreated at 250 °C for 2 h with flowing He, then cooled down to 100 °C. After the pretreatment, the catalyst was adsorbed with 1%NH_3/He gas at 100 °C for 0.5 h, and then the sample was swept with flowing He at 100 °C for another 0.5 h. Then the temperature of the sample tube was increased from 100 °C to 750 °C with the rate of 15 °C/min and NH_2 ($m/z = 16$) species in the desorption gas was recorded.

The morphologies of the catalysts were characterized by High Resolution Transmission Electron Microscopy (HR-TEM) with JEM-2010 JEOL equipped with an energy dispersive spectrometer (EDS).

The actual amounts of Cl remained in the catalysts were analyzed with X-Ray Fluorescence (XRF), using Shimadzu XRF-1800 instrument.

2.3. Glycerol hydrogenolysis

The reactions were carried out in a 100 mL stainless steel autoclave. In a typical run, 0.15 g of the catalyst, which was reduced at 250 °C or 500 °C before used, and 10 mL 40% glycerol aqueous was added into the autoclave. After checking the leakage of the autoclave with 8 MPa H_2, 3 MPa H_2 was purged and released for 3 times to remove the residual air in the autoclave. The temperature of the autoclave was increased to 200 °C and 8 MPa H_2 was purged, and then the reaction was carried out for 18 h with 700 rpm stirring.

After the reaction, the autoclave was cooled down to 5 °C and gas phase products were analyzed by a TCD gas chromatography (Weisifu SP-6890). The mixture of liquid and solid catalysts was separated by centrifugation. The liquid phase products were analyzed by a FID gas chromatography (Lunan-6890).

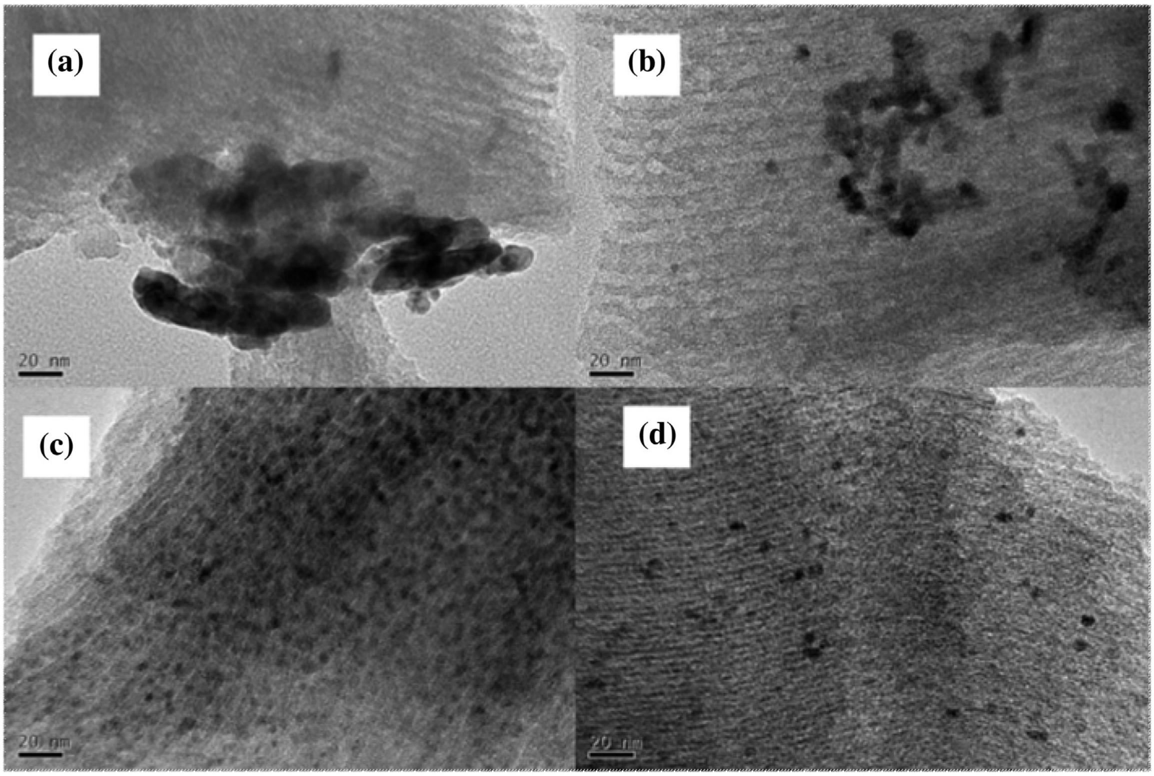

Fig. 4. TEM images of Pd(N)-Re/SBA-15 prepared with different amount of HCl addition and treated with H_2 at 250 °C. (a) without HCl addition, (b) Pd:HCl = 5:1, (c) Pd:HCl = 1:1, (d) Pd:HCl = 1:5.

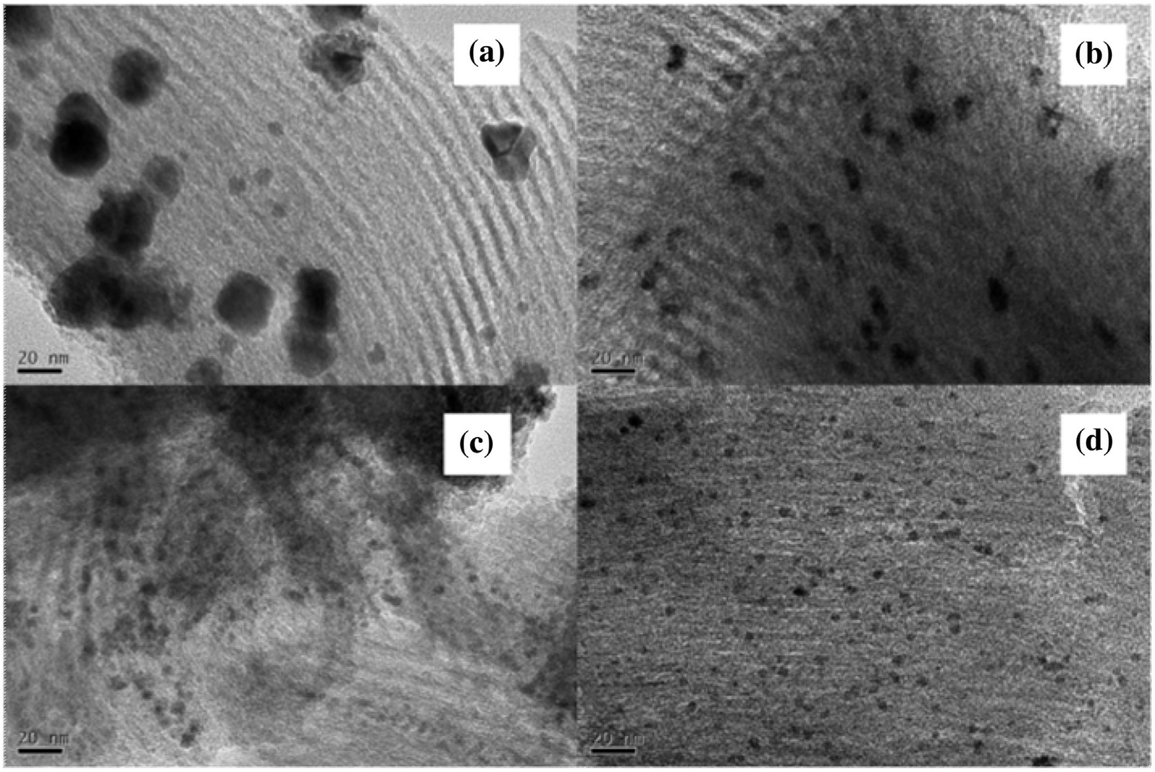

Fig. 5. TEM images of Pd(A)-Re/SBA-15 prepared with different amount of HCl addition and treated with H_2 at 250 °C. (a) without HCl addition, (b) Pd:HCl = 5:1, (c) Pd:HCl = 1:1, (d) Pd:HCl = 1:5/.

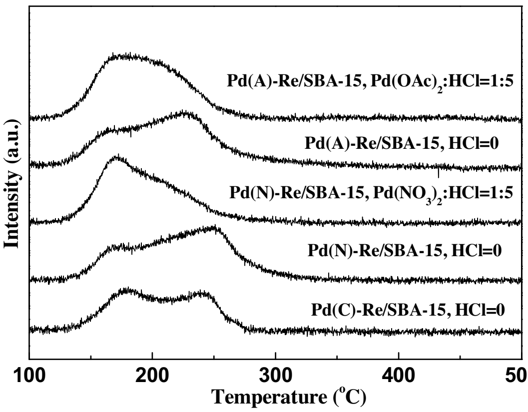

Fig. 6. NH_3-TPD profiles of Pd-Re/SBA-15 prepared with different amount of HCl addition and treated with H_2 at 250 °C.

The conversion of glycerol and selectivity to product were calculated by equations as below.

$$Conversion(\%) = \frac{Sum\ \ of\ C\ mol\ of\ all\ products}{Added\ \ glycerol\ \ \ before\ reaction\ \ (C\ mol)} \times 100\%$$

$$Selctivity(\%) = \frac{C\ \ mol\ \ of\ \ each\ \ product}{Sum\ \ of\ \ C\ \ mol\ of\ \ all\ \ products} \times 100\%$$

The carbon balances for all reactions were about 95 ± 5%.

3. Results and discussion

3.1. The texture properties of Pd-Re/SBA-15 prepared with different Pd precursors

The texture properties of Pd-Re/SBA-15 prepared with different precursors were all characterized by N_2 adsorption-desorption method and the results are shown in Table S1. From the results, it can be seen that the texture properties of these catalysts were quite similar. The specific surface areas were in the range of 600–680 m^2/g, which were lower than that of support SBA-15. The pore volumes and average pore sizes of the catalysts were also lower than those of support SBA-15. Pd-Re/SBA-15 with different Pd precursors all had similar N_2 adsorption-desorption isotherms and pore size distributions (Fig. S1), indicating that all catalysts maintained the mesoporous structure of SBA-15 after impregnation and reduction.

3.2. The effect of different Pd precursors on the properties and catalytic performance of Pd-Re/SBA-15

The effect of different Pd precursors on the catalytic performance of Pd-Re/SBA-15 catalysts in glycerol hydrogenolysis is shown in Table 1. When the reduction temperatures of the catalysts were 250 °C, the conversion of glycerol over Pd(C)-Re/SBA-15 was the highest (40.7%) among the three catalysts, while Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 had similar conversion of glycerol (19.3% and 18.0%, respectively). Even increasing the reduction temperature from 250 °C to 500 °C, the glycerol conversion over Pd(C)-Re/SBA-15 (41.4%) was still higher than those over Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 (15.4% and 22.1%, respectively). The selectivities to 1,2-PD was in the range of 55–68% over these catalysts when the reduction temperature was 250 °C, and they were in the order of Pd(A)-Re/SBA-15 (67.4%) > Pd(C)-Re/SBA-15 (59.9%) > Pd(N)-Re/SBA-15 (55.7%). All catalysts showed similar selectivity to 1,3-PD (8–11%) at the conditions of 200 °C, 8 MPa H_2 and 18 h. After reduction at 500 °C, the catalysts all showed a relatively lower selectivity to 1,2-PD, while a higher selectivity to 1,3-PD. For example, on Pd(A)-Re/SBA-15, the reduction at 500 °C decreased the selectivity to 1,2-PD from 67.4% to 60.4%, while the selectivity to 1,3-PD increased from 9.5% to 11.0%. From the results mentioned above, it could be seen that the different Pd precursors could affect the activities of Pd-Re catalysts. Pd(C)-Re/SBA-15 prepared with $PdCl_2$ as the precursor had better activity than those prepared with $Pd(NO_3)_2$ or $Pd(OAc)_2$ as the precursor.

The crystal phases of Pd-Re/SBA-15 catalysts prepared with different Pd precursors are shown in Fig. 1. For the samples using $PdCl_2$ as the precursor (Fig. 1(a)), after evaporated and dried at 110 °C, there was no obvious diffraction peak of Pd or Re on Pd(C)-Re/SBA-15. When the Pd(C)-Re/SBA-15 was reduced at 250 °C, the diffraction peaks of Pd(111) at $2\theta = 40°$, Pd(200) at $2\theta = 46°$ and Pd(220) at $2\theta = 68°$ could be observed [24,25]. For the bi-component sample using $Pd(NO_3)_2$ as the precursor (Fig. 1(b)), its crystal structure was different from that of using $PdCl_2$ as the precursor. After evaporated and dried at 110 °C, the diffraction peak of PdO $2\theta = 34°$ could be observed on Pd(N)-Re/SBA-15, and the crystal phase of PdO changed into Pd° after reduced at 250 °C. Similar results were also found over Pd(A)-Re/SBA-15 (Fig. 1(c)), Pd° crystal phase was observed after dried at 110 °C. Therefore, different Pd precursors would affect the particle size of Pd on the Pd-Re catalysts, and this might result in the different activities of these catalysts.

H_2-TPR profiles of Pd-Re catalysts prepared by different Pd precursors are shown in Fig. 2(a). For step I of TPR experiment (keeping at 30 °C constant), all catalysts showed similar TPR profiles (the results are shown in Fig. S2). From step II (from 30 °C to 500 °C) of all Pd-Re/SBA-15, the reduction behaviors of these catalysts were different from either mono-component Pd/SBA-15 or Re/SBA-15 (Fig. S3). This meant that Pd and Re had interaction no matter what Pd precursor was used. But the reduction behaviors of Pd-Re catalysts prepared with different palladium precursors were quite different from each other. For Pd(C)-Re/SBA-15, the main reduction peaks were at 130 °C and 220 °C, while for Pd(N)-Re/SBA-15, the main reduction peak was at 200 °C. The reduction peaks of Pd(A)-Re/SBA-15 were also at 130 °C and 220 °C, but the peak shapes were different from Pd(C)-Re/SBA-15. The reduction peak of Pd(A)-Re/SBA-15 at 130 °C was much sharper than that of Pd(C)-Re/SBA-15. And the reduction peak of Pd(A)-Re/SBA-15 at 220 °C was also more visible. Moreover, for Pd(A)-Re/SBA-15, a weak reduction peak at 330 °C could be found, which might belong to ReOx, which meant that the Pd and Re interaction was not as strong as that of Pd(C)-Re/SBA-15.

3.3. The effect of Cl component on the properties and catalytic performance of Pd-Re/SBA-15

As mentioned above, Pd-Re catalysts prepared with different Pd precursors showed different activities in glycerol hydrogenolysis. Different Pd precursors have different negative ions. Pd(C)-Re/SBA-15 had better activity than Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15, and the Cl component on the Pd(C)-Re/SBA-15 might be the reason. In order to further investigate the influence of Cl on the properties and catalytic performance of Pd-Re/SBA-15, HCl or NaCl was added into the catalysts as Cl precursor.

Table 2 shows the influence of Cl addition on Pd(N)-Re/SBA-15 in glycerol hydrogenolysis. From No. 1–6, as the addition amount of HCl increased, the conversion of glycerol over Pd(N)-Re/SBA-15 increased from 19.3% to 45.3%, while the selectivity to 1,2-PD decreased from 59.1% to 43.6%. As the addition amount (mol) of HCl was 5 times of that of $Pd(NO_3)_2$, the selectivity to 1,2-PD was the lowest (43.6%), but the addition of HCl influenced little on the selectivity to 1,3-PD (maintained between 7–10%). This decrease of 1,2-PD selectivity might be caused by the higher activities of the catalysts with Cl addition on further hydrogenolysis of 1,2-PD to

Table 1
Catalytic performance of Pd-Re/SBA-15 prepared with different Pd precursors in glycerol hydrogenolysis.

Catalyst	Treatment Condition	Glycerol Conv. (%)	Select. (%)				
			C_{1-2}	1-PO	2-PO	1,2-PD	1,3-PD
Pd(C)-Re/SBA-15	H_2-250	40.7	5.2	24.6	2.1	59.9	8.2
Pd(C)-Re/SBA-15	H_2-500	41.4	4.7	25.3	3.5	57.0	9.5
Pd(N)-Re/SBA-15	H_2-250	19.3	4.2	29.4	3.6	55.7	7.1
Pd(N)-Re/SBA-15	H_2-500	15.4	5.7	27.7	2.8	54.8	9.0
Pd(A)-Re/SBA-15	H_2-250	18.0	4.1	17.6	1.5	67.4	9.5
Pd(A)-Re/SBA-15	H_2-500	22.1	4.2	22.1	2.3	60.4	11.0

Reaction conditions: 0.15 g Pd catalyst, 40% glycerol aqueous solution 10 mL, 200 °C, 8 MPa H_2, 18 h, 700 rpm.
C_{1-2}: methane, methanol, ethanol and ethylene glycol, PO: propanol, PD: propanediol.

Table 2
Influence of addition Cl on the catalytic performance of Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 prepared with $Pd(NO_3)_2$ and $Pd(OAc)_2$ as precursor.

No.	Catalyst	Cl precursor type	Pd:Cl (mol ratio)	Glycerol Conv. (%)	Select. (%)				
					C_{1-2}	1-PO	2-PO	1,2-PD	1,3-PD
1	Pd(N)-Re/SBA-15	–	–	19.3	4.2	29.4	3.6	55.7	7.1
2	Pd(N)-Re/SBA-15	HCl	5:1	21.4	3.4	24.6	3.2	59.1	9.7
3	Pd(N)-Re/SBA-15	HCl	2:1	25.0	3.5	27.8	3.0	56.1	9.5
4	Pd(N)-Re/SBA-15	HCl	1:1	36.6	3.1	35.9	4.3	48.3	8.3
5	Pd(N)-Re/SBA-15	HCl	1:2	38.7	3.9	31.6	3.0	51.4	10.1
6	Pd(N)-Re/SBA-15	HCl	1:5	45.3	3.0	40.5	4.8	43.6	8.2
7	Pd(N)-Re/SBA-15	NaCl	1:2	45.8	3.4	32.4	4.5	51.1	8.6
8	Pd(N)-Re/SBA-15	$NaNO_3$	–	20.0	5.8	17.0	1.9	67.7	7.6
9	Pd(A)-Re/SBA-15	–	–	18.0	4.1	17.6	1.5	67.4	9.5
10	Pd(A)-Re/SBA-15	HCl	5:1	24.4	3.8	28.8	2.9	55.7	8.8
11	Pd(A)-Re/SBA-15	HCl	2:1	25.8	3.5	40.2	2.6	43.9	9.8
12	Pd(A)-Re/SBA-15	HCl	1:1	32.7	2.7	35.4	2.4	49.4	10.2
13	Pd(A)-Re/SBA-15	HCl	1:2	42.0	2.8	32.7	3.1	52.5	8.9
14	Pd(A)-Re/SBA-15	HCl	1:5	59.5	4.5	39.1	5.6	45.0	5.8

Reaction Conditions: 0.15 g Pd catalyst, 40% glycerol aqueous solution 10 mL, 200 °C, 8 MPa H_2, 18 h,700 rpm.
C_{1-2}: methane, methanol, ethanol and ethylene glycol, PO: propanol, PD: propanediol.

Table 3
Actual amount of Cl in Pd-Re/SBA-15 prepared with different treatments.

Catalyst	Pd Precursor	Pd:HCl (mol ratio)	Treatment	Cl content(%)
Pd(N)-Re/SBA-15	$Pd(NO_3)_2$	1:5	Only evaporation	3.76
Pd(N)-Re/SBA-15	$Pd(NO_3)_2$	1:5	Only dried at 110	1.51
Pd(N)-Re/SBA-15	$Pd(NO_3)_2$	1:5	H_2-250	0.17
Pd(A)-Re/SBA-15	$Pd(OAc)_2$	1:5	Only evaporation	3.22
Pd(A)-Re/SBA-15	$Pd(OAc)_2$	1:5	Only dried at 110	0.51
Pd(A)-Re/SBA-15	$Pd(OAc)_2$	1:5	H_2-250	0.12
Pd(C)-Re/SBA-15	$PdCl_2$	–	Only evaporation	0.98
Pd(C)-Re/SBA-15	$PdCl_2$	–	Only dried at 110	0.91
Pd(C)-Re/SBA-15	$PdCl_2$	–	H_2-250	0.14

Table 4
Acid amounts of Pd-Re/SBA-15 prepared with different Pd precursors.

Catalyst	Precursor	Pd:HCl[a] (mol ratio)	Total Acid amount[b] μ mol/g	Amount of weak acid sites[b] μ mol/g	Amount of moderate acid sites[b] μ mol/g
Pd(C)-Re/SBA-15	$PdCl_2$	–	175	100.4	74.2
Pd(N)-Re/SBA-15	$Pd(NO_3)_2$	–	232	59.7	172.3
Pd(N)-Re/SBA-15	$Pd(NO_3)_2$	1:5	194	95.4	98.6
Pd(A)-Re/SBA-15	$Pd(OAc)_2$	–	226	78.6	147.6
Pd(A)-Re/SBA-15	$Pd(OAc)_2$	1:5	196	95.4	100.3

[a] Addition amount of HCl during preparation.
[b] Obtained from NH_3-TPD.

1-PO. The selectivity to 1-PO increased to the highest of 40% with the ratio of Pd/HCl = 5/1. During the impregnation, the HCl addition might change the pH value of the impregnation solution. For comparison, NaCl was also used as Cl precursor for preparing Pd(N)-Re/SBA-15. The result (Table 2, No. 7) revealed that, the addition of NaCl into Pd(N)-Re/SBA-15 could also increase the conversion of glycerol from 19.3% to 45.8% while the selectivity to 1,2-PD became a little lower, and the selectivity to 1,3-PD was still kept at 8.6%. Furthermore, for comparison NaCl, $NaNO_3$ was also used to examine the effect of Na on the activity of Pd(N)-Re/SBA-15 (Table 2, No. 8), and the conversion of glycerol was 20.0%, which was similar to that of Pd(N)-Re/SBA-15 without Cl addition (19.3%), while the selectivity to 1,2-PD was the highest (67.7%). This might be the reason of the basic property of Na which was favor to 1,2-PD formation in the hydrogenolysis. In our previous study [21], the Pd-Re catalysts with base supports (like CeO_2, MgO, La_2O_3) had higher selectivity to 1,2-PD compared with those Pd-Re catalysts with neutral and acid supports. From these results, it can be seen that the addition of Cl could surely increase the activity of Pd(N)-Re/SBA-15. For mono-component Pd and Re catalysts, the influence of HCl addition was also tested. The activity of mono-component Pd or Re catalyst was very low, and as shown in Table S2, the addition of HCl affected little on the activity of Pd(N)/SBA-15 or Re/SBA-15. The conversions of glycerol were below 5%, but the selectivities changed. For Pd(N)/SBA-15, after addition of HCl, the selectivity to 1,2-PD increased from 35.6% to 70.4%, which was quite similar with the selectivity to 1,2-PD on Pd(C)/SBA-15 (72.2%).

The reduction behaviors of Pd(N)-Re/SBA-15 prepared with different amounts of HCl addition are shown in Fig. 2(b). It clearly showed that when the amount of HCl was small (Pd:HCl = 5:1), the intensity of reduction peak at 130 °C in TPR profile was stronger, while the reduction peak at 200 °C shifted to 210 °C. As the addition amount of HCl increased, the intensity of reduction peak at 130 °C became stronger, but the reduction peak at 210 °C became weaker. When the addition amount of HCl was 2 times of that of $Pd(NO_3)_2$, the TPR profile of the Pd(N)-Re/SBA-15 was very like that of Pd(C)-Re/SBA-15. When the amount (mol) of HCl was 5 times of that of $Pd(NO_3)_2$, the main reduction peak in the TPR profile was at 130 °C, while the reduction peak at 210 °C was almost disappeared. The differences of reduction behaviors of these Pd(N)-Re/SBA-15 samples might be due to the addition of Cl component, and this would finally result in the different activities of Pd(N)-Re/SBA-15. To further investigate the effect of HCl, mono-component Pd and Re catalysts were also prepared with HCl addition, respectively. From the TPR results of Pd(N)/SBA-15 with HCl addition, the reduction peak at 130 °C was observed (Fig. S3(a)). On the other hand, for the TPR profiles of Re/SBA-15 samples (Fig. S3(b)), the reduction temperature of Re/SBA-15 with HCl addition decreased from 330 °C to 270 °C compared with that of Re/SBA-15 without HCl addition. These results showed that the Cl would also affect the reduction behaviors of ReOx, and finally also influence the performance of Pd-Re catalysts.

Fig. 3(a) shows the XRD patterns of Pd(N)-Re/SBA-15 prepared with different amounts of HCl addition. When the samples were reduced at 250 °C, all Pd(N)-Re/SBA-15 showed similar Pd° diffraction peaks in the XRD patterns. When the addition amount (mol) of HCl was 5 times of that of $Pd(NO_3)_2$, the Pd° diffraction peaks in the XRD patterns of Pd(N)-Re/SBA-15 (Pd:HCl = 1:5) were very weak.

The morphologies of Pd(N)-Re/SBA-15 prepared with different amounts of HCl addition were characterized by HR-TEM. The results are shown in Fig. 4. For Pd(N)-Re/SBA-15 without HCl addition (Fig. 4(a)), Pd-Re particles agglomerated into very large ones, while Pd and Re components were both existed in the particles according to EDX analysis. After a certain amount of HCl was added (Pd:HCl = 5:1, Fig. 4(b)), Pd-Re particles on the sample were still agglomerated, but the dispersion of these particles were clearly better than that one without HCl addition. When the addition amount of HCl increased to Pd:HCl = 1:1 (Fig. 4(c)), Pd-Re particles on the sample were obviously dispersed better and grew along the SBA-15 channels, and particle sizes of Pd-Re were in the range of 4–5 nm. Further increasing the amount (mol) of HCl to 5 times of that of $Pd(NO_3)_2$ (Fig. 4(d)), Pd-Re particles dispersed more homogenously, and the particle sizes of Pd-Re particles were also 4–5 nm. From these results, it clearly indicated that the addition of HCl would surely decrease the particle size and increase the dispersion of Pd-Re particles.

In order to further make sure the effect of Cl, Pd(A)-Re/SBA-15 catalysts were also prepared with HCl addition during an impregnation process. The reaction results using these catalysts are listed in Table 2 (No. 9–14). Similar as the case of Pd(N)-Re/SBA-15, for Pd(A)-Re/SBA-15 without HCl addition, it had the lowest activity (conversion of glycerol was 18.0%), while it had the highest selectivity to 1,2-PD (67.4%). The addition of HCl into Pd(A)-Re/SBA-15 also increased the activity of the catalysts. As the addition amount (mol) of HCl increased from 0 to 5 times of that of $Pd(OAc)_2$, the conversion of glycerol over these catalysts increased from 18.0% to 59.5%, while the selectivity to 1,2-PD became lower. To further examine the influence of HCl addition on the distribution of products, reaction times over the catalysts were changed to maintain conversions of glycerol in the range of 18–27% (Table S3). It can be seen that using the catalysts prepared with the addition of HCl could increase the activity of Pd-Re while the selectivity to 1,2-PD was decreased. For Pd(N)-Re/SBA-15, the addition of HCl decreased the selectivity to 1,2-PD from 55.7% to 51.3%, while the addition of HCl decreased the selectivity to 1,2-PD from 67.4% to 50.5% over Pd(A)-Re/SBA-15 (Table S3). In all these catalysts, the selectivities to 1,3-PD were all maintained at 7–12%. In glycerol hydrogenolysis, 1,2-PD could undergo further hydrogenolysis reaction to 1-PO. The increase of the activity of Pd-Re catalyst with Cl addition in hydrogenolysis of —OH group might be favorable to convert 1,2-PD into 1-PO. This might be the reason of lower selectivity to 1,2-PD and higher selectivity to 1-PO.

Furthermore, H_2-TPR was also used to characterize the reduction properties of Pd(A)-Re/SBA-15 prepared with different amounts of HCl addition (Fig. 2(c)). The addition of HCl could also change the reduction behaviors of Pd(A)-Re/SBA-15. When the ratio of Pd:HCl was 5:1, the reduction peak at 130 °C in the TPR profile of Pd(A)-Re/SBA-15 prepared with HCl addition was not as sharp as that of without HCl addition, while the intensity of the reduction peak at 330 °C became stronger. As the addition amount (mol) of HCl increased to 5 times of that of $Pd(OAc)_2$, the TPR profile of Pd(A)-Re/SBA-15 was very like that of Pd(C)-Re/SBA-15. This result was also as similar as that of Pd(N)-Re/SBA-15 prepared with HCl addition.

From Fig. 3(b), the crystal structures of Pd(A)-Re/SBA-15 prepared with different amounts of HCl addition had no obviously differences except for the sample of Pd:HCl = 1:5. For Pd(A)-Re/SBA-15 prepared with Pd:HCl = 1:5, the Pd° diffraction peaks in the XRD pattern were weaker than those of others. This result was similar with that of Pd(N)-Re/SBA-15. HR-TEM was also used to characterize the morphologies of Pd(A)-Re/SBA-15 prepared with different amounts of HCl addition, and the results are shown in Fig. 5 (The histograms established from TEM images of Pd(A)-Re/SBA-15 are performed in Fig. S4). Really, the addition of HCl during the preparation of the catalysts also increased the dispersion of Pd-Re particles on Pd(A)-Re/SBA-15. For Pd(A)-Re/SBA-15 prepared without HCl addition (Fig. 5(a)), most of the Pd-Re particles grew on the outside of the support, and the average particle size was 17 nm, which was much larger than that of Pd(C)-Re/SBA-15. When a little amount of HCl was added into Pd(A)-Re/SBA-15 during the preparation of the catalyst (Pd:HCl = 5:1, Fig. 5(b)), the average particle size of Pd-Re was 10 nm and particles dispersed more homogenously. At the same time, the Pd-Re particles grew along the SBA-15 channels and their shapes became rod like. Further increasing the HCl amount, the Pd-Re particles of Pd(A)-Re/SBA-15 became smaller. When Pd:HCl was 1:5 (Fig. 5(d)), the average Pd-Re particle size of Pd(A)-Re/SBA-15 was 4 nm. These results were also as similar as that of Pd(N)-Re/SBA-15 prepared with HCl addition.

The actual amounts of Cl in the catalysts were characterized by XRF, and the results are listed in Table 3. For Pd(N)-Re/SBA-15 prepared with Pd:HCl = 1:5 addition, the actual amount of Cl on the catalyst was 3.76% after the sample was evaporated, while only 1.51% of Cl remained on the catalyst after it was dried at 110 °C overnight. Furthermore, when the sample was reduced at 250 °C, the Cl amount on the catalyst further decreased to only 0.17%. For Pd(A)-Re/SBA-15 prepared with Pd:HCl = 1:5 addition, it had similar results. That is, during the treatment steps of evaporation, drying and reduction, part of the Cl component on the catalyst lost. Only 0.12% of Cl remained on the catalyst after the reduction at 250 °C.

These results indicated that most of the Cl might be removed by the reduction step.

Acid properties of Pd-Re catalysts prepared with HCl addition were characterized by NH_3-TPD. Fig. 6 shows the NH_3-TPD profiles of Pd-Re catalysts, and the acid amounts calculated from NH_3-TPD are listed in Table 4. For bi-component Pd-Re catalysts, the NH_3-TPD profiles of Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 prepared without HCl addition had similar peak type, and the intensity of the desorption peak at 240 °C (moderate acid sites) was stronger than that of at 160 °C (weak acid sites), while the moderate acid amounts were higher than weak acid amounts. Meanwhile, the total acid amounts of these two catalysts were also similar (232 and 226 μmol/g, respectively). For Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 prepared with HCl addition, the NH_3-TPD profiles changed a lot. The desorption peaks at 160 °C became much stronger than those of 240 °C, and the weak acid amounts become higher than the moderate acid amounts. Meanwhile, the total acid amounts were similar with Pd(C)-Re/SBA-15, which were all between 175–196 μmol/g. It's worth noting that the weak acid amounts of Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 prepared with HCl addition were similar with that of Pd(C)-Re/SBA-15 (95–100 μmol/g). Meanwhile, the glycerol hydrogenolysis reactions were carried out at 200 °C, which meant the weak acid sites had a greater impact on the activities of Pd-Re catalysts. From NH_3-TPD results combined with H_2-TPR, it can be seen that the addition of Cl component during preparation might increase the interaction between Pd and Re. This kind of interaction lead to the change of reduction behaviors and acid properties of Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15.

From the results mentioned above, the addition of Cl in the preparation of the catalysts could change the reduction behaviors of Pd(N)-Re/SBA-15 and Pd(A)-Re/SBA-15 catalysts, and decrease the particle sizes of Pd-Re on the catalysts. These results were as similar as a reference reported by Wang and Lu [26]. They found that the existence of Cl could vary the dispersion of Pd in Pd-Cu bimetallic catalysts. Michel et al. [27] studied Pt-Re catalysts and found that ReOCl species could be formed, and this ReOCl could move on the support surface, which led Pt-Re be reduced much easier.

4. Conclusions

Different Pd precursors showed influence on the properties and the catalytic performance of Pd-Re/SBA-15 catalysts in glycerol hydrogenolysis. The conversions of glycerol over Pd-Re/SBA-15 catalysts prepared with different precursors were in the order of $PdCl_2 > Pd(NO_3)_2 \approx Pd(OAc)_2$. Those catalysts showed the different reduction behaviors and had different Pd-Re particle sizes. The existence of Cl on the catalysts could change the reduction behaviors, Pd-Re particle sizes and acid properties of the catalysts, and finally affected their activities in glycerol hydrogenolysis. When $Pd(NO_3)_2$ or $Pd(OAc)_2$ was used as Pd precursor, the appropriate amount of Cl addition could promote the dispersion of Pd-Re particles, and then improve the activities of the catalysts in glycerol hydrogenolysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2016.04.029.

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