SCIENCE CHINA
Chemistry

• ARTICLES •

July 2010 Vol.53 No.7: 1571–1577
doi: 10.1007/s11426-010-3205-y

Selective hydrogenation of citral over Au-based bimetallic catalysts in supercritical carbon dioxide

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Received March 19, 2010; accepted April 21, 2010

Selective hydrogenation of citral was investigated over Au-based bimetallic catalysts in the environmentally benign supercritical carbon dioxide ($scCO_2$) medium. The catalytic performances were different in citral hydrogenation when Pd or Ru was mixed (physically and chemically) with Au. Compared with the corresponding monometallic catalyst, the total conversion and the selectivity to citronellal (CAL) were significantly enhanced over TiO_2 supported Pd and Au bimetallic catalysts (physically and chemically mixed); however, the conversion and selectivity did not change when Ru was physically mixed with Au catalyst compared to the monometallic Ru/TiO_2, and the chemically mixed $Ru-Au/TiO_2$ catalyst did not show any activity. The effect of CO_2 pressure on the conversion of citral and product selectivity was significantly different over the Au/TiO_2, $Pd-Au/TiO_2$, and Pd/TiO_2 catalysts. It was assumed to be ascribed to the difference in the interactions between Au, Pd nanoparticles and CO_2 under different CO_2 pressures.

supercritical CO_2, citral, hydrogenation, bimetallic catalysts, synergistic effects

1 Introduction

Supercritical carbon dioxide ($scCO_2$) as a benign medium has received much attention in chemistry and reaction engineering, because it satisfies several green chemistry and engineering principles such as pollution prevention, lower toxicity, and use of an "abundantly available" resource with no increase in environmental burden and easy separation from products through depressurization [1, 2]. In addition, CO_2 is chemically inert toward the substrates in most cases. Therefore, $scCO_2$ is regarded as a particular promising solvent for chemical reactions, especially, for the heterogeneous catalytic reactions involving gases such as H_2 and O_2, due to its complete miscibility with these gases, and the coke and products absorbed on the surface of catalysts can be removed by $scCO_2$, prolonging the life of the catalysts [3]. As reported, the tunable solvent properties of $scCO_2$ make it possible to adjust the reaction rate and product selectivity through changing pressure [4–6].

Recently, the use of Au in heterogeneous catalysis has attracted much attention in controlling product selectivity in hydrogenation reactions such as selective hydrogenation of unsaturated ketones [7], acrolein [8] and 1,3-butadiene [9], although the overall rate of hydrogenation reaction over Au catalysts is much lower compared with that over conventional Pd, Pt and Ni catalysts [10–14]. For example, it was reported that Au/TiO_2 was much less active than Pt/TiO_2, but it was highly selective to produce crotyl alcohol in hydrogenation of crotonaldehyde [15]. However, practical applications require the total activity of Au to be improved with the specific selectivity unchanged. Many attempts have been made to develop efficient Au-based catalyst, for example, alloying Au with other components to form bimetallic catalysts was an efficient way, as these bimetallic catalysts often show highly improved activity due to the geometric

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*Corresponding author (email: zhaofy@ciac.jl.cn) and electronic effects [16, 17]. The Au-Pd alloy catalysts showed superior activities compared to the monometallic Pd or Au nanoparticles in hydrogenation of aromatic compounds [18, 19], acetylene [20, 21], and hydrodehalogenation reactions [22–24]. Furthermore, it was reported that the incorporation of Au with Pd- or Pt-based catalysts could improve the resistance toward deactivation in hydrodesulphurization [25] and hydrogenation reactions [26] through preventing the formation of undesired carbon and/or CO deposits covering or adsorbing on active metallic surface. In our previous work, the TiO_2-supported physically and chemically mixed Au and Pd bimetallic catalysts showed significant synergetic effect on the reaction rate and the selectivity of citronellal during hydrogenation of citral in $scCO_2$. Compared with *n*-hexane solvent, the overall reaction rate was enhanced due to high H_2 solubility and fast mass transfer rate in $scCO_2$, and the selectivity to citronellal was improved due to the molecular interaction between CO_2 and the reactant [27].

The above results have stimulated us to conduct a further study on the reaction features of selective hydrogenation of citral over the Au-based catalysts in $scCO_2$. Our intention is to investigate the potentiality of Au in the Pd-Au/TiO_2 bimetallic catalyst and the effect of CO_2 pressure on the product selectivity and conversion in $scCO_2$.

2 Experimental

2.1 Catalyst preparation

Several supported monometallic and bimetallic catalysts were prepared using an anatase TiO_2 (surface area of 120 $m^2\,g^{-1}$) support supplied from Nanjing Haitai Nanomaterial Co. 1 wt% Au/TiO_2 monometallic catalyst was prepared by deposition-precipitation as reported in our previous work [27]. Typically, an aqueous solution of $HAuCl_4$ (Sinopharm Chemical Reagent Co., Ltd.) was prepared and its pH was adjusted to 10 with 5 M NaOH solution. The TiO_2 support was added to this solution with vigorous stirring and the resulting suspension was aged at room temperature for 2 h with stirring. An aqueous solution of $NaBH_4$ was dropwise added into this suspension with vigorous stirring. The $NaBH_4$ aqueous solution was prepared in an ice water bath, and the molar ratio of $NaBH_4$ to Au is 10. Upon the addition of the $NaBH_4$ solution, the color of the mixture turned to pink purple, indicating the reduction of the auric ions. After aging for 3 h, the solid materials were separated by centrifugation at 10000 rpm. The supernatant was clear and colorless. The precipitates obtained were washed thoroughly with deionized water and absolute ethanol and separated again by centrifugation. The washing and the centrifugation were repeated four times. Then, the solid materials were dried in a vacuum oven at 80 °C overnight.

1 wt% Pd/TiO_2 and 1 wt% Ru/TiO_2 catalysts were prepared by a wet impregnation method. A precursor $PdCl_2$ (Shanghai Reagent Co.,) was dissolved into an HCl solution and this $PdCl_2$ solution was diluted by deionized water. The support TiO_2 was added to this solution and the resulting slurry was vigorously stirred for 24 h at room temperature. After that, an ice cooled aqueous solution of $NaBH_4$ was added dropwise into this suspension with vigorous stirring. Upon the addition of the $NaBH_4$ solution, the color of the mixture turned gray, indicating the reduction of the palladium ions. After aging for 3 h, the solid materials were separated, washed, and dried in the same manner as described above for the Au/TiO_2 samples. Ru/TiO_2 catalyst was prepared with the same procedure except that the aqueous solution of $RuCl_3{\cdot}1.8H_2O$ (Aldrich) was used directly as a precursor without being dissolved in the HCl solution.

Bimetallic 0.5 wt%Pd-0.5 wt%Au/TiO_2 catalyst was prepared by co-impregnation method and reduced by $NaBH_4$ in similar procedures as used for the monometallic Pd/TiO_2 catalyst.

2.2 Activity test

The catalytic performance of the catalysts listed in Table 1

Table 1 Results of hydrogenation of citral over various TiO_2-supported Pd, Ru, and Au catalysts in $scCO_2$ a)

Entry	Catalyst	Time (h)	Conversion (%)	Selectivity (%)					
				DCAL	CAL	COL	G & N	IOL	others
1	Au/TiO_2	4	6	8	70	3	16	3	0
2	Pd/TiO_2	4	27	4	78	4	8	5	1
3	Ru/TiO_2	4	15	8	61	5	22	3	2
4	Pd/TiO_2+Au/TiO_2	1	69	4	90	1	4	1	0
5	Ru/TiO_2+Au/TiO_2	4	16	6	57	4	23	3	8
6	Pd-Au/TiO_2	4	51	13	61	4	2	21	0
7	Pd-Au/TiO_2 b)	4	49	10	62	2	1	25	0

a) Reaction conditions: citral, 2 mmol; H_2 4 MPa; CO_2 8 MPa; 80 °C, catalyst weight 25 mg for monometallic catalysts, 50 mg for bimetallic catalysts, 25 mg for each physically mixed catalyst. The total metal loading of the catalysts used was 1 wt%, and each metal is 0.5 wt% in the bimetallic catalysts. b) is the recycling of the catalyst used in entry 6.

was tested for the selective hydrogenation of citral. The reaction runs were carried out in a stainless steel batch reactor (50 cm^3). Certain amounts of citral and the catalysts were added into the reactor and the reactor was sealed and flushed with 2 MPa CO_2 at least three times. Then, the reactor was heated up to 80 °C and introduced with 4 MPa H_2 first and then the desired pressure CO_2 with a high-pressure liquid pump. The reaction was started with a continuous agitation at a speed of 800 rpm, where the mass transfer resistance was neglected, as confirmed in our previous work [28]. At the end of the reaction, the reactor was cooled to room temperature and the gases (H_2 and CO_2) were vented. Finally, the reaction mixture was extracted with *n*-hexane. The resulting solutions were analyzed with gas chromatography (GC-Shimadza-14C, FID, Capillary column Rtx-Wax 30 m 0.53 mm 0.25 mm) and gas chromatography/mass spectrometry (GC/MS, Agilent 5890).

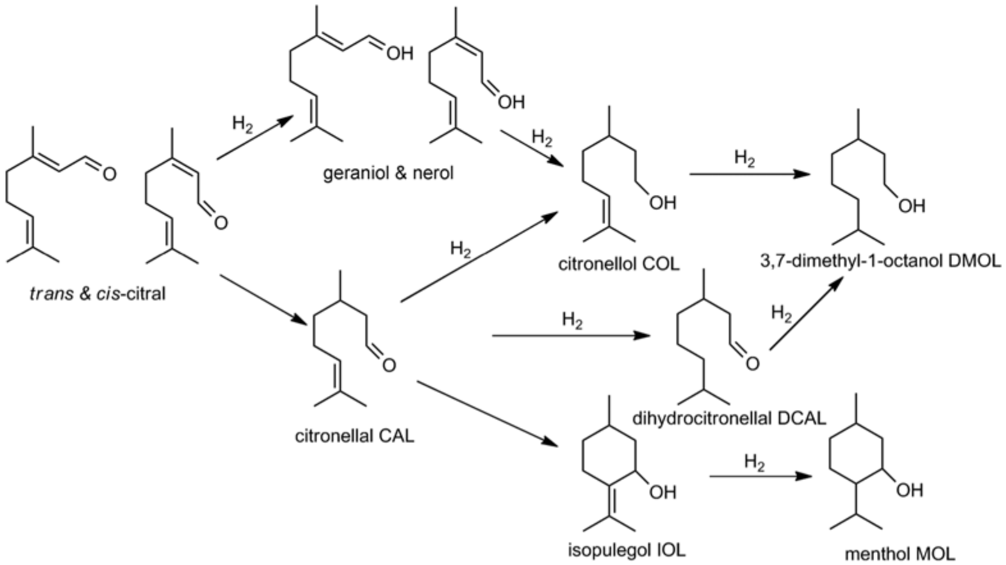
3 Results and discussion

3.1 Catalytic performance of the TiO_2-supported metallic catalysts

The lattice of Pd and Au is similar. Au and Pd both have a face-centered-cubic structure and these two components are completely miscible over the entire range, while Au and Ru are essentially completely immiscible in the bulk, and the crystal structures of them are different, with ruthenium having a hexagonal-close-packed structure [29]. In this work, Pd and Ru were chosen to mix with Au, forming bimetallic catalysts, and different catalytic performances were expected.

The catalytic performances of the TiO_2-supported Pd, Ru, and Au catalysts were evaluated in selective hydrogenation of citral in $scCO_2$. Citral hydrogenation is a significant reaction in the flavor, fragrance and pharmaceutical industries. The hydrogenation of citral is a complex reaction with various products such as citronellal (CAL), citronellol (COL), geraniol & nerol (G & N), menthol (MOL) and others shown in Scheme 1. Thus, it was often selected as a model reaction to test the performance of catalysts [30]. The hydrogenation results obtained are listed in Table 1.

The monometallic Au/TiO_2 was even less active, giving 6% conversion of citral and 70% selectivity of CAL, which was produced from hydrogenation of conjugated C=C bond (Table 1, entry 1). Pd/TiO_2 and Ru/TiO_2 were slightly more active than Au/TiO_2 catalyst, giving 27% and 15% conversion of citral, which are three times and twice as high as that over 1 wt% Au/TiO_2 under the same conditions, respectively. The difference in the total conversion of citral was ascribed to the capacity of hydrogen dissociation over the above active metal components. The selectivity to CAL was 78% for Pd/TiO_2 catalyst, which was higher than that for Ru/TiO_2 (61%). When the same quantities of Au/TiO_2 and Pd/TiO_2 were physically mixed and used for the reaction (Table 1, entry 4), the conversion of citral hydrogenation for 1 h was enhanced sharply to 69%, and the selectivity to CAL was increased to 90%. The synergistic effect and hydrogen spillover over the bimetallic catalysts were confirmed to be responsible for the enhancement in conversion and selectivity as reported in our previous work [27]. By contrast, the conversion and product selectivity did not change so much for the physically mixed Ru/TiO_2 and Au/TiO_2 catalysts compared with the monometallic Ru/TiO_2. The chemically mixed Ru-Au/TiO_2 bimetallic catalysts were almost inert in citral hydrogenation under the conditions used (the results were not given). However, the chemically mixed Pd-Au/TiO_2 bimetallic catalyst presented a large



Scheme 1 Network of citral hydrogenation.

conversion (51%), which is eight times higher than that of monometallic Au/TiO_2, while the selectivity to CAL decreased to 61%, along with an increase in the selectivity to DCAL and isopulegol (IOL). It suggested that the catalytic performance depended on the nature of metal atoms on the surface of the catalysts (physically and chemically mixed). The recycling of bimetallic Pd-Au/TiO_2 catalyst was also investigated (Table 1, entries 6 and 7). Compared with the results for the first run (Table 1, entry 6), the conversion of citral and product selectivity did not change in the second run (Table 1, entry 7). The particle size of bimetallic Pd-Au/TiO_2 catalyst after the second run was almost unchanged, being about 1–2 nm, similar to the fresh one as shown in Figure 1.

3.2 Effect of CO_2 pressure

Figure 2 shows the effect of CO_2 pressure on the conversion and product selectivity of citral hydrogenation over bimetallic Pd-Au/TiO_2 and physical mixture of Au/TiO_2 and Pd/TiO_2 catalysts in the presence of 4 MPa H_2 at 80 °C, respectively. For the bimetallic Pd-Au/TiO_2 catalyst, the total conversion of citral increased from 51% to 72% when the CO_2 pressure changed from 6 to 12 MPa, but it decreased sharply when CO_2 pressure was above 12 MPa. With respect to the product selectivity, in the subcritical region (6 MPa CO_2) the selectivity to CAL was 61%, and it was around 55% almost independent on CO_2 pressure in the supercritical region. CO_2 pressure showed different effects over the physical mixture Au/TiO_2 and Pd/TiO_2 catalysts. The conversion decreased gradually from 56% to 40% with CO_2 pressure in the range investigated, and the selectivity of citronellal increased from ~62% to ~73%.

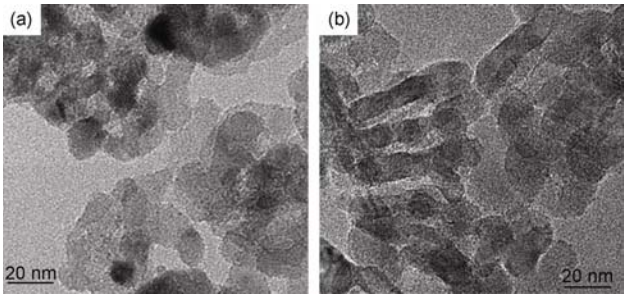


Figure 1 TEM image of bimetallic Au-Pd/TiO_2. (a) The fresh sample; (b) after the second run.

For comparison, the effects of CO_2 pressure on the monometallic Pd/TiO_2 and Au/TiO_2 catalysts were also investigated under the same conditions, and the results are shown in Figures 3(a) and (b). A strong influence of CO_2 pressure has been observed on the conversion and product selectivity. For the monometallic Pd/TiO_2 catalyst, the conversion increased from 54% to 68% and the selectivity of CAL did not change as the CO_2 pressure changed from 6 to 8 MPa, but the conversion deceased significantly from 68% to 25% when CO_2 pressure was enhanced from 8 to 14 MPa. Meanwhile the selectivity of CAL increased from 51% to 74%, along with a decrease in the selectivity of DCAL and IOL. As reported in our previous work, 2 mmol of citral can be completely solubilized into 8 MPa CO_2 in the presence of 4 MPa H_2 at 80 °C [31, 32]. The initial increase of conversion is attributed to the increase of substrate concentration in $scCO_2$ phase and the elimination of the phase transfer resistance at 8 MPa (homogeneous formed), and the dilution effect might result in the following successive decrease of conversion.

For the monometallic Au/TiO_2 catalyst, the conversion of citral showed a volcano-trend as CO_2 pressure increased, which was similar to the results of the chemically mixed bimetallic catalyst of Au-Pd/TiO_2. The conversion over Au/TiO_2 catalyst reached the maximum at 12 MPa CO_2, which was the same with the case of Au-Pd/TiO_2. However, for Pd/TiO_2 catalyst, the maximum conversion appeared at 8 MPa. With respect to the product distribution, CAL was produced as the main product over the above three catalysts, and the selectivity to CAL increased slightly from 47% to 57% as CO_2 pressure increased. It indicated that the catalytic feature of the bimetallic Pd-Au/TiO_2 catalyst behaved more like Au/TiO_2, as the present Pd-Au/TiO_2 catalyst was surface-rich with Au from the EDS measurement (Figure 4).

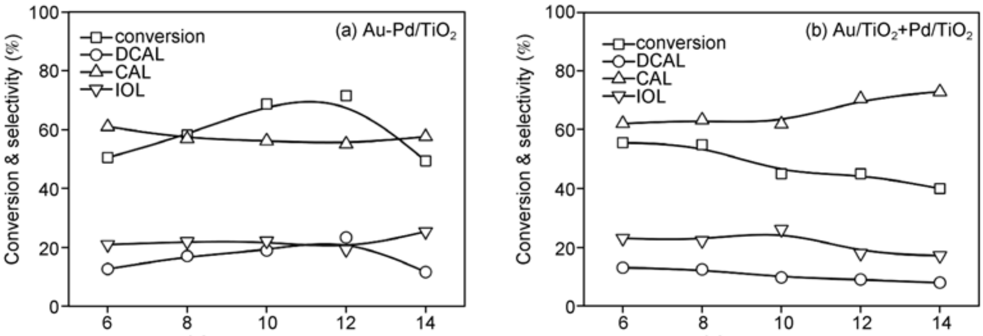


Figure 2 Effect of CO_2 pressure on conversion and selectivity in hydrogenation of citral over (a) bimetallic Pd-Au/TiO_2, (b) physical mixture of Au/TiO_2 and Pd/TiO_2. Reaction conditions: citral 2 mmol, H_2 4 MPa, 80 °C; (a) Pd-Au/TiO_2 50 mg, 4 h; (b) Au/TiO_2 20 mg, Pd/TiO_2 20 mg, 2 h.

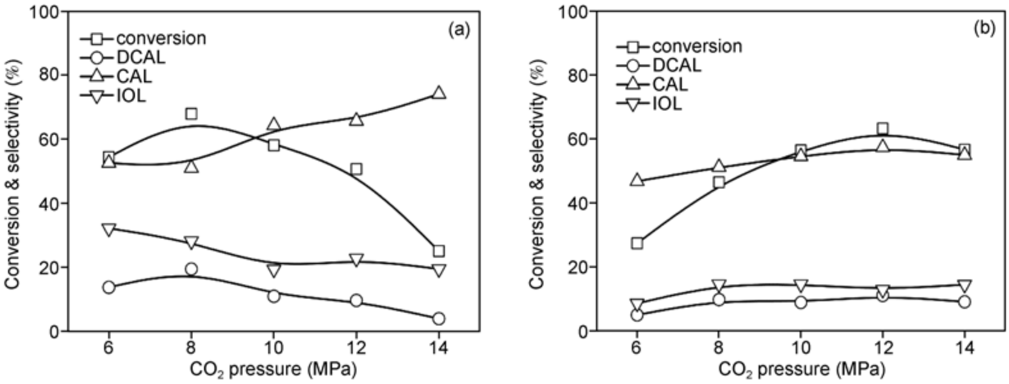


Figure 3 Effect of CO_2 pressure on the conversion and selectivity in hydrogenation of citral over the monometallic Pd/TiO_2 and Au/TiO_2. Reaction conditions: H_2 4 MPa, 4 h, 80 °C; (a) Pd/TiO_2 citral 2 mmol, catalyst 50 mg; (b) Au/TiO_2, citral 0.6 mmol, catalyst 100 mg.

By contrast, the catalytic performance of the physical mixture of Au/TiO_2 and Pd/TiO_2 was different from bimetallic Pd-Au/TiO_2 catalyst, but it behaved as the simple sum of two monometallic Pd and Au samples from the results of the influence of CO_2 pressure.

The electronic state of supported Au and Pd nanoparticles was assumed to be influenced by CO_2 pressure and then affected the activity, resulting in the maximum conversion appearing at different CO_2 pressures. We have tried to use XPS spectra to analyze the electronic state of Au and Pd nanoparticles supported on TiO_2, however, no signal was observed due to the low metal loading. It was reported that the electron density of gold and silver metal particles decreased with increasing CO_2 pressure in scCO_2 from the shift of the wavelength of their maximum plasmon optical absorption [33, 34]. It was also reported that the electronic state of supported platinum particles could be affected by the scCO_2 solvent in selective hydrogenation of α,β-unsaturated aldehydes over supported platinum catalysts [35, 36], in which the conversion and selectivity to unsaturated alcohols in scCO_2 were higher than those in ethanol and also increased with an increase of CO_2 pressure. The authors claimed that the interaction between metal particles and CO_2 could promote the adsorption of the α,β-unsaturated aldehydes on the platinum particles with π electrons of their C=O bonds, enhancing the hydrogenation of C=O bonds. The evolution of the product distribution is closely related to the working state of the catalytic systems and the stability of intermediate species on the catalyst surfaces at a particular pressure of CO_2. It was reported that the product distribution of citral hydrogenation strongly depended on CO_2 pressure over micelle-hosted Pd and Ru nanoparticles in scCO_2. The authors pointed out that at lower pressure, although in a supercritical state, the density of the fluid is close to a gas-like phase, and the volatile citral molecules can easily gain access to the catalyst surface and be exhaustively hydrogenated to DCAL before its desorption to the mobile phase. However, at higher pressure, the fluid becomes more liquid-like, enabling solubility of chemical species therein. This enhances desorption of partially hydrogenated intermediate species from the metal surface to the mobile phase [37, 38]. Another example is the hydrogenation of 4-*tert*-butylphenol over Rh/C in scCO_2. As the CO_2 pressure increased, the selectivities to *cis*- and *trans*-4-*tert*-butylcyclohexanol decreased, whereas the selectivity to 4-*tert*-butylcyclohexanone increased due to the higher solubility of the intermediate product 4-*tert*-butylcyclohexene-1-ol at higher CO_2 pressures, resulting in its further hydrogenation to 4-*tert*-butylcyclohexanone [39]. The similar effect also appeared in hydrogenation of naphthalene and tetralin in scCO_2 [40–42]. In addition, the adsorption mode of the reactants on the surface of the catalysts can be tuned through changing CO_2 pressure, resulting in a variation in product distribution. Chatterjee *et al.* [43] reported that compared with ethanol solvent, the scCO_2 medium promoted the selective formation of cyclohexanone (~98%) and the selectivity to cyclohexanone increased as CO_2 pressure increased in the hydrogenation of phenol over palladium supported Al-MCM-41 catalyst. They suggested that scCO_2 is a quadrupolar solvent and the interaction between CO_2 and phenol will be weaker than that for ethanol-phenol with more phenol attracted to the catalyst active site in scCO_2. As a result, phenol was preferred to adsorb on the catalyst

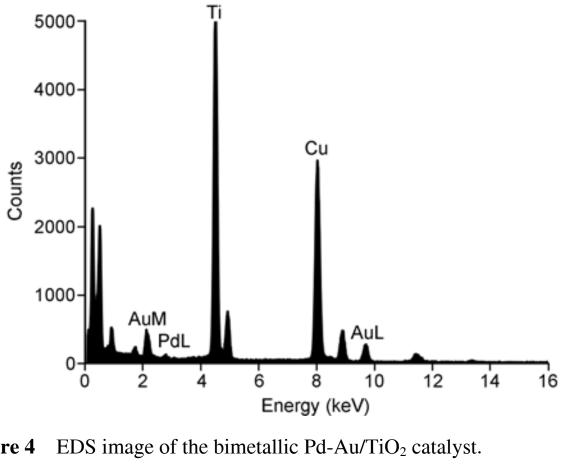


Figure 4 EDS image of the bimetallic Pd-Au/TiO_2 catalyst.

surface in a non-planar way to produce cyclohexanone. It was suggested that the improvement in the product selectivity and reaction rate in $scCO_2$ was possibly because the CO_2 molecule may act as a modifier on the catalyst surface to block the active sites for a certain reaction step. For example, when hydrogenation of halonitroaromatics was carried out over supported Pt catalysts in $scCO_2$, CO generated from CO_2 during the reaction might preferentially cover the active sites for dehalogenation of halonitroaromatics, resulting in a significant increase in halo-aniline selectivity [44]. Recently, Han *et al*. reported that CO_2 could serve as a weak Lewis acid to promote the selectivity of cyclohexanone significantly in the selective hydrogenation of phenol [45]. The true reason for the improvement in selectivity and conversion along with CO_2 pressure is still a debatable issue as mentioned previously, but there is no doubt that the CO_2 pressure has a strong influence, and in most cases the effects are positive as we expected.

The product selectivity was related with conversion, so the changes of product selectivity with conversion over Pd-Au/TiO_2 in the hydrogenation of citral are given in Figure 5. The selectivity to CAL was around 60% at the conversions lower than 70%, and it decreased as the conversion further increased, for that CAL was deeply hydrogenated to DCAL (complete hydrogenation of C=C bonds). For the Pd/TiO_2 catalyst, the selectivity to CAL decreased linearly with the conversion, as the subsequent hydrogenation of CAL was relatively easy on the surface of Pd/TiO_2 [46]. It was reported that DCAL was produced almost in 100% selectivity over the supported Pd catalysts in $scCO_2$. Those results indicated that the presence of Au in the bimetallic Pd-Au/TiO_2 catalyst could improve the selectivity of CAL in $scCO_2$ [47].

4 Conclusions

In summary, it has been demonstrated that significant difference in synergistic effect between Au and Pd, Ru appeared in selective hydrogenation of citral in $scCO_2$ when the physically and chemically mixed TiO_2-supported Pd, Ru, and Au catalysts were used. The catalytic activity increased when Au was mixed with Pd catalyst irrespective of the physical or chemical mix, while the activity was the same when Au was physically mixed with Ru catalyst, but it even disappeared with the chemically mixed Au-Ru/TiO_2 catalyst. The effect of CO_2 pressure on conversion of citral and product selectivity was significantly different for Au/TiO_2, Pd-Au/TiO_2, Pd/TiO_2 and Au/TiO_2+Pd/TiO_2 catalysts, with the maximum conversion appearing at 12 MPa CO_2 for the first two catalysts and at 8 MPa CO_2 for Pd/TiO_2 catalyst, but for the physical mixture of Au/TiO_2+Pd/TiO_2, the conversion decreased slowly with CO_2 pressure. It was assumed that the difference in the interaction of Au, Pd nanoparticles with CO_2 would affect the activity of the catalysts at different CO_2 pressures, which needs further investigation and discussion.

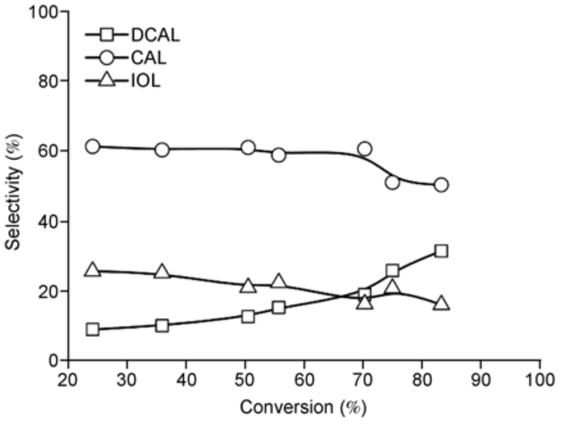


Figure 5 Plots of selectivity against conversion for selective hydrogenation of citral over the bimetallic Pd-Au/TiO_2 catalyst. Reaction condition: citral 2 mmol, Pd-Au/TiO_2, 50 mg, H_2, 4 MPa, CO_2, 8 MPa, 80 °C.

This work was financially supported by the One Hundred Talents Program and YW.H16 from the Chinese Academy of Sciences, the National Natural Science Foundation of China (20573104), and the CAS-JSPS International Joint Project GJHZ05.

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