Research Article

Pyrrolidone Modifying Gold Nanocatalysts for Enhanced Catalytic Activities in Aerobic Oxidation of Alcohols and Carbon Monoxide

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Enhancing the catalytic activity of supported metal nanoparticle is a great demand but extremely challenging to make. We reported a simple strategy for enhancing the activities by employing the polyvinylpyrrolidone (PVP) additive, where a series of supported Au nanoparticle catalysts including Au/C, Au/BN, Au/TiO_2, and Au/SBA-15 exhibited significantly higher activities in the oxidation of various alcohols and carbon monoxide by molecular oxygen after adding PVP to the reaction system. The XPS study indicates that PVP could electronically interact with Au to form high active Au sites for molecular oxygen, thus causing improved activities for the various oxidation reactions.

1. Introduction

Since the pioneer work of Haruta and Hutchings [1–6], Au catalysts have been demonstrated to be promising catalysts for various reactions, including aerobic oxidation [7–10], homocoupling [11–14], and selective hydrogenation [15–18]. Particularly, the oxidation of hydrocarbons including alcohols [19] and olefins and alkanes [20, 21] has attracted much attention. However, the catalytic activities of the gold nanoparticles are always unsatisfactory, which limited their wide application. A key step in the Au-catalyzed oxidation reactions is the activation of molecular oxygen on Au surface. Many parameters of the Au nanoparticle catalysts have been well understood to be sensitive for their catalytic activities to molecular oxygen, such as the nanoparticles sizes [22], valence state [23], and strong metal-support interactions [24]. However, rationally controlling the factors for the goals of high catalytic activity in oxidation is still challenging.

In recent years, much success has been achieved in synthesizing active Au catalysts. For examples, Turner et al. synthesized ultrasmall Au nanoclusters exhibiting high

activity in the activation of molecular oxygen [25]; Wang et al. synthesized 2D-Au nanostructure with layer thickness and rich low-coordinative Au atoms, which is very active in the activation of molecular and oxidation of carbon-hydrogen bonds [26]. Notably, these methods are mainly focused on changing the size and morphology of the Au nanoparticles, which are difficult in synthesizing these catalysts as well as controlling their stability. Constructing strong interaction between Au nanoparticles and the support is regarded to be effective in creating highly active metal sites for the oxidation, which has been widely used in the Au/TiO_2 [27], Au/hydrotalcite [28], and Au/organic polymer [29] catalysts. In these cases, an important discovery in this field is that the polyvinylpyrrolidone (PVP) could strongly interact with the soluble Au nanoparticles in water solvent, leading to high activity in oxidation of alcohols [30, 31]. Up to date, much attention has been focused on PVP-stabilized nanoparticles as soluble catalysts [32], because PVP is cheap, harmless, and easily available. However, this system has disadvantage in the separation and regeneration of the soluble Au nanoparticles. Notably, the employment of PVP additive is

rarely reported for the Au nanoparticles supported on solid support [30, 31]. It is still uncertain whether the PVP additive would work for the supported Au nanoparticle catalysts. Herein, we systemically studied the effect of PVP additive for various supported Au catalysts of Au/C, Au/BN, Au/TiO$_2$, and Au/SBA-15. Interestingly, the addition of PVP could significantly enhance the catalytic activity of these catalysts in the oxidation of alcohols and CO. Particularly, the Au/SBA-15 presented the highest activity compared to other catalysts due to the mesoporous structure of SBA-15 support, which facilitates the adsorption/enrichment of the PVP species and promotes the PVP-Au interaction.

2. Experimental

2.1. Materials. All reagents were of analytical grade and used as purchased without further purification.

2.1.1. Synthesis of SBA-15. The mesoporous silica of SBA-15 was synthesized according the method in literature [33]. As a typical run, 0.82 g of copolymer surfactant P123 was dissolved in 24 mL of water with 3 mL HCl (12 M), followed by the addition of 2.4 mL TEOS (tetraethyl orthosilicate). After stirring at 40°C for 20 h, the mixture was transferred into an autoclave for further condensation at 100°C for 24 h. The as-synthesized samples were collected by filtration and calcined at 500°C for 4 h in oxygen to remove the surfactants.

2.1.2. Synthesis of Au/TiO$_2$, Au/SBA-15, Au/C, and Au/BN. These catalysts were synthesized by the classic impregnation method [34]. As a typical run for the synthesis of Au/TiO$_2$, 1 g of anatase was added to 80 mL of HAuCl$_4$ and urea solution. After stirring at 90°C for 4 hours in a closed reactor kept away from the light, the liquid mixture was cooled in an ice bath at 0°C, followed by adding NaBH$_4$ solution (50 mg of NaBH$_4$ in 6 mL of water). Finally, the solid sample was filtrated and washed with a large amount of water, dried at 100°C for 12 hours, and calcined at 400°C for 4 hours, obtaining the final Au/TiO$_2$ catalyst. By using activated carbon (HNO$_3$ treatment to change the surface to be hydrophilic) and BN (boron nitride) as support, Au/C and Au/BN were synthesized in the same method.

2.1.3. Synthesis of PVP-Modified Au/TiO$_2$, Au/SBA-15, Au/C, and Au/BN. As a typical run for the synthesis of PVP-modified Au/SBA-15, 1 g of SBA-15 and 80 mg of PVP were mixed in a mixture of 10 g of water and 10 g of ethanol. After stirring at room temperature for 6 h and removing the liquor under vacuum at 60°C, the PVP-modified Au/SBA-15 was obtained.

2.2. Characterization. X-ray photoemission spectroscopy (XPS) measurements were carried out using a Thermo Fisher Scientific ESCALAB 250i with photoelectron spectroscopy system using a 300 W monochromatic Al Kα (1486.6 eV) X-ray source. The instrument work function was calibrated to give an Au 4f$_{7/2}$ metallic gold binding energy (BE) of 83.96 eV. The spectrometer dispersion was adjusted to give a BE of 368.21 eV for metallic Ag3d$_{5/2}$ and 932.62 eV for metallic

Cu2$p_{3/2}$. The XPS spectra were collected in constant analyzer energy (CAE) mode. Instrument base pressure was 2.0×10^{-10} mbar and high-resolution spectra were collected using a spot size of 500 μm, with pass energy of 20 eV. The charge neutralization being monitored using the C 1s (284.6 eV) signal for adventitious carbon. Thermogravimetric curves (TG) were performed on a SDT Q600 Simultaneous DSC-TGA in flowing air with heating rate of 10°C/min. In the TG curves, the weight loss during the 400–600°C is regarded to be the loss of PVP species. The weight loss weight percentage is 6.3% over the PVP-modified Au/TiO$_2$, while the loss weight percentage is only ~1.0% over the PVP-free Au/TiO$_2$ sample. The adsorption amount of PVP on the solid sample was tested with 0.5 g of solid sample in a PVP solution (30 mL water and 0.2 g of PVP). The adsorption amount was measured by a weight method. The high-resolution transmission electron microscopy (HR-TEM) was over a JEOL JEM-3000F microscope. ICP (Inductive Coupled Plasma Emission Spectrometer) has been used to measure the Au content [26, 35]. As a typical run for analyzing the Au loading on Au/SBA-15, the solid samples were dried at 120°C under vacuum overnight, then ~13 mg of the sample (the amount was precisely measured) was digested in a mixed aqueous solution of HF, HNO$_3$, and HCl. The suspension was heated at 35°C for completely dissolving the sample. Then the solution was diluted to 100 mL. For each sample, the Sn content was tested at least five times. The Au contents were calculated by the mean value. The Sn content in the solid sample was calculated from the concentration according to the following equation:

$$P_{\text{Au}} = \left[\frac{(C_{\text{Au}} * V_{\text{solution}})}{W} \right] * 100\%. \tag{1}$$

where P_{Au} is the weight percentage of Au in the solid sample, C_{Au} is the concentration of Au measured by ICP, V_{solution} is 100 mL, and W is the amount of solid sample for preparing the solution.

2.3. Catalytic Tests. Catalytic oxidation of alcohols was performed in a 40-mL high-pressure autoclave with a magnetic stirrer (commercially obtained from the Xinyu Co.). The substrate and catalyst were mixed in the reactor and oxygen was introduced, and then the reaction system was heated to a given temperature. After the reaction, in the catalytic tests, the product was taken out from the reaction system and analyzed by gas chromatography (GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column (length at 100 m) coated with FFAP (free fatty acid phase). The columns are localized in a programmed temperature control system, where the temperature started at 60°C and increased to 200°C at a rate of 10°C/min and then kept at 200°C for 45 min. The dodecane was used as internal standard. The calibration factors of various molecules to dodecane were used as internal standard.

CO oxidation tests were carried out in a fixed-bed reactor with length of 500 mm and diameter of 5 mm at 1 atm and temperature controlled by an oven. The catalysts were pressured, crushed, sieved into 40–60 mesh, and diluted with

TABLE 1: Catalytic oxidation of benzyl alcohol, phenylethyl alcohol, cyclohexanol, and 1-hexanol over various catalysts. The substrate conversions and selectivities to the aldehyde/ketone products are presented.

Entry	Benzyl alcohol[a]		Phenylethyl alcohol[b]		Cyclohexanol[c]		1-Hexanol[d]	
	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)	Conv. (%)	Sel. (%)
Au/C	16.2	98.8	43.3	>99.5	6.3	>99.5	4.4	97.9
Au/C + PVP[e]	35.5	98.0	66.9	>99.5	15.1	>99.5	14.1	99.1
Au/BN	10.0	99.0	21.2	>99.5	4.2	>99.5	4.9	99.0
Au/BN + PVP[e]	21.9	99.5	29.0	>99.5	10.0	>99.5	17.1	98.4
Au/TiO$_2$	29.1	97.9	66.6	>99.5	16.1	>99.5	9.9	98.9
Au/TiO$_2$ + PVP[e]	55.0	96.5	75.6	>99.5	31.9	>99.5	21.2	98.3
Au/SBA-15	32.1	99.0	70.0	>99.5	11.0	>99.5	11.0	98.9
Au/SBA-15[f]	58.1	99.0	84.2	>99.5				
Au/SBA-15[g]	66.0	99.4	87.3	>99.5				
Au/SBA-15 + PVP[e]	59.0	99.0	91.3	>99.5	22.4	>99.5	25.0	99.2
Au/SBA-15 + PVP[fh]	79.6	99.1	97.5	>99.5				
Au/SBA-15 + PVP[gi]	93.2	98.0	99.0	>99.5				

[a]Reaction conditions: 1 mmol of alcohol, 3 mL of toluene solvent, 5 bar of oxygen, 30 mg of catalyst, 100°C, 3 h; [b]Reaction conditions: 1 mmol of alcohol, 3 mL of toluene solvent, 30 mg of catalyst, 80°C, 3 h; [c]Reaction conditions: 1 mmol of alcohol, 3 mL of toluene solvent, 30 mg of catalyst, 100°C, 5 h; [d]Reaction conditions: 1 mmol of alcohol, 3 mL of p-xylene solvent, 30 mg of catalyst, 120°C, 5 h; [e]15 mg of PVP was physically mixed with the catalysts; [f]60 mg of catalyst was used. The molar ratio of S/C (substrate/catalyst) is about 192; [g]120 mg of catalyst was used. The molar ratio of S/C (substrate/catalyst) is about 96; [h]30 mg of PVP was added; [i]60 mg of PVP was added.

quartz in the volume ratio of 1/1. The catalysts localized in the middle part of the reactor were pretreated with 20% O$_2$/He at 120°C for 1 h. The gas component of 1% CO/19% O$_2$/80% He was used as feed with GHSV at 70000 mL/g$_{Au}$/h. The productive gas was analyzed by a chromatograph equipped with thermal conductivity detector (TCD) and a column (TDX-1) at constant temperature of 90°C.

The oxidation of ethanol was carried out in a continuous-flow fixed-bed reactor with length of 400 mm and diameter of 6 mm. Pure oxygen was used as oxidant. Ethanol was introduced with a pump and the flow rate of oxygen was controlled by a flow instrument. The reactants and products were collected by cold trap and then analyzed by a gas chromatography equipped with FID detector and Agilent HP6890 Gas chromatography-mass spectrometry. The oxidation was performed with 30 mg of catalyst with 40–60 mesh diluted with 0.15 g of quartz sands (40–60 mesh), ethanol inlet rate of 0.1 mL/h, and O$_2$ flow rate of 6.8 mL/min.

3. Results and Discussion

The Au/C, Au/BN, Au/TiO$_2$, and Au/SBA-15 catalysts were synthesized according to the impregnation method using activated carbon, boron nitride, anatase, and mesoporous SBA-15 as support. By ICP analysis, the Au loading on Au/C, Au/BN, Au/TiO$_2$, and Au/SBA-15 is established to be 1.6, 1.6, 1.7, and 1.6 wt%, respectively.

The investigation in catalytic activity of these catalysts starts from the catalytic oxidation of various alcohols including benzyl alcohol, phenylethyl alcohol, cyclohexanol, and 1-hexanol. The catalytic data of various catalysts are summarized in Table 1. Interestingly, the PVP-modified Au catalysts (Figure 1, the presence of PVP on the Au sample

was confirmed by thermogravimetry analysis) always exhibit higher conversions than the catalysts without PVP. For example, in the oxidation of benzyl alcohol, Au/C, Au/BN, Au/TiO$_2$, and Au/SBA-15 give benzyl alcohol conversions at 16.2, 10.0, 29.1, and 32.1%, respectively. After adding small amount of PVP to the reaction liquor, the conversions of benzyl alcohol over PVP-modified Au/C, Au/BN, Au/TiO$_2$, and Au/SBA-15 could reach as high as 35.5, 21.9, 55.0, and 59.0%, respectively. Notably, the only difference between each catalyst in the couple (e.g., Au/SBA-15 and PVP-modified Au/SBA-15 catalysts) is the presence or absence of PVP species, which can completely avoid the influence of Au nanoparticle diameters for the catalytic reactions. Figure 1 shows the turnover frequencies (TOFs) over various catalysts in the oxidation of benzyl alcohol. The PVP-modified catalysts exhibit higher TOFs than the PVP-free ones, indicating the important role of PVP in enhancing the catalytic activities. Notably, this strategy in enhancing the catalytic activities of Au catalysts by PVP modification not only is limited to the oxidation of alcohols but also can be extended to the oxidation of other aromatic alcohols of phenylethyl alcohol and aliphatic alcohols of cyclohexanol and 1-hexanol. In these cases, significant enhanced catalytic activity and alcohol conversion could be obtained by simply adding PVP in the reaction liquor.

Notably, it is worth noting that the PVP enhanced the activities of Au/SBA-15 and Au/C more significantly than the activities of Au/BN and Au/TiO$_2$ (Figure 2). Considering the same amount of PVP was used in the reaction liquor of different catalysts, we rationally studied the adsorption of PVP on the solid catalysts in water solvent. Taking Au/SBA-15 and Au/TiO$_2$ as an example, the Au/SBA-15 adsorbed PVP continuously with the adsorption time, giving an adsorption
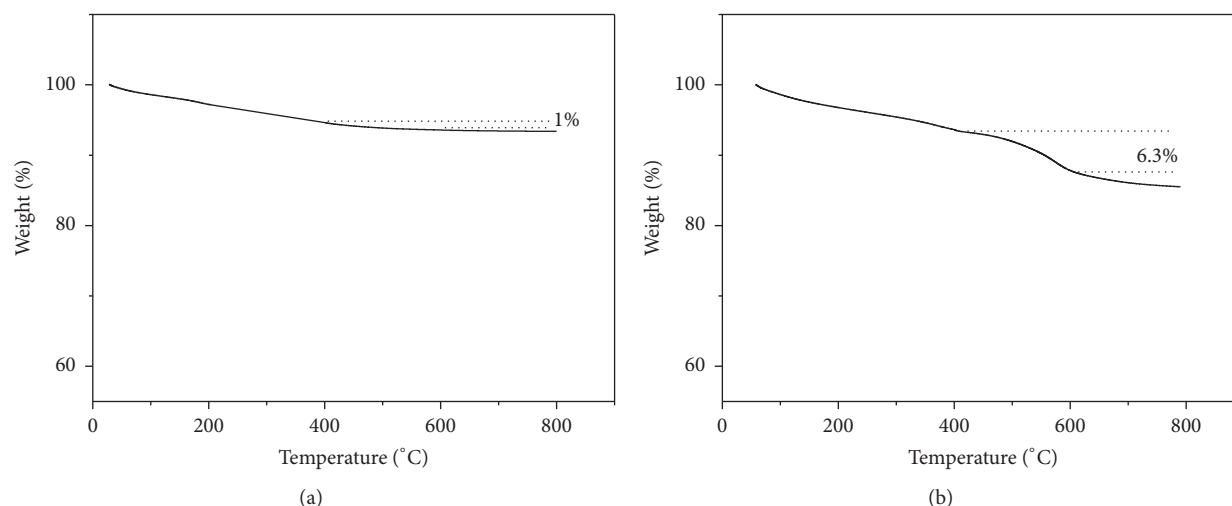
(a)

(b)

FIGURE 1: TG curves of the Au/TiO$_2$ before (a) and after (b) PVP modification. The significant weight decrease at 400 to 600 °C is attributed to the removal of PVP species. In contrast, the as-synthesized Au/TiO$_2$ gives the weight decrease at ~1% in the same temperature region, demonstrating the lack of PVP.
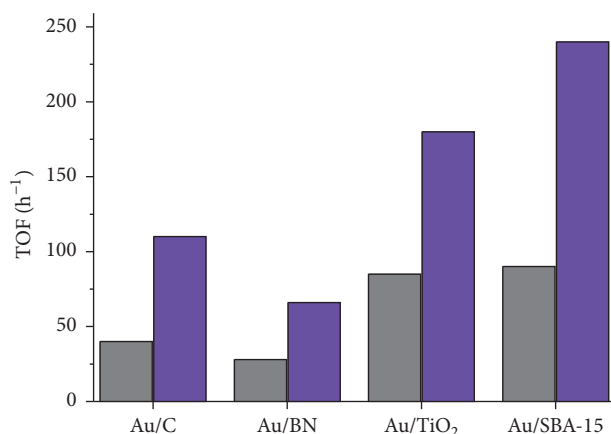

FIGURE 2: TOFs of various catalysts in the oxidation of benzyl alcohol. The gray and purple correspond to the as-synthesized and PVP-modified catalysts, respectively. Reaction conditions: 3 mmol of alcohol, 3 mL of toluene solvent, 5 bar of oxygen, and 10 mg of catalyst, 100°C, 20 min.

amount at ~125 mg/g in 60 min. In contrast, Au/TiO$_2$ only adsorbed a small amount at ~12 mg/g (Figure 3(a)). This phenomenon might be attributed to the rich mesoporosity of Au/SBA-15, which benefits the adsorption and enrichment of PVP in the mesopores. Therefore, the Au nanoparticles localized in the mesopores of SBA-15, as present in Figure 3(b) where the Au nanoparticle diameters are calculated to be at 2–10 nm with mean size at 3.6 nm, prefer to be modified by PVP.

Furthermore, we reasonably adjusted the molar ratio of substrate and PVP-modified Au/SBA-15 catalyst in the oxidation of benzyl alcohol and phenylethyl alcohol (Table 1). Clearly, in both cases, the alcohol conversions significantly increased with more Au species in the reaction system, which could reach as high as 93.2% for benzyl alcohol and 99.0%

for phenylethyl alcohol. But the PVP-modified catalysts are always more active than the PVP-free ones, demonstrating the positive role of PVP in promoting the reaction.

These results motivated us to study the role of PVP interacting with Au nanoparticles. Figure 4 shows the Au4f XPS spectra of Au/SBA-15 and PVP-modified Au/SBA-15 samples. The spectrum of Au/SBA-15 exhibits Au4f binding energy at 84.1 eV, which is the typical binding energy of metallic Au [12, 36]. Interestingly, after PVP-modification treatment, the Au4f binding energy is 83.4 eV, with a shift of 0.7 eV from the metallic Au. Considering the two samples have the same SBA-15 support and Au nanoparticles, the different binding energy should be reasonably attributed to the PVP additive. The negatively charged Au is known to be very active in the activation of molecule oxygen [37–39], thus exhibiting higher activities than the conventional PVP-free catalysts in the oxidation reactions.

Motivated by the successes in oxidation of alcohols in liquid phase, we then carried out the aerobic oxidation of ethanol in gas phase in a fixed-bed reactor, which is an important reaction for obtaining acetaldehyde. Figure 5 shows the dependence of ethanol conversion on time over as-synthesized and PVP-modified Au/SBA-15 catalysts. At a reaction temperature of 120°C (Figure 5(a)), which is a relatively low temperature for ethanol oxidation [40–42], the Au/SBA-15 catalyst is inactive for the reaction. Interestingly, the PVP-modified SBA-15 exhibits ethanol conversion at 12.4% with acetaldehyde (selectivity at >98.0) as a major product. In a reaction period of 11 h, the PVP-modified SBA-15 catalyst exhibits a constant conversion at ~12.0% with >98.0% selectivity of acetaldehyde. These results indicate the positive effect of PVP in enhancing the catalytic activity of Au catalyst in ethanol oxidation. When the reactions were performed at high temperature of 170°C, the ethanol conversions are higher than those at 120°C, where the PVP-modified Au/SBA-15 catalyst always exhibits higher ethanol
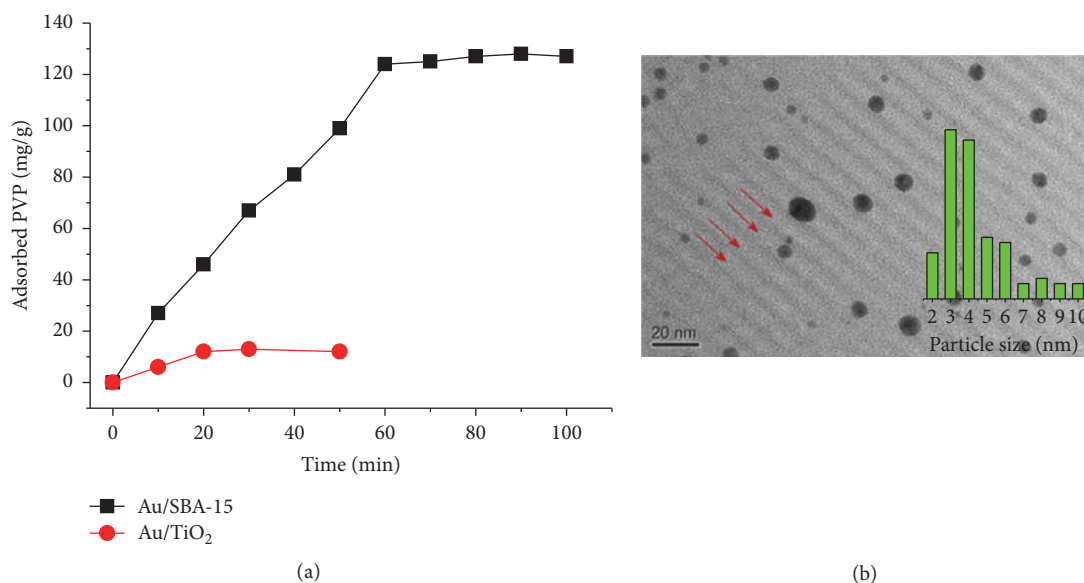
FIGURE 3: (a) Dependence of adsorption amount of PVP over Au/SBA-15 and Au/TiO$_2$ catalysts. (b) High-resolution TEM image of Au/SBA-15. The red arrows highlight the mesopores.
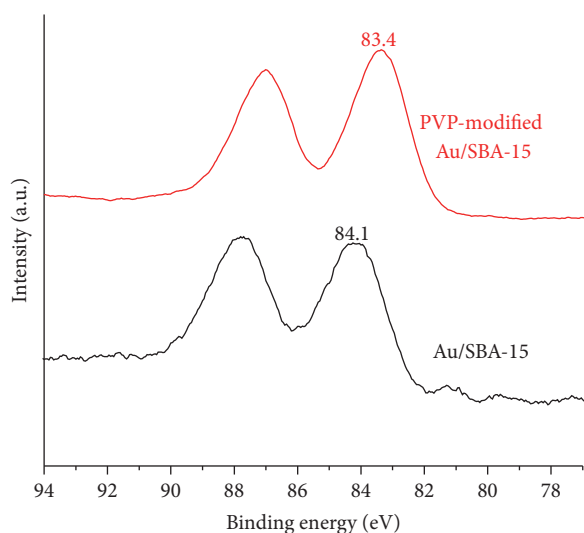

FIGURE 4: Au4f XPS spectra of Au/SBA-15 and PVP-modified Au/SBA-15.

conversion than the PVP-free Au/SBA-15, further confirming the promotion role of PVP. Notably, in the reaction after 12 h at 120°C or 6 h at 170°C, a significant decrease in ethanol conversion could be observed, which might be due to the leaching of PVP species during the reaction process. After retreatment of the catalyst using PVP, the catalyst activity was easily regenerated.

Furthermore, we extended the method of using PVP to enhance the catalytic activity to the oxidation of CO (Figure 6), which is an important reaction and widely investigated over various Au nanocatalysts. The silica supported Au nanoparticles are known as poorly active catalyst for the reaction because of the inert silica support. Similar phenomenon

could also be observed in the Au/SBA-15 catalyst, which exhibits very low CO conversion (<5%) at even 150°C. Interestingly, the CO conversion could be significantly enhanced after treating Au/SBA-15 with PVP, giving 12.8% at 150°C. Although this performance is not so good as the highly active metal oxides support Au nanoparticles in literature [43–45], it still gives clear evidence to confirm the positive effect of PVP in promoting the Au-catalyzed oxidation reaction, in good agreement with the results obtained from alcohol oxidation.

4. Conclusions

In summary, we demonstrate that adding PVP could effectively enhance the catalytic activity of supported Au nanoparticles, because the PVP could electronically interact with Au to form high active Au sites for molecular oxygen. Other catalysts with PVP modification are mostly soluble ones, which have significant disadvantages in separation and regeneration, particularly for the noble metal catalysts. Our work extended the concept of PVP modification and promotion to the supported Au nanoparticle catalysts, remarkably enhancing the activity of supported metal catalysts. The features of the PVP-modification method, including low cost, being easily available, general usability, and harmlessness of PVP, make it potentially important for wide applications. Although the PVP might leach during the reaction recycles, it could not pollute the products because the PVP could be easily separated from the product molecules due to its high molecule weight. The method involved in this work might be potentially important for developing more catalysts with enhanced activities in the future.

Conflicts of Interest

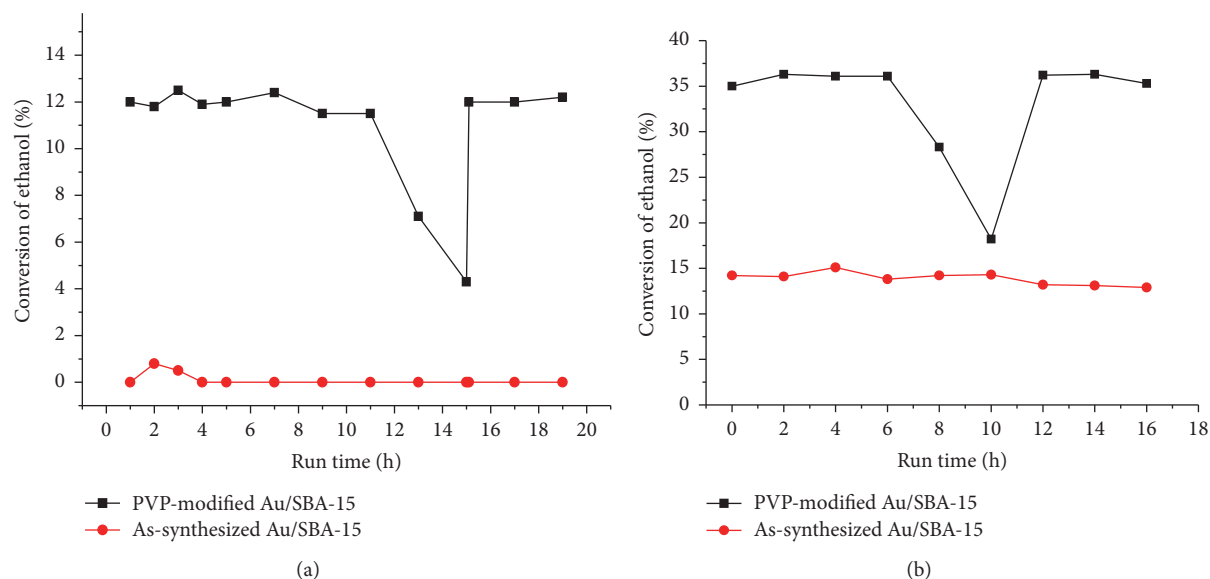The authors declare that they have no conflicts of interest.

(a)

(b)

FIGURE 5: Catalytic data in aerobic oxidation of ethanol over the Au catalysts at (a) 120 and (b) 170°C. In the case of PVP-modified Au/SBA-15, the deactivated catalyst was treated with PVP again after reaction for 15 h at 120°C and 10 h at 170°C and further used in the reaction. The acetaldehyde selectivities are over 98% at 120°C and over 95% at 170°C with acetic acid as by-product.
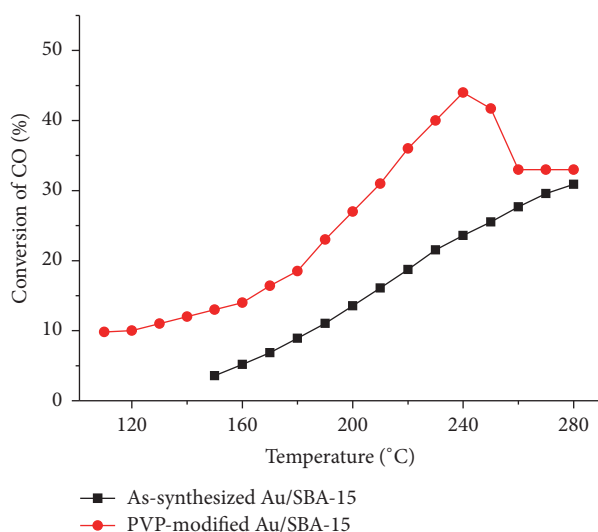

FIGURE 6: Catalytic oxidation of CO over the Au catalysts.

Acknowledgments

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