



Physically and chemically mixed TiO₂-supported Pd and Au catalysts: unexpected synergistic effects on selective hydrogenation of citral in supercritical CO₂

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ABSTRACT

The selective hydrogenation of citral was studied with various TiO₂-supported monometallic and bimetallic Pd and Au catalysts and their physical mixtures in supercritical CO₂ (scCO₂). Significant synergistic effects appeared when active Pd species was chemically or physically mixed with less active Au species. The total rate of conversion was greatly enhanced and the selectivity to citronellal (CAL) was improved. The physical properties of those catalysts were characterized by TEM, HRTEM-EDS, XPS, and UV/Vis and their features of H₂ desorption were examined by TPD. The physical and chemical characterization results were used to discuss the reasons for the unexpected synergistic effects observed. The same selective hydrogenation was also conducted in a conventional non-polar organic solvent of *n*-hexane to examine the roles of scCO₂. The use of scCO₂ was effective for accelerating the hydrogenation of citral and improving the selectivity to CAL.

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1. Introduction

The use of Au in heterogeneous catalysis has been attracting much attention [1,2], since the discovery that Au is catalytically effective for low temperature oxidation of CO [3]. Although the overall rate of hydrogenation reaction with Au is smaller compared with conventional Pd, Pt, and Ni catalysts [4–8], the application of Au catalysts would be interesting for selective hydrogenation in which the control of product selectivity is more important. In the literature, several authors have applied Au catalysts for selective hydrogenation of unsaturated ketones [9–11], acrolein [12–14], and 1,3-butadiene [15]. It is noted for hydrogenation of crotonaldehyde, for example, that Au/TiO₂ is even less active than Pt/TiO₂ but it is highly selective for the production of the corresponding unsaturated alcohol, crotyl alcohol [16]. It is also reported that the reaction with Au/TiO₂ is structure sensitive and the specific activity (turnover frequency) of small Au particles (ca. 2 nm) is larger by a factor of 7 compared with that of larger Au particles (4–9 nm). The practical application of Au catalysts for hydrogenation reac-

tions is interesting but, at present, it is still desired that the total activity should be improved while keeping the specific selectivity unchanged. One way is to prepare the efficient Au-based catalysts by alloying Au with other components, and such modified catalysts may show unexpected catalytic features due to geometric and electronic effects [4,6,17,18]. The former effect involves the variation in composition, configuration, and availability of active sites for a given reaction and the latter involves electronic interactions between electronically dissimilar components. For acetylene hydrogenation, for example, a Pd-promoted Au/TiO₂ catalyst exhibits significantly higher ethylene selectivity and stability compared with monometallic Pd/TiO₂ [19,20]. Another efficient way is physical mixing of Au catalysts with others. However, only a few studies on the physical mixtures of supported Au catalysts with other ones have appeared until now [21–24]. It was reported that a physical mixture of Au/Al₂O₃ + Pd/Al₂O₃ showed higher reaction rate and different selectivity compared with the monometallic Au/Al₂O₃ and Pd/Al₂O₃ catalysts and with chemically mixed Au–Pd/Al₂O₃ bimetallic catalysts in gas-phase hydrogenation of *p*-chloronitrobenzene [22]. In some cases, the mixing of supported metal catalysts and metal-free support materials is also effective. The incorporation of Au/ZnO with ZnO, Al₂O₃, or zeolite-Y drastically altered the product distribution in low-pressure synthesis of

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methanol and dimethyl ether from syngas [21]. Methanol was produced over ZnO and dimethyl ether on Al₂O₃ and zeolite-Y, whereas methane was produced over the physical mixture of Al₂O₃ and zeolite-Y with Au/ZnO catalysts. The mixture of Pt/Al₂O₃ and Al₂O₃ showed an enhanced activity for hydrogenation of benzene, compared with monometallic Pt/Al₂O₃, due to hydrogen spillover effect [25].

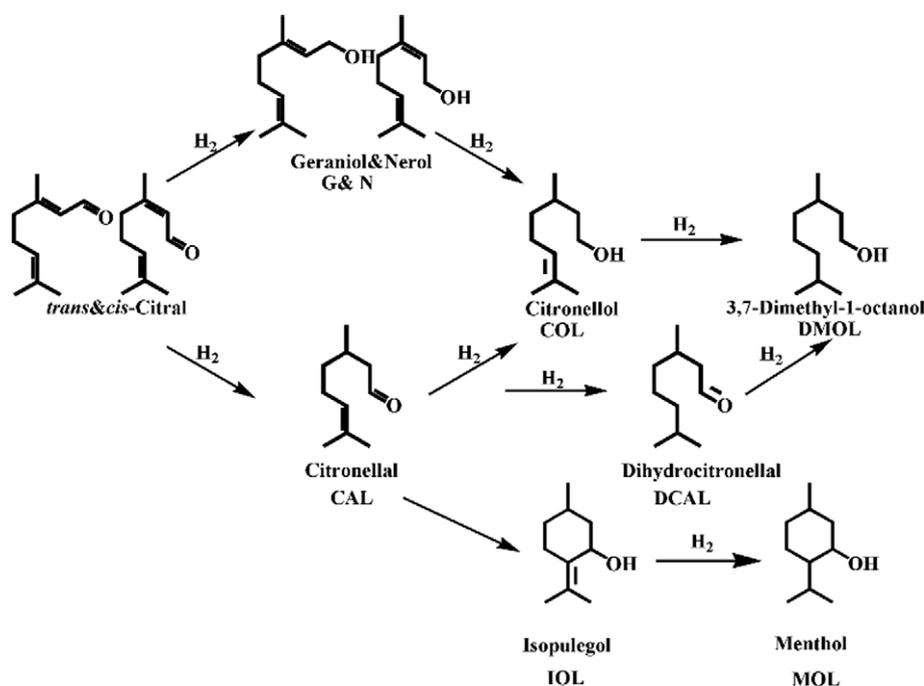
The above-mentioned results have stimulated us to make a comparative study on the performance of chemically and physically mixed Au/TiO₂ and Pd/TiO₂ catalysts in a green medium of scCO₂. Our intention was to exploit a highly active and selective catalytic hydrogenation system for hydrogenation of citral using the intrinsic high performance of Pd, the potentiality of Au to control the product selectivity, and the interesting functions of scCO₂ [26]. Selective hydrogenation of citral is an important reaction in the flavor, fragrance, and pharmaceutical industries. The reaction pathways of hydrogenation of citral are complicated, giving various products such as citronellal, citronellol, geraniol, nerol, menthol, and others through hydrogenation reactions of C=C and C=O bonds involved (Scheme 1). It is therefore important to control the product selectivity as well as the overall conversion in the citral hydrogenation, and thus it was selected as a model reaction for testing the performance of catalysts [27]. In the literature, only a few works were reported on hydrogenation reactions with binary Au–Pd catalysts [4,20,22,28–37], including hydrogenation of aromatic compounds [4,28,29], acetylene [20,35,36], 1,3-butadiene [33], and hydrodehalogenation reaction of CCl₂F₂ and C₂HCl₃ over supported Au–Pd bimetallic catalysts [31,32,37]. It was reported that the selectivity toward the desired product was increased upon introducing Au to Pd and this enhancement was strongly dependent on the alloying degree of Pd–Au bimetallic catalysts. The addition of Au was also reported to have positive impacts on Pd- or Pt-based catalysts in oxidation [38], hydrodesulfurization [4,34], and hydrogenation reactions [20]. It is pointed out that the incorporation of Au could improve the resistance toward deactivation, through preventing the undesired formation of carbon deposits covering active metallic surface.

In the present work, the authors prepared TiO₂-supported monometallic and bimetallic catalysts containing Au and/or Pd and their physically mixed catalysts. Those catalysts were studied for the selective hydrogenation of citral in scCO₂ and a conventional organic solvent of *n*-hexane. The activities of these Au and/or Pd catalysts were compared to give light on the possibility of synergistic effects of physical and chemical mixture of Au and Pd on the selective hydrogenation. It has been found that significant synergistic effects appear for physically mixed systems of Au/TiO₂ and Pd/TiO₂ catalysts and for those of monometallic Pd or bimetallic Au–Pd catalysts and metal-free TiO₂ support. The properties of the single and mixed metal catalysts were also characterized by various techniques and the causes of the synergistic effects observed were discussed by chemical state and size of supported metal particles, the distribution of metal species on the surface of metal particles, and their effects on hydrogen adsorption and spillover.

2. Experimental

2.1. Catalyst preparation

Various supported monometallic and bimetallic Au and Pd catalysts were prepared using a commercial anatase TiO₂ with a surface area of 120 m² g⁻¹, supplied from Nanjing Haitai Nanomaterial Co. Monometallic Au/TiO₂ catalysts were prepared by deposition-precipitation. Typically, an aqueous solution of HAuCl₄ (Sinopharm Chemical Reagent Co. Ltd.) was prepared and its pH was adjusted to 10 with 5 M NaOH solution. The TiO₂ support was added to this solution with vigorous stirring and the resulting suspension was aged at room temperature for 2 h while stirring. An aqueous solution of NaBH₄, which was prepared in an ice water bath, was dropwise added into this suspension with vigorous stirring until the final molar ratio of NaBH₄ to Au reached 10. On the addition of the NaBH₄ solution, the color of the mixture turned to pink purple, indicating the reduction of the auric ion. After aging



Scheme 1. Network of citral hydrogenation.

for 3 h, the solid materials were separated by centrifugation at 10,000 rpm. The supernatant was clear and colorless. The precipitates obtained were washed thoroughly with deionized water and absolute ethanol, and the solid materials were again separated 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. These catalysts so prepared will be referred to as Au(0)/TiO₂.

Monometallic Pd/TiO₂ catalysts were prepared by a wet impregnation method. A precursor PdCl₂ (Shanghai Reagent Co.) was dissolved in an HCl solution and this PdCl₂ solution was diluted by deionized water. The support TiO₂ was added to this solution and the resulting slurry was vigorously stirred for 24 h at room temperature. The solid materials were separated, washed, and dried in the same manner as described above for the Au(0)/TiO₂ samples. The Pd/TiO₂ samples so prepared were reduced in H₂ (99.999%) stream at 300 °C for 3 h. These Pd catalyst samples before and after the reduction will be referred to as Pd(2)/TiO₂ and Pd(0)/TiO₂.

Bimetallic catalysts were prepared by loading Pd onto Au(0)/TiO₂ samples in similar procedures as used for the preparation of monometallic Pd samples. The bimetallic samples so prepared will be referred to as Pd(2)/Au(0)/TiO₂ and Pd(0)/Au(0)/TiO₂ for unreduced and reduced (with H₂) ones, respectively. The properties of the monometallic and bimetallic Au and Pd catalysts prepared are given in Table 1. In the present sample abbreviations, 0 and 2 in the parentheses simply indicate the presence and absence of reduction procedures, respectively, but not the oxidation state correctly.

2.2. Activity test

The catalytic performance of the catalysts listed in Table 1 and their physical mixtures were tested for the selective hydrogenation of citral (Scheme 1). The reaction runs were carried out in a stainless steel batch reactor (50 cm³). Certain amounts of citral and catalysts were added into the reactor and the reactor was sealed and flushed with 2 MPa CO₂ at least three times. Then, the reactor was heated up to 80 °C and introduced with 4 MPa H₂ first and then with 8 MPa CO₂ with a high-pressure liquid pump. The reaction was started with a continuous agitation at a speed of 800 rpm, at which the mass transfer resistance was neglected, as confirmed in our previous work [39]. At the end of reaction, the reactor was cooled to room temperature and the gases (H₂ and CO₂) were vented. Finally, the reaction mixture was extracted with *n*-hexane. The resulting solutions were analyzed with gas chromatography (GC-Shimadzu-14C, FID, Capillary column Rtx-Wax 30 m–

0.53 mm–0.25 μm) and gas chromatography/mass spectrometry (GC/MS, Agilent 5890). For the reaction runs in *n*-hexane, the same procedures were used, except for the introduction of CO₂.

2.3. Catalyst characterization

The metal loadings were determined by inductively coupled plasma-optical emission spectrometry (ICP-MS; Thermo Scientific ICAP6000, USA) after the extraction of metal species from the support by aqua regia. The structural properties of the supported monometallic and bimetallic particles were analyzed by high-resolution TEM (JEOL 100 CX II microscope) along with EDX. The TEM samples were prepared by dispersing the catalyst powder in ethanol under ultrasonic and then allowing a drop of the suspension to evaporate on copper grids covered with holey carbon film. Diffuse reflectance UV/Vis spectra were recorded with a Shimadzu UV-3100 PC spectrophotometer. X-ray photoelectron spectroscopy (XPS, VG Microtech 3000 Multilab) was used to examine the electronic properties of the supported metal catalysts.

The H₂ adsorption/desorption behavior was examined by temperature-programmed desorption (TPD). A single or multi-component catalyst sample was loaded into a U-shaped pyrex glass cell. The weight of sample used was 30 mg for a single component catalyst and 15 mg + 15 mg for a mixture of binary component catalysts. The sample was pretreated with Ar stream at about 20 cm³ min⁻¹ and at 50 °C for 30 min. Then, the sample was exposed to pure H₂ stream at 20 cm³ min⁻¹ and at room temperature for 60 min. After that, the physisorbed H₂ was removed by pure Ar stream until TCD response became stable. For TPD, the sample was heated up to 550 °C at a rate of 5 K/min while passing pure Ar at 20 cm³ min⁻¹. The amount of H₂ desorbing was measured at several-minute intervals by GC with TCD. The catalyst samples used for the hydrogenation runs as listed in Table 1 were also tried for the TPD measurements. For some samples, however, significant desorption of H₂ was not detected. So, different catalysts were prepared in the same manner and used for TPD, in which the loading of Au was similar but that of Pd was larger: 0.56 wt% Pd/TiO₂ and 0.71 wt% Pd/1.66 wt% Au(0)/TiO₂.

3. Results and discussion

3.1. Physical properties of catalysts

Various chemically and physically mixed Au and Pd catalysts were prepared. Table 1 lists the metal loading and particle size of the monometallic and bimetallic catalysts prepared with different reduction processes. The supported metal particles were examined by TEM (Fig. 1). The Pd particle size of Pd(0)/TiO₂ reduced at 300 °C was small (1 nm). It was difficult to differentiate the particles for unreduced Pd(2)/TiO₂ sample, probably due to high dispersion of the Pd precursors. The Au particle size of Au(0)/TiO₂ reduced with NaBH₄ was 3.5 nm, which was larger than that (1 nm) of Pd(0)/TiO₂ although the reduction was mild for the Au(0) sample. This was because the Au loading was larger by a factor of about 20 compared to Pd. When a small quantity of Pd was added to Au(0)/TiO₂, the size of the particles increased to around 5 nm. On reduction at 300 °C, larger bimetallic particles were formed, giving a size of about 12 nm. These large particles were also examined by HRTEM and EDS (Fig. 2). The HRTEM image shows that the lattice spacing is 0.230 nm, which is between those of Pd(1 1 1) plane (0.225 nm) and Au(1 1 1) plane (0.235 nm), suggesting the formation of Pd–Au alloy, in agreement with Vegard's law [40]. In addition, the EDS result indicates that Au is rich in the surface layer of this Pd–Au alloy particle. A similar HRTEM-EDS analysis was also made for the unreduced Pd(2)/Au(0)/TiO₂ sample. The lattice spacing is

Table 1
Various catalyst samples prepared and used in this work.

Catalyst ^a	Reduction method ^b		Metal loading ^c (wt%)		Particle size ^d (nm)
	Au	Pd	Au	Pd	
Au(0)/TiO ₂	NaBH ₄	–	1.8	–	3.5 (2–4)
Pd(2)/TiO ₂	–	–	–	0.08	–
Pd(0)/TiO ₂	–	H ₂	–	0.08	1 (0.8–1)
Pd(2)/Au(0)/TiO ₂	NaBH ₄	–	1.9	0.13	5 (4–7)
Pd(0)/Au(0)/TiO ₂	NaBH ₄	H ₂	1.9	0.13	12 (10–15)

^a Au(0) and Pd(0) mean the reduced samples while Pd(2) the unreduced ones. However, this notation does not indicate that all the metal species exist in the zero-valent or di-valent state in those samples.

^b Reduction conditions: for Au, the reduction was made with NaBH₄; for Pd, the reduction was made with H₂ at 300 °C.

^c Metal loading measured by ICP.

^d Average size of metal particles determined by TEM. The values in parentheses indicate the range of metal particle sizes observed. The particle size distributions were determined with 100 particles for Au(0)/TiO₂, Pd(0)/TiO₂, and Pd(2)/Au(0)/TiO₂ each and with 50 particles for Pd(0)/Au(0)/TiO₂.

0.235 nm, indicative of Au(111) plane; unfortunately, the EDS analysis failed, due to the smaller particle size of this sample. It may be assumed, however, that sintering of the particles and redistribution of the two metal species occur during the reduction process, resulting in the formation of larger alloy particles rich in Au content at the surface. It was previously reported that core-

shell structure appeared in supported bimetallic particles prepared by similar methods as used in this work [41]. However, such a core-shell structure was not observed for our bimetallic Pd–Au catalysts under the preparation conditions used.

As a source of complementary information on the chemical state and particle size of gold particles, diffuse reflectance UV/Vis

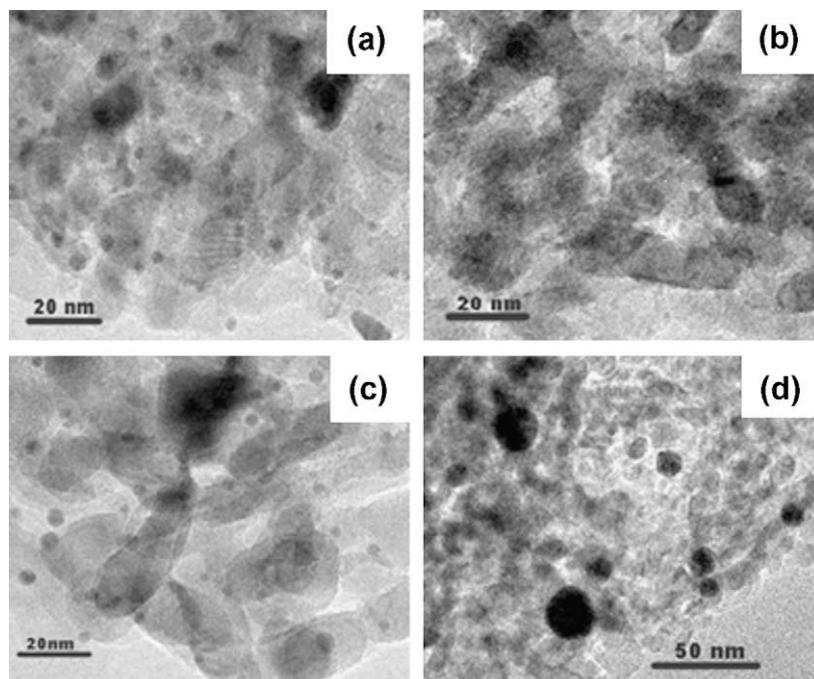


Fig. 1. TEM images of (a) Au(0)/TiO₂, (b) Pd(0)/TiO₂, (c) Pd(2)/Au(0)/TiO₂, and (d) Pd(0)/Au(0)/TiO₂ samples.

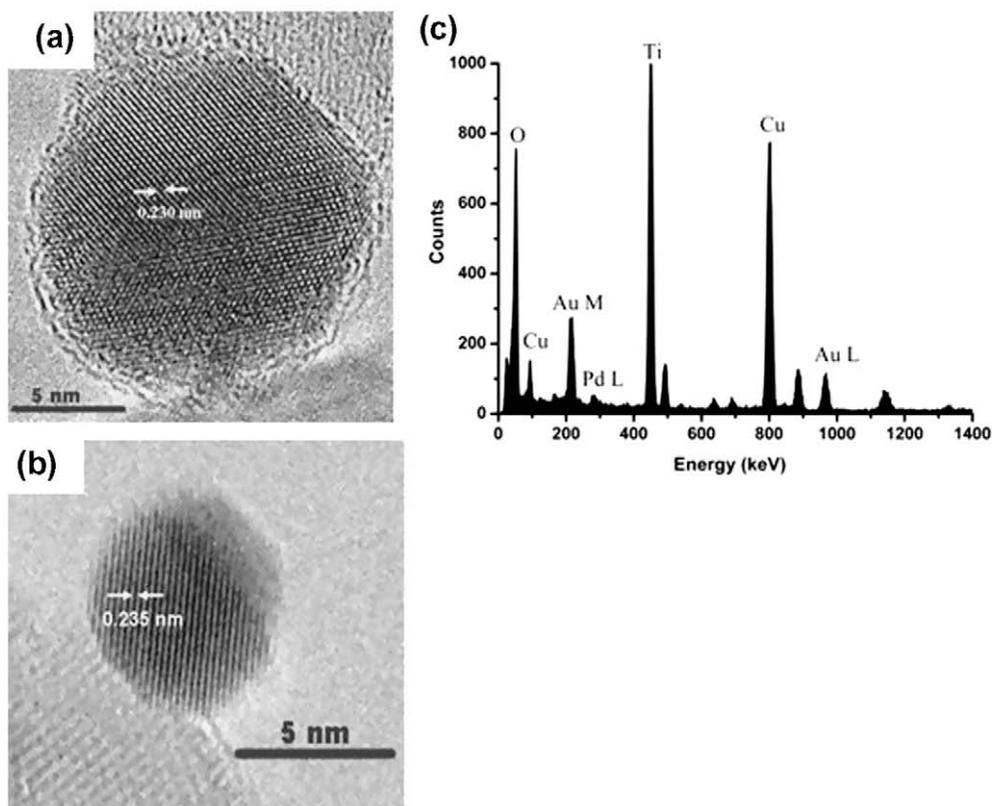


Fig. 2. HRTEM images of (a) Pd(0)/Au(0)/TiO₂ and (b) Pd(2)/Au(0)/TiO₂ catalysts. (c) EDS of a large metal particle of (a).

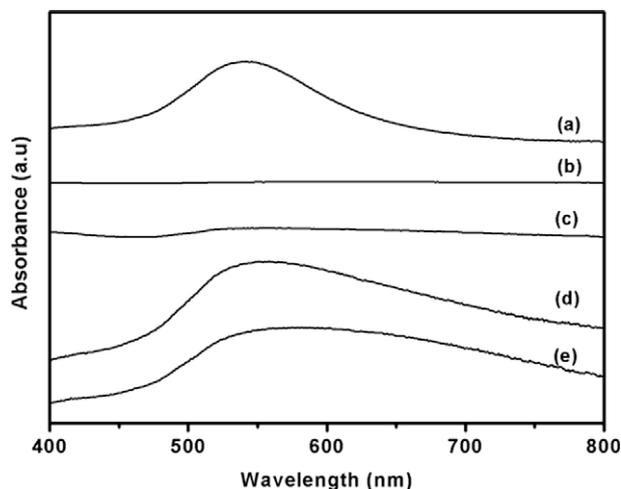


Fig. 3. UV/Vis absorption spectra for (a) Au(0)/TiO₂, (b) Pd(2)/TiO₂, (c) Pd(0)/TiO₂, (d) Pd(2)/Au(0)/TiO₂, and (e) Pd(0)/Au(0)/TiO₂ samples.

spectra of the TiO₂-supported Au and Pd samples were measured. Fig. 3 shows UV/Vis spectra for TiO₂-supported Au and Pd catalysts. For Au(0)/TiO₂ an absorption band was clearly observed, in which the absorption is the strongest at 540 nm. There existed small Au particles in this sample, and the average particle size was 3.5 nm from TEM (Table 1). No absorption was seen for Pd(2)/TiO₂ and very weak absorption was detected at >480 nm for reduced Pd(0)/TiO₂. For Pd-loaded Au(0)/TiO₂ samples, absorption started to occur at a similar wavelength around 440 nm but in a wider range compared to Au(0)/TiO₂. The absorption was weaker for reduced Pd(0)/Au(0)/TiO₂ than for unreduced Pd(2)/Au(0)/TiO₂. These results indicated that Au and Pd species were not in separate monometallic particles but in contact with one another in individual particles in these Pd(0)/Au(0)/TiO₂ and Pd(2)/Au(0)/TiO₂ samples. It was further suggested that the electronic state of mixed Pd and Au species should be different between the two reduced and unreduced samples. Those results may also suggest the formation of Pd–Au alloy particles in Pd-loaded Au(0)/TiO₂ samples.

The surface properties of monometallic and bimetallic particles were examined by XPS. Unfortunately, no significant Pd 3d signals were detected for the monometallic and bimetallic Pd catalysts of Pd(2)/TiO₂, Pd(0)/TiO₂, Pd(2)/Au(0)/TiO₂, and Pd(0)/Au(0)/TiO₂, due to the low loading of Pd in these samples. The Au 4f spectra for the monometallic and bimetallic catalysts are shown in Fig. 4. The XPS peaks of Au 4f_{7/2} and 4f_{5/2} for Au(0)/TiO₂ catalyst appeared at 83.8 and 87.5 eV, respectively, in agreement with the literature data [42], indicating that the Au existed in zero-valent state on the surface of this monometallic catalyst. For the Pd(0)/Au(0)/TiO₂ catalyst, Au 4f_{7/2} and 4f_{5/2} peaks existed at lower binding energies of 83.4 and 87.1 eV, respectively. This may be attributable to a charge transfer from Pd(0) to Au(0), corresponding to the alloy formation as assumed by HRTEM (Fig. 2). The binding energy of Au 4f_{7/2} and 4f_{5/2} in the Pd(2)/Au(0)/TiO₂ catalyst was the same as for the Au(0)/TiO₂ catalyst but the peak became broad, possibly due to the electron transfer from Au(0) to Pd(2). In addition, it was confirmed that no residual sodium or boron remained on the Au(0) catalysts from XPS and EDS analysis, in consistent with the previous results of Au/TiO₂ catalyst prepared with the same NaBH₄ reduction in the literature [43].

3.2. Catalytic activities in selective hydrogenation

The catalytic performance of various TiO₂-supported Au and Pd catalysts was evaluated in selective hydrogenation of citral in

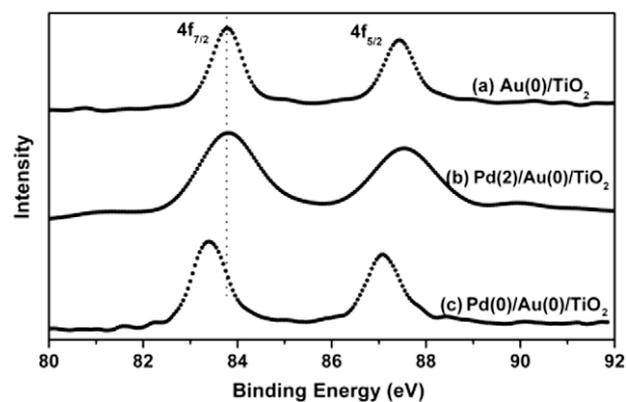


Fig. 4. XPS Au 4f spectra of (a) Au(0)/TiO₂, (b) Pd(2)/Au(0)/TiO₂, and (c) Pd(0)/Au(0)/TiO₂ catalysts.

scCO₂. The pressurized CO₂ was chosen due to its several merits such as low cost, environmental benign, high mass transfer rate, complete miscibility with H₂, and molecular interactions with some functional groups of substrates and/or intermediates [26]. The results of hydrogenation reactions obtained are presented in Table 2. The turnover frequency (TOF) value, a measure of average activity, was determined from the total number of Pd and Au atoms involved in the reactions for the physically and chemically mixed Pd and Au catalysts.

The Au(0)/TiO₂ catalyst was even less active (TOF 26 h⁻¹), giving CAL, produced from hydrogenation of conjugated C=C bond, as the main product with a selectivity of 67% (entry 1). The unsaturated alcohols of geraniol and nerol were produced with a total selectivity of about 24%, which was much lower than that (95%) over Au/Fe₂O₃ in ethanol [27]. Both Pd(2)/TiO₂ and Pd(0)/TiO₂ gave similar conversion levels of around 25% under the conditions used but were different in the product distribution (entries 2 and 3). The selectivity to CAL was smaller and that to IOL was larger for the former compared to the latter. This would be explained by that Pd(2)/TiO₂ was *in situ* reduced to Pd(0)/TiO₂ with the generation of HCl and/or H₂O during the hydrogenation reaction. The presence of HCl and H₂O + CO₂ would make the reaction environment acidic and this would promote the cyclization of CAL to IOL [44]. The loading of Pd used in the catalyst was 0.08 wt% and the amount of Cl species present in the catalyst used in the reaction was 25 μmol. When a comparable, small quantity of HCl (62 μmol) in 1 cm³ solution was added to the reaction mixture, the selectivity to IOL was found to increase along with benzene, ethylbenzene, isopropylbenzene, and others formed through acid-catalyzed reactions. In the present hydrogenation (entry 2), however, such byproducts were not detected and so the influence of the HCl and H₂O was less significant. The TOF values of the two Pd/TiO₂ catalysts are similar (entries 2 and 3) and higher by two orders of magnitude than that of Au(0)/TiO₂. ICP analysis was used to examine the possibility of Pd leaching from the unreduced Pd(2)/TiO₂ catalyst into the liquid phase under the conditions used but no Pd leaching was detected. The leaching and re-deposition of Pd onto the same Pd particles and/or the other Au particles were unlikely to modify the properties of physical and chemical mixtures of Pd(2) and Au(0) catalysts during the reaction.

The hydrogenation was significantly accelerated by physically mixing less active Au(0)/TiO₂ with Pd/TiO₂ catalysts (entries 4 and 5). The TOF was enhanced to 2059 h⁻¹ for Pd(2)/TiO₂ + Au(0)/TiO₂, which was larger than those of not only Au(0)/TiO₂ but also Pd(2)/TiO₂. It was also enhanced to 686 h⁻¹ for Pd(0)/TiO₂ + Au(0)/TiO₂, which was higher than that of Au(0)/TiO₂ but slightly lower than that of Pd(0)/TiO₂. It is interesting that the selectivity

Table 2
Results of hydrogenation of citral with various TiO₂-supported Pd and/or Au catalysts in the presence of scCO₂.

Entry	Catalysts	Time (h)	Conv. (%)	Selectivity (%)				TOF ^b (h ⁻¹)
				DCAL	CAL	IOL	Others ^a	
1	Au(0)/TiO ₂	4	8	5	67	3	24	26
2	Pd(2)/TiO ₂	4	24	11	62	20	7	956
3	Pd(0)/TiO ₂	4	27	13	72	7	9	1075
4	Pd(2)/TiO ₂ + Au (0)/TiO ₂	0.5	85	14	80	3	3	2059
5	Pd(0)/TiO ₂ + Au (0)/TiO ₂	1.5	85	5	89	0	5	686
6	Pd(2)/Au (0)/TiO ₂	0.5	43	10	61	25	5	948
7	Pd(0)/Au (0)/TiO ₂	4	55	3	88	2	6	152
8	Pd(2)/TiO ₂ + TiO ₂	1	15	8	64	12	16	2390
9	Pd(0)/TiO ₂ + TiO ₂	1	11	8	68	8	17	1753
10	Au(0)/TiO ₂ + TiO ₂	4	4	5	65	5	25	13
11	Pd(2)/Au (0)/TiO ₂ + TiO ₂	0.5	71	20	52	24	4	1565
12	Pd(0)/Au (0)/TiO ₂ + TiO ₂	4	35	5	86	3	7	97

Reaction conditions: citral 2 mmol, H₂ 4 MPa, CO₂ 8 MPa, 80 °C, catalyst weight 16.7 mg for single component samples (entries 1–4, 7 and 8), 16.7 mg + 16.7 mg for the multi-component samples (entries 5, 6, and 9–13).

^a Geraniol and nerol (entries 1 and 10). Trace amounts of geraniol, nerol, citronellol, 3,7-dimethyloctanol, and menthol (entries 2–9, 11 and 12).

^b TOF = (moles of citral converted)/((total moles of Au and Pd)(time)).

to CAL was increased up to >80% while that to IOL was decreased to <3% for the physically mixed catalysts (entries 4 and 5). One of the chemically mixed bimetallic catalysts, Pd(2)/Au(0)/TiO₂, showed a TOF of 948 h⁻¹ (entry 6), which was about 36 times as large as that of monometallic Au(0)/TiO₂, while the product distribution did not change so much (entries 2 and 6). In contrast, the TOF of the other bimetallic catalyst Pd(0)/Au(0)/TiO₂ was 152 h⁻¹, which was still larger than that of Au(0)/TiO₂ but much lower than that of Pd(0)/TiO₂ (1075 h⁻¹). The lower activity of Pd(0)/Au(0)/TiO₂, as compared to Pd(0)/TiO₂, may be attributable to the larger size of metal particles (the smaller degree of metal dispersion) in the former catalyst (Table 1). But, the selectivity to CAL was increased, along with a decrease in the selectivity to DCAL and IOL (entries 3 and 7). These results demonstrate that synergistic effects can appear on the total conversion and the product selectivity for those physically and chemically mixed Au and Pd catalysts.

Attempts were also made to physically mix the metal-loaded catalysts with neat TiO₂ support (entries 8–12). The TiO₂ support itself was found to be inactive for the reaction. Although the addition of TiO₂ to Au(0)/TiO₂ had a negative impact on the total conversion (entries 1 and 10), the addition of TiO₂ was effective for increasing the total conversion over Pd(2)/TiO₂ and Pd(0)/TiO₂ (entries 2, 3, 8 and 9). A similar positive impact of TiO₂ addition was observed for Pd(2)/Au(0)/TiO₂ but not for Pd(0)/Au(0)/TiO₂ (entries 11 and 12). Sancier et al. previously reported that the hydrogenation of benzene with Pd/Al₂O₃ was accelerated by mixing with Al₂O₃ support [25]. These authors explained this acceleration by hydrogen spillover from the parent Pd catalyst to the mixed inert support, which increased the total quantity of the active hydrogen species on the surface of Al₂O₃ to be effectively used for the hydrogenation.

For the active catalyst mixture of Pd(0)/TiO₂ + Au(0)/TiO₂, the influence of the amount of Au(0)/TiO₂ used was examined. Table 3 shows that the monometallic Pd(0)/TiO₂ gave a conversion of 10% and a selectivity to CAL of 75% under the reaction conditions used. When Pd(0)/TiO₂ was physically mixed with Au(0)/TiO₂, the total conversion was significantly enhanced up to a maximum of 77% at a Au/Pd ratio of 10.1 (entry 4), after which the conversion was decreased. When Au(0)/TiO₂ was added, the number of active sites for hydrogenation should increase; however, a larger amount of Au(0)/TiO₂ would cause a dilution of the active Pd(0)/TiO₂ catalyst in the reaction mixture and so decrease the conversion. The monometallic Au(0)/TiO₂ was less active but more selective to the formation of CAL, as above-mentioned (Table 2) and, therefore, the

selectivity to CAL was also enhanced from 76% for Pd(0)/TiO₂ alone to 90% for the physically mixed catalyst (entries 1 and 5) but it did not change so much with the amount of Au(0)/TiO₂ added.

For the chemically and physically mixed Pd and Au(0) catalysts, the changes in the product yield and selectivity with total conversion were examined (Fig. 5). The selectivity to CAL was large, being ~90% for the catalysts including Pd(0) irrespective of the total conversion (Fig. 5b and d); only trace amounts of DCAL and IOL were detected. The yield of CAL simply increased with the total conversion. That is, citral was hydrogenated to CAL but did not go through further hydrogenation to DCAL and cyclization to IOL. For the catalysts including Pd(2), however, the selectivity to CAL tended to decrease with the conversion (a, c) due to its further hydrogenation to DCAL.

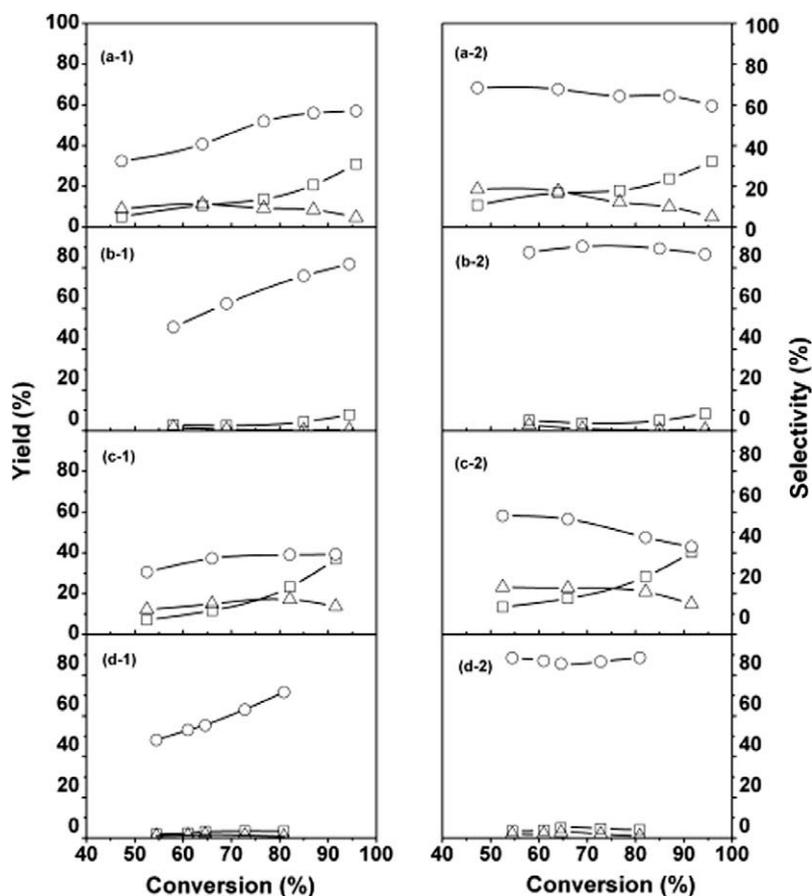
3.3. Synergistic effects on selective hydrogenation

It was demonstrated that synergistic effects appeared with physically and chemically mixed TiO₂-supported Pd and Au catalysts for the selective hydrogenation of citral in scCO₂ (Table 2). It was reported that catalytic activity and resistance to deactivation were significantly improved for silica-supported Pt–Ni bimetallic catalysts compared with the corresponding monometallic Pt and Ni catalysts in the atmospheric gas-phase hydrogenation of acetonitrile [45]. It was supposed that the electronic and geometric effects in the bimetallic catalysts were main factors inducing such an improvement. Moreover, synergistic effects were reported for a ternary Co–P–B amorphous alloy catalyst in liquid-phase hydrogenation of maltose, owing to that Co became electronic-rich in the presence of B and new active Co clusters were formed with the presence of P [46]. In addition, synergistic effects in a mixture of Pt/Al₂O₃ and Al₂O₃ in hydrogenation of benzene were ascribed to hydrogen spillover [25]. In the present work, the hydrogen spillover was discussed in more detail for the synergistic effects observed. H₂-TPD was used to examine the adsorption and desorption behavior of hydrogen on the physically and chemically mixed catalysts.

Fig. 6 gives TPD patterns of some selected catalysts. The amount of H₂ desorbing from Au(0)/TiO₂ sample was comparable to those from the Pd/TiO₂ samples although the adsorption of H₂ was more difficult for the former. This is because the metal loading of Au(0)/TiO₂ is larger by a factor of 3 than that of the Pd/TiO₂ samples. For monometallic Au(0)/TiO₂ catalyst (Fig. 6a), the desorption of H₂ was observed to start at about 250 °C and end at 550 °C, while the H₂ desorption started at lower temperatures for Pd(2)/TiO₂

Table 3Influence of the amount of Au(0)/TiO₂ added to Pd(0)/TiO₂ for selective hydrogenation of citral with the physical mixtures of Au(0)/TiO₂ + Pd(0)/TiO₂.

Entry	Catalyst weight		Au/Pd ratio (mol/mol)	Conv. (%)	Selectivity (%)			
	Au(0)/TiO ₂	Pd(0)/TiO ₂			DCAL	CAL	IOL	Others ^a
1	0	16.7	0	10.4	14	75.6	8.2	2.2
2	2.5	16.7	3.4	38.7	6.5	80.4	8.2	4.9
3	5	16.7	6.7	48.3	5.6	81.8	5.3	7.3
4	15	16.7	10.1	76.5	5.2	87.2	1.8	5.8
5	16.7	16.7	11.3	69	3.7	90.4	1	4.9
6	20	16.7	13.5	56.9	2.7	87.7	2.4	7.2
7	30.2	16.7	20.2	39.6	6.7	83.4	5.2	4.7
8	16.7	0	–	3.7	9.6	90.4	0	0

Reaction conditions: citral 2 mmol, H₂ 4 MPa, CO₂ 8 MPa, 80 °C, 1 h.^a Others include trace of geraniol and nerol, citronellol, 3,7-dimethyloctanol, and menthol.**Fig. 5.** Plots of yield (a1–d1) and selectivity (a2–d2) against conversion for selective hydrogenation of citral with chemical and physical mixtures of TiO₂-supported Au and Pd catalysts. (a) Pd(2)/TiO₂ + Au(0)/TiO₂, (b) Pd(0)/TiO₂ + Au(0)/TiO₂, (c) Pd(2)/Au(0)/TiO₂, and (d) Pd(0)/Au(0)/TiO₂. (○) CAL; (□) DCAL; (△) IOL. Reaction conditions: citral 2 mmol, catalyst weight 16.7 mg for chemically mixed catalysts, 16.7 mg + 16.7 mg for physically mixed catalysts, H₂ 4 MPa, CO₂ 8 MPa, 80 °C.

and Pd(0)/TiO₂ catalysts with desorption maxima at around 350 °C. For the former Pd(2)/TiO₂ catalyst, exposed Pd species were likely to be reduced by H₂ during the adsorption of H₂ at room temperature for 1 h and so these were able to adsorb H₂. Such a reduction of Pd(2)/TiO₂ may also occur during the hydrogenation reactions at H₂ 4 MPa. The number of exposed Pd species of this catalyst is larger than that of Pd(0)/TiO₂ reduced by H₂ at 300 °C, which may cause sintering of Pd species. Interestingly, the amount of H₂ desorbing was significantly enhanced when either Pd(2)/TiO₂ or Pd(0)/TiO₂ was physically mixed with Au(0)/TiO₂ (Fig. 6b), which was even larger than that expected from the simple sum of the desorption results of the two monometallic Pd and Au samples. That is, the adsorption of H₂ was promoted in these catalyst mix-

tures; probably the H₂ species formed via dissociative adsorption on Pd sites should spillover to the counter catalyst of Au(0)/TiO₂. A similar promotional effect on the adsorption of H₂ also appeared when Pd(0)/TiO₂ was mixed with neat TiO₂ support (Fig. 6d). A smaller H₂ desorption was observed for Pd(2)/Au(0)/TiO₂, for which the reduction of exposed Pd species was more difficult due to interactions with Au compared with the monometallic Pd(2)/TiO₂ sample, resulting in the smaller desorption (Fig. 6c). The reduced Pd(0)/Au(0)/TiO₂ sample was likely to have an alloy structure, in which the surface was rich with Au and the size of metal particles was large. Hence, this catalyst was unable to adsorb a large amount of H₂. The adsorption of H₂ on the Pd(2)/Au(0)/TiO₂ was much larger than that over the Pd(0)/Au(0)/TiO₂ catalyst,

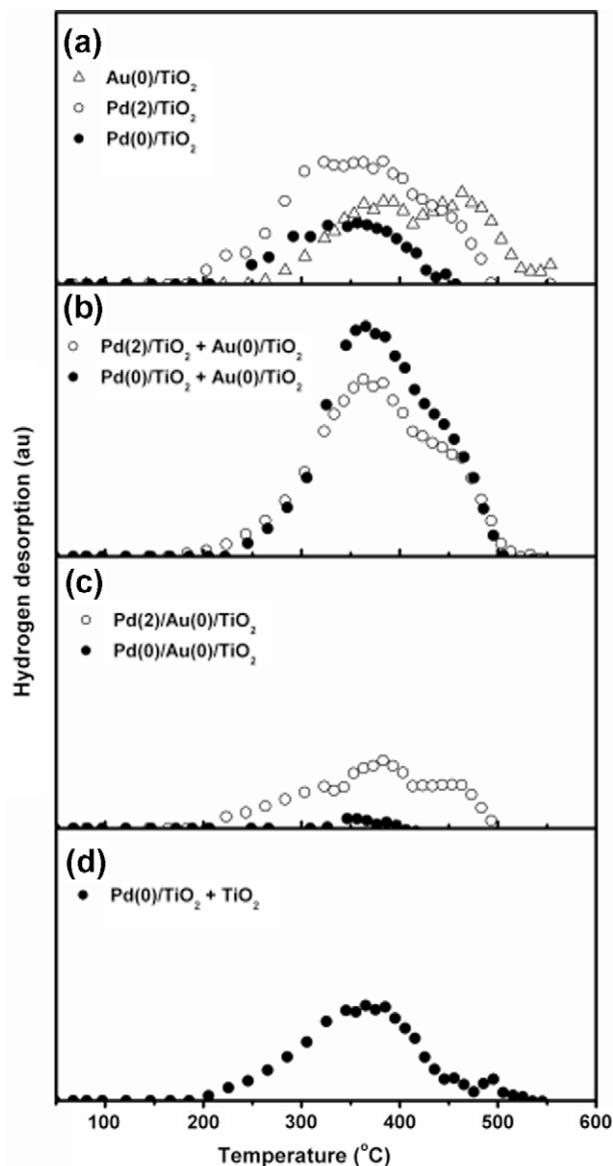


Fig. 6. H_2 -TPD profiles for various Pd and Au catalyst samples. (a) Monometallic, (b, d) physical mixed, and (c) chemically mixed samples.

which may be attributable to the difference in the size of metal particles.

The TPD results indicate differences in the H_2 adsorption/desorption behavior among the physically and chemically mixed Pd and Au catalysts (Fig. 6). The increased amount of H_2 adsorption is one of the significant factors for the synergistic effects on the total conversion in hydrogenation of citral. In these catalysts, Pd(0) should be the main active component giving active hydrogen species and either Au(0)/TiO₂ or TiO₂ serves as an active hydrogen acceptor. When active hydrogen is supplied to Au(0)/TiO₂, the Au species may act as more active sites for hydrogenation than does it alone. Hence, the total rate of hydrogenation is even larger for the physically mixed catalysts relative to the monometallic and bimetallic catalysts. In addition, the Pd(2)-containing catalysts show much higher activity than those of the corresponding Pd(0)-containing catalysts (Table 2). As demonstrated from TPD results, there are more active hydrogen adsorbed on the surface of Pd(2) catalysts than Pd(0) ones except for the physically mixed catalysts Pd(2)/TiO₂ + Au(0)/TiO₂ and Pd(0)/TiO₂ + Au(0)/TiO₂. It is likely that the Au and Pd species were highly dispersed in Pd(2)-

containing samples and that the Pd(2) were reduced during the adsorption of H_2 in TPD or the hydrogenation reaction, resulting in the larger amount of H_2 desorption and the larger conversion of citral hydrogenation. For the physically mixed catalysts Pd(2)/TiO₂ + Au(0)/TiO₂ and Pd(0)/TiO₂ + Au(0)/TiO₂, the adsorption of H_2 over the former is a little small (Fig. 6b), this may result from the consumption of some desorbing hydrogen for the partial reduction of Pd(2) species during the process of hydrogen desorption. Fig. 6 shows that the amount of H_2 desorbing was even smaller for Pd(0)/Au(0)/TiO₂ than for Au(0)/TiO₂, which was in disagreement with the trend of catalytic activity (Table 2). That is, the capacity of H_2 adsorption cannot explain the activities of these two catalysts for hydrogenation of citral. These catalysts are different in the surface properties of metal particles, as assumed from TEM, XPS, and UV/Vis results, and so the reaction kinetics should be different. Indeed, apparent activation energy values determined at 40–80 °C were 13 kJ/mol and 37 kJ/mol for Au(0)/TiO₂ and Pd(0)/Au(0)/TiO₂ catalysts, respectively.

The selectivity to CAL maintained about 90% over the Pd(0)-containing catalysts (Fig. 5), while it was smaller for the Pd(2) catalysts (both chemical and physical mixtures) due to the deep hydrogenation of CAL in the presence of excess amount of active hydrogen, similar to the monometallic Pd catalyst. As the active hydrogen species was easy to form on the surface of Pd particles, over-hydrogenation of citral to dihydrocitronellal would usually occur over Pd catalysts [47]. As compared with the monometallic Pd(0)/TiO₂, the physical mixture of Pd(0)/TiO₂ + Au(0)/TiO₂ and the bimetallic Pd(0)/Au(0)/TiO₂ catalyst with Au-rich surface produced CAL in the larger selectivity. For these catalysts, active hydrogen species on the exposed Pd sites could be diluted by the presence of Au and this could suppress the further hydrogenation of CAL.

3.4. Comparison with the hydrogenation in organic solvent

The present results indicate the significant synergistic effects of physically and chemically mixed TiO₂-supported Pd and Au catalysts in selective hydrogenation of citral in scCO₂. To examine the roles of scCO₂, the same hydrogenation reactions were run in a non-polar organic solvent of *n*-hexane using selected catalysts and catalyst mixtures. The results obtained are given in Table 4. The catalytic features (relative activities and product distribution patterns) of the monometallic Au and Pd catalysts (entries 1–3) are similar to those observed in scCO₂ (Table 2). When the Pd catalysts were physically mixed with Au(0)/TiO₂, the hydrogenation reaction was significantly accelerated (entries 4 and 5); the TOFs of Pd(2)/TiO₂ + Au(0)/TiO₂ and Pd(0)/TiO₂ + Au(0)/TiO₂ were 2059 and 686 h⁻¹, respectively, which were larger by factors of 79 and 26 than those of the corresponding monometallic Au/TiO₂ catalysts. For the chemically mixed catalysts, the TOF values were also increased relative to that of the monometallic Au/TiO₂ catalyst (entries 6 and 7), but less significant compared to the physical mixtures. Compared to Pd(0)/TiO₂ catalyst (entry 2), the selectivity to CAL was larger over the mixed catalysts containing Pd(0) and the selectivity to CAL increased to above 77% from 67% (entries 3, 5 and 7), while it was smaller over the mixed catalysts containing Pd(2) (entries 4 and 6). It was observed again that the addition of neat TiO₂ was effective for increasing the total conversion and the selectivity to CAL (entries 3 and 8).

From the results of Tables 2 and 4, it is obvious that the total conversion obtained in scCO₂ is larger than that in *n*-hexane under the reaction conditions used. Furthermore, for the physically and chemically mixed Pd and Au catalysts, the selectivity to CAL is larger in scCO₂ than in the organic solvent at similar conversion levels. The difference in the total conversion would be ascribed to differences in the H_2 solubility between the two different reaction media. The total amount of active hydrogen species on the

Table 4Results of hydrogenation of citral with various TiO₂-supported Pd and/or Au catalysts in *n*-hexane.

Entry	Catalysts	Time (h)	Conv. (%)	Selectivity (%)				TOF ^b (h ⁻¹)
				DCAL	CAL	IOL	Others ^a	
1	Au(0)/TiO ₂	6	1	34	66	0	0	2
2	Pd(2)/TiO ₂	6	22	4	58	23	15	488
3	Pd(0)/TiO ₂	6	28	15	67	12	6	621
4	Pd(2)/TiO ₂ + Au (0)/TiO ₂	2	85	19	70	10	1	430
5	Pd(0)/TiO ₂ + Au (0)/TiO ₂	2	36	6	77	8	9	182
6	Pd(2)/Au (0)/TiO ₂	3	66	19	53	20	8	151
7	Pd(0)/Au (0)/TiO ₂	3	47	7	78	8	7	108
8	Pd(0)/TiO ₂ + TiO ₂	6	37	6	79	9	6	821

Reaction conditions: citral 2 mmol, H₂ 4 MPa, *n*-hexane 5 cm³, 80 °C, catalyst weight 20 mg for single component samples (entries 1–3, 6 and 7), 20 mg + 20 mg for the multi-component samples (entries 4, 5 and 8).

^a Same as in Table 3.

^b Same as in Table 2.

catalysts may be larger in scCO₂ than in hexane. Another difference might be in the rate of hydrogen transfer over the surface of a catalyst particle and from a catalyst particle to another in scCO₂ medium. Detailed kinetic analysis should be needed for further discussion. The reactions were enhanced as the availability of hydrogen in the vicinity of the adsorbed reactants on the surface of the catalysts in the scCO₂ solvent increased. As known, a hydrogen-rich environment increased the risk of over-hydrogenation in the successive reaction. But as reported in our previous work, the selectivity of the corresponding unsaturated alcohols was improved because the C=O bond was activated through the molecular interactions between CO₂ and the C=O group of α,β -unsaturated aldehydes [48–51]. Such a molecular interaction should also exist in the present hydrogenation, but the selectivity to the unsaturated alcohols was not improved, instead of that the selectivity to CAL was enhanced in scCO₂. It should be attributed to the following two factors: the main catalytic species of Pd prefers to hydrogenate C=C bond rather than C=O bond; the conjugated C=C bond was relatively activated in dense CO₂ compared with the isolated C=C bond due to the electrons de-localized in the conjugated C=C–C=O bond, even though the interaction between C=C and CO₂ was much weaker compared to that of C=O and CO₂.

4. Conclusions

It is demonstrated that significant synergistic effects present themselves in selective hydrogenation of citral in scCO₂, when the physically and chemically mixed TiO₂-supported Pd and Au catalysts are used. The total conversion and the selectivity to CAL were enhanced over those physically mixed catalysts of Pd/TiO₂ with less active Au/TiO₂. The addition of neat TiO₂ to Pd/TiO₂ catalysts is also effective for accelerating the hydrogenation rate. The hydrogen spillover takes place over the physically mixed catalysts (from TPD), and this should be the main factor for enhancing the hydrogenation rate. For the chemically mixed bimetallic catalysts, the electron transfer between Pd and Au species (from XPS) should be responsible for the improvement in the catalytic activity. Moreover, the activity of Pd(2)-containing mixed catalysts is higher than that of the Pd(0)-containing ones because of the higher metal dispersion in the former, in which the reduction of highly dispersed Pd precursors occurs *in situ* during the hydrogenation at a lower temperature of 80 °C, compared with the Pd(0) catalysts pre-reduced at 300 °C. Furthermore, with comparison to the results in *n*-hexane, the use of scCO₂ has such merits that the overall rate of citral hydrogenation can be enhanced and the selectivity to CAL can be improved, in addition to its environmentally benign nature and easy separation by depressurization.

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