



The effect of titania polymorph on the strong metal-support interaction of Pd/TiO₂ catalysts and their application in the liquid phase selective hydrogenation of long chain alkadienes

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Abstract

In situ EPR and IR investigation by using CO as probe molecules show that even pre-reduced by H₂ at lower temperature results in SMSI for anatase titania supported palladium catalyst, but not for rutile titania supported palladium catalyst, which is attributed that the Ti³⁺ ions produced by reduction of Ti⁴⁺ are fixed in the surface lattice of TiO₂, as rutile titania is more thermodynamically and structurally stable than anatase titania so that the Ti³⁺ ions fixed in the surface lattice of anatase TiO₂ is easier to diffuse to surface of palladium particle than one in the surface lattice of rutile TiO₂. Anatase titania supported palladium catalyst 0.075% Pd/TiO₂ (A) pre-reduced by H₂ at lower temperature has higher selectivity of alkenes for the liquid phase selective hydrogenation of long chain alkadienes than rutile titania supported palladium catalysts 0.075% Pd/TiO₂ (R). For titania (rutile or anatase) supported palladium catalysts, the elevation of pre-reduction temperature from 200 to 450 °C gives rise to sharp change of catalytic properties, especially for selectivity of alkenes. The very different catalytic properties between 0.075% Pd/TiO₂ (R) and 0.075% Pd/TiO₂ (A) catalyst pre-reduced at lower temperature, and the rapid increasing of selectivity of 0.075% Pd/TiO₂ (A) and 0.075% Pd/TiO₂ (R) with the elevation of pre-reduction temperature are reasonably explained by the presence of SMSI both for anatase titania supported palladium catalyst pre-reduced at lower temperature, and titania (rutile and anatase) supported palladium catalyst pre-reduced at higher temperature.

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1. Introduction

Strong metal-support interaction (SMSI) has attracted much attention since its first report because noble metal supported on reduced oxides (with SMSI) shows important differences in the catalytic activity and selectivity of hydrogenation reaction when reduced at high temperature, compared with one reduced at lower temperature or the corresponding noble metal supported on un-reducible supports (without SMSI) [1–8]. Most of all studies of SMSI concentrated on titania supported noble metal catalyst. Traditional criterion for SMSI is the rapid reduction of H₂ or CO ad-

sorption capacity without a significant enlargement of metal particles with the elevation of pre-reduction temperature. Usually, SMSI is observed when the reduction temperature is above 300 °C. It is well known that titania exists in three main crystalline form e.g. anatase, rutile, and brookite, and each structure exhibits different physical properties. It is inferred that noble metal supported on titania with different crystalline forms might exhibit different physio-chemical properties and catalytic properties. However, to our best knowledge, there have been no reports of such difference up to now.

Olefin stream produced in the plant for producing the feedstock of detergent-linear alkyl benzene by dehydrogenation of C₁₀–C₁₃ alkanes contains 1–3% of alkadienes. The presence of these alkadienes will cause a lot of side re-

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actions in the subsequent alkylation, resulting in a decrease of the yield and quality of alkyl benzene [9]. Therefore, it is of both scientific and industrial significance to make an investigation on the selective hydrogenation of alkadienes to alkenes. Palladium catalysts have by far been proved to be the most active and selective for selective hydrogenation of alkadienes and alkynes to alkenes. At present, alumina supported palladium is used as a catalyst in industry for selective hydrogenation of C₁₀–C₁₃ alkadienes. However, it is less effective (with lower selectivity of alkenes) at higher temperature and pressure, which is required by this industrial process to avoid using huge cooling system. In order to improve the selectivity of alkenes on alumina supported palladium catalyst, multi-steps hydrogenation process instead of one-step process are used in industry [9]. Therefore, it is of significance to make an investigation into improving the selectivity of alkenes for supported palladium catalyst.

In this work, we make comparative investigation into SMSI for anatase and rutile titania supported palladium catalyst by EPR and IR using CO as probe molecules, CO chemisorption, and TEM, and their catalytic properties for the selective hydrogenation of C₁₀–C₁₃ alkadienes. It is discovered that anatase titania supported palladium catalyst shows very different properties from rutile titania supported palladium catalyst, and even pre-reduced by H₂ at lower temperature results in SMSI for anatase titania supported palladium catalyst, but not for rutile titania supported palladium catalyst. This anatase titania supported palladium catalyst shows much better selectivity of alkenes than alumina supported palladium catalyst.

2. Experimental

2.1. Preparation of catalysts

The 0.125 mol TiCl₄ was added dropwise into 500 ml distilled water in an ice–water bath. Then 2 mol l⁻¹ dilute NH₃H₂O was added to the above aqueous TiCl₄ solution (0.25 mol l⁻¹) until the pH value was above 9. Subsequently, the precipitated hydrous titania was separated from the solution by filtering, and repeatedly washed with distilled water to make the precipitant free of chloride. The hydrous titania was dried at 120 °C for 24 h, the anatase titania TiO₂ (A) was obtained by calcining the dried titania at 500 °C for 3 h. For the preparation of rutile titania TiO₂ (R), 0.25 mol TiCl₄ was added drop wise into 1000 ml distilled water. Then the above aqueous solutions were kept at 40 °C for hydrolysis of TiCl₄ in a temperature-controlled bath. In order to promote crystallization of titania, a small amount of nano rutile TiO₂ (ca.70 mg) with average crystal size of 6.9 nm and a specific area of 141.0 m² g⁻¹ were added into the above solutions. After hydrolysis and crystallization for several days, the precipitates formed in the solutions were filtered and washed thoroughly with distilled water, and dried at 150 °C in air

for 24 h, then calcined at 500 °C for 3 h. The details of the preparation of rutile titania was described in our previous work [10].

The Pd/TiO₂ (A) and Pd/TiO₂ (R) catalyst were prepared by impregnating 20 g TiO₂ (A) and TiO₂ (R) with 0.017 mol l⁻¹ PdCl₂ solution (pH 0.1), respectively. The catalyst samples were dried at 120 °C overnight. The catalyst samples were oxidized and de-chlorinated by flowing air saturated by water (80 °C) at a rate of 80 ml(STP) min⁻¹ into the catalysts in a quartz tube at 500 °C for 12 h. There is no detected Cl⁻ in Pd/TiO₂ by AgNO₃ aqueous solution. We use industry used 0.3% Pd/Al₂O₃ (Al₂O₃: 237 m² g⁻¹) to make comparison with Pd/TiO₂.

2.2. Characterization of catalysts

Powder X-ray diffraction analysis was performed with Ni-filtered Cu K α radiation on a Shimadzu XD-3A X-ray diffractometer. The working voltage of 35 kV and the electronic current of 25 mA were employed. The average crystal size of anatase and rutile titania is determined by Scherrer formula: $L = 0.89\lambda/\beta \cos \theta$ from the broadening of corresponding X-ray spectral peaks at 25.4 and 27.3°, respectively [10].

The EPR spectra were taken at 123 K on EMXEPR spectrometer (Bruker). The quartz reactor with valves was equipped with side arm EPR tube where the pre-reduced catalyst was transferred. The catalyst was reduced by H₂ for 1 h at lower temperature (200 °C) or higher temperature (450 °C). After the reduction the valves were turn off, and the catalysts in quartz reactor was transferred to side arm EPR tube for EPR measurement. Then the catalyst in the quartz reactor was evacuated to remove H₂, and CO ($P = 200$ Torr) (99.95%) deoxygenated by MnO/SiO₂ was introduced into the quartz reactor to make catalyst absorbed CO for second EPR measurement in order to know the effect of CO on the stability of Ti³⁺ in catalyst.

BET surface area of the catalysts was measured on a MICROMERITICS ASAP-2000 adsorption analyzer using nitrogen as adsorbate.

Pulsed chemisorption technique [11] was employed to measure the amount of irreversibly chemisorbed CO on the prepared catalysts. As-synthesized catalyst was reduced by H₂ at a rate of 80 ml(STP) min⁻¹ at 200 °C for 1 h, then flushed by He (99.999%) purified by an oxygen trap (MnO/SiO₂) at a rate of 30 ml(STP) min⁻¹ at 200 °C for 1 h, finally, cooled to room temperature for CO pulsed chemisorption. Pulse of a known quantity (1.96 μ mol) of CO (99.95%) deoxygenated by MnO/SiO₂ were injected every 5 min on the sample at room temperature in flowing He (99.999%) purified by an oxygen trap (MnO/SiO₂). The injection was continued until probe molecules saturated the surface. After each injection, the quantity of probe molecules not chemisorbed was measured using a conventional device equipped with a TCD. TEM images were taken with using JEM-100CX electron microscope.

The Fourier transform infrared (FTIR) spectra were recorded at room temperature on a Perkin-Elmer 1750 spectrometer, at resolution 2 cm^{-1} using around 100 scans. Sample disks (diameter 18 mm) of catalysts were put into an infrared cell equipped with CaF_2 windows, designed to treat the sample in a controlled atmosphere. They were submitted to the following pretreatment: (1) outgassing at room temperature until $P < 10^{-5}$ Torr, (2) reduction under hydrogen at 200 or 450 °C, (3) outgassing at 200 or 450 °C until $P < 10^{-5}$ Torr, before introduction of CO ($P = 200$ or 0.5 Torr) and IR measurements. The spectral presented here were obtained after subtracting the gas phase and solid contributions.

2.3. Catalytic activity measurement

The measurement of reaction of catalysts for selective hydrogenation of longer chain alkadienes were accomplished on homemade apparatus by using a technical process of hydrogenation of feedstock saturated by hydrogen, which is similar to industrial process [9]. The feedstock composed of 84.38% alkanes, 10.40% alkenes, 1.26% alkadienes, and 3.96% aromatic hydrocarbons were firstly saturated by hydrogen in a 2 l autoclave at 100 °C and 17 atm. Then the feedstock saturated by hydrogen was delivered into a fixed-bed micro-reactor of 20 mm i.d. \times 400 mm stainless tube from the autoclave by a valve for hydrogenation. Every catalyst was pretreated in H_2 at a rate of $80\text{ ml(STP) min}^{-1}$ under atmospheric pressure at 200 or 450 °C for 1 h before hydrogenation. The details of the reaction conditions and method of product analysis were reported in our previous work [12].

The conversion of alkadienes and selectivity of alkenes or alkanes were defined as follows:

Conversion of alkadienes (%)

$$= \frac{\text{content of alkadienes in the feedstock} - \text{content of alkadienes in product}}{\text{content of alkadienes in the feedstock}} \times 100$$

Selectivity of alkenes (%)

$$= \frac{\text{content of alkenes in product} - \text{content of alkenes in feedstock}}{\text{content of alkadienes in feedstock} - \text{content of alkadienes in product}} \times 100$$

3. Results and discussion

3.1. XRD and EPR

Fig. 1 shows the XRD patterns of as-synthesized TiO_2 . As can be seen from Fig. 1, the as-synthesized titania has pure anatase or rutile crystalline structure, respectively.

The EPR spectra of TiO_2 (R), TiO_2 (A), Pd/ TiO_2 (R), and Pd/ TiO_2 (A) catalyst pretreated under different conditions were shown in Figs. 2 and 3, respectively. The signals of g values less than 2 were assigned to Ti^{3+} ($3d^1$) [13,14]. No Ti^{3+} EPR signal is observed for TiO_2 (R) reduced at 200 °C, and there is a small Ti^{3+} EPR signal for TiO_2 (A) reduced at 200 °C. This result shows that Ti^{4+} in both TiO_2 (A) and TiO_2 (R) is difficult to be reduced to Ti^{3+} . However, both the Pd/ TiO_2 (R) and Pd/ TiO_2 (A) catalyst reduced at 200 °C

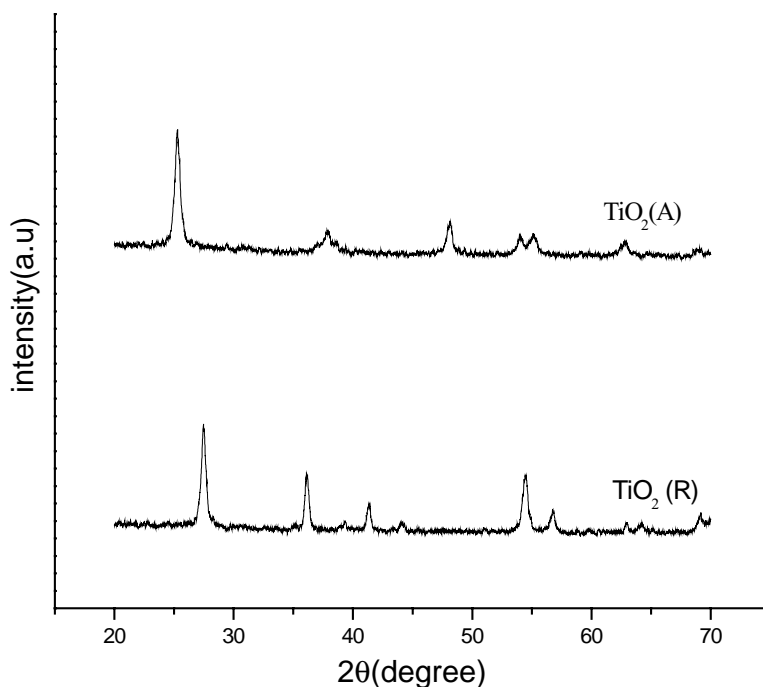


Fig. 1. XRD patterns of the as-synthesized anatase and rutile TiO_2 .

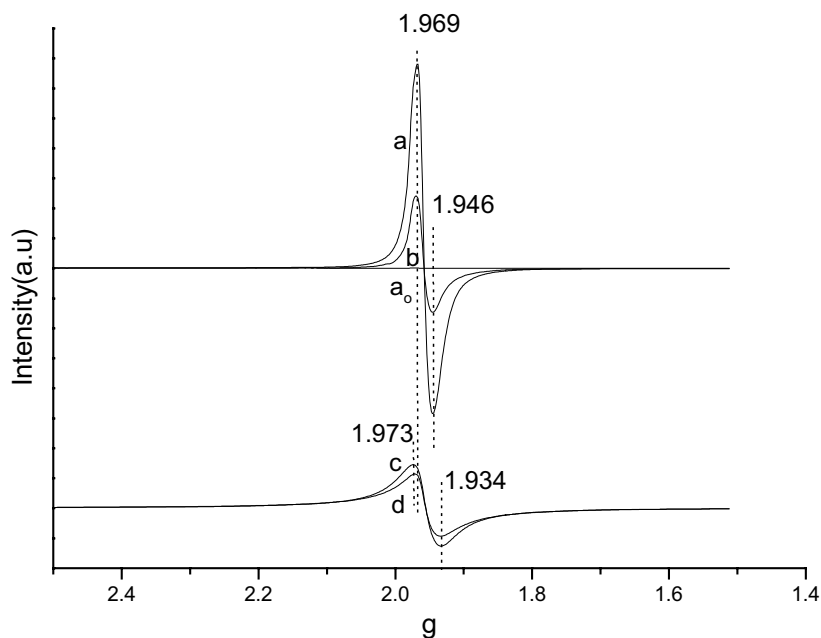


Fig. 2. EPR spectra of 0.075% Pd/TiO₂ (R) catalysts pre-reduced at different temperature (in bracket) with or without CO adsorbed on them: (a₀) TiO₂ (R), (a) 0.075% Pd/TiO₂ (R) (200 °C), (b) 0.075% Pd/TiO₂ (R) (200 °C) CO, (c) 0.075% Pd/TiO₂ (R) (450 °C), (d) 0.075% Pd/TiO₂ (R) (450 °C) CO.

all have strong Ti³⁺ EPR signal. The result shows that Ti⁴⁺ can be very easily reduced to Ti³⁺ in the presence of Pd even at lower temperature (200 °C), which is caused by the dissociatively chemisorbed hydrogen on palladium diffusing from Pd to TiO₂ and reducing Ti⁴⁺ to Ti³⁺ [15,16]. The elevation of reduction temperature from 200 to 450 °C leads to widening and weakening of Ti³⁺ EPR signal both for Pd/TiO₂ (R) and Pd/TiO₂ (A) catalyst, which is contributed to the formation of diamagnetically coupled Ti³⁺ pairs and the coupling

of no-diamagnetic Ti³⁺ ions [17,18] under higher reduction temperature.

For Pd/TiO₂ (R) reduced at lower temperature (200 °C), the signal at $g_{\perp} = 1.969$, $g_{\parallel} = 1.946$ is assigned to surface Ti³⁺ ions which are not in contact with palladium [19]. The adsorption of CO on this catalyst leads to the rapidly decreasing of intensity of Ti³⁺ signal. The disappearance of most Ti³⁺ ions is caused by the oxidation of Ti³⁺ to Ti⁴⁺ ions by O atoms produced at the metal interface during

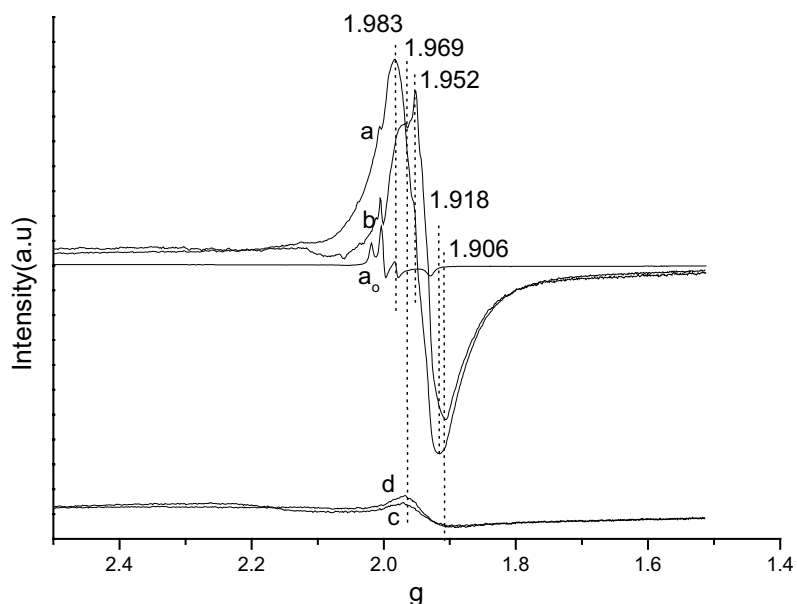


Fig. 3. EPR spectra of 0.075% Pd/TiO₂ (A) catalysts pre-reduced at different temperature (in bracket) with or without CO adsorbed on them: (a₀) TiO₂ (A), (a) 0.075% Pd/TiO₂ (A) (200 °C), (b) 0.075% Pd/TiO₂ (A) (200 °C) CO, (c) 0.075% Pd/TiO₂ (A) (450 °C), (d) 0.075% Pd/TiO₂ (A) (450 °C) CO.

CO dissociation [20,21]. When pre-reduction temperature increases to 450 °C, a new signal is observed at $g_{\perp} = 1.973$, $g_{\parallel} = 1.934$, which is assigned to Ti^{3+} ion located at the contact of Pd-surface [19].

For Pd/TiO₂ (A) reduced at lower temperature (200 °C), compared with Pd/TiO₂ (R), the profile of Ti^{3+} EPR signal of Pd/TiO₂ (A) is widened, and its g values are very different from the former, there are two shoulder peaks at $g = 1.969$ and 1.952 , which is obviously caused by overlapping of different Ti^{3+} EPR signals. This EPR signal at $g \approx 1.91$ or so (including 1.918 and 1.906) was ascribed to vacancy-stabilized Ti^{3+} in the lattice sites or even to Ti_2^{7+} , or similar center in the subsurface layer of TiO₂ [22,23]. The adsorption of CO on this catalyst leads to decreasing of the intensity of EPR signal at $g = 1.983$, and the appearance of two peaks at $g = 1.969$ and 1.952 . Based on the analysis of EPR signal for Pd/TiO₂ (R), the EPR signal at $g = 1.983$ is reasonably ascribed to the Ti^{3+} ions which are not in contact with palladium, and the two peaks at $g = 1.969$ and 1.952 are assigned to the two kind of Ti^{3+} ions located at the contact of Pd-surface. The stability of most Ti^{3+} in Pd/TiO₂ (A) catalyst reduced at 200 °C in the presence of CO shows that there is SMSI which could stabilize Ti^{3+} in Pd/TiO₂ (A) catalyst even reduced by H₂ at lower temperature. We assume that the produced Ti^{3+} ions are fixed in the surface lattice of TiO₂, as rutile titania is more thermodynamically and structurally stable than anatase titania [14] so that the Ti^{3+} ions fixed in the surface lattice of anatase TiO₂ is easier to diffuse to surface of palladium particle than one in the surface lattice of rutile TiO₂.

After introduction of CO into both Pd/TiO₂ (A) and Pd/TiO₂ (R) catalyst reduced at 450 °C in the EPR tube, the intensity of Ti^{3+} signal almost keep unchanged. The stability of Ti^{3+} in both Pd/TiO₂ (A) and Pd/TiO₂ (R) catalyst reduced at 450 °C in the presence of CO suggests that there is SMSI between Ti^{3+} and Pd that could stabilize Ti^{3+} . The thermal diffusion of Ti^{3+} ion produced at higher temperature is much easier than at lower temperature so that it could overcome the binding of surface lattice of both anatase and rutile titania to move to the surface or surrounding of palladium particle, and give rise to SMSI between Ti^{3+} and Pd.

3.2. BET, CO chemisorption and TEM

Table 1 shows the properties of catalysts and the CO adsorption. Compared with rutile titania supported palladium

catalyst 0.075% Pd/TiO₂ (R) reduced at 200 °C, anatase titania supported palladium catalyst 0.075% Pd/TiO₂ (A) reduced at 200 °C has much higher CO chemisorption. As the surface area of TiO₂ (A) (45 m² g⁻¹) is two times higher than one of TiO₂ (R) (22 m² g⁻¹), the much higher CO chemisorption of 0.075% Pd/TiO₂ (A) than 0.075% Pd/TiO₂ (R) may be caused by the higher dispersion of Pd for 0.075% Pd/TiO₂ (A) than one for 0.075% Pd/TiO₂ (R). It is estimated that 0.15% Pd/TiO₂ (A) should have same dispersion of Pd with 0.075% Pd/TiO₂ (R), but 0.15% Pd/TiO₂ (A) reduced at 200 °C still has much higher CO chemisorption than 0.075% Pd/TiO₂ (R). Obviously, such difference of CO chemisorption could not be explained only by the difference of Pd dispersion for 0.075% Pd/TiO₂ (R) and 0.075% Pd/TiO₂ (A). Moreover, the elevation of reduction temperature from 200 to 450 °C leads to rapidly decreasing of CO chemisorption for both 0.075% Pd/TiO₂ (A) and 0.075% Pd/TiO₂ (R), which may be caused by sintering of Pd particles at higher temperature. As the loading of Pd in 0.075% Pd/TiO₂ (A) or (R) is so small that the number of Pd particle is too small to be difficult to be observed by TEM, we use 1.5% Pd/TiO₂ instead of 0.075% Pd/TiO₂ to illustrate whether the elevation of reduction temperature results in the sintering of small Pd particles. Fig. 4 shows the photographs of 1.5% Pd/TiO₂ catalysts reduced by H₂ at different temperature. Obviously, there is no obvious sintering of both small Pd particles and large titania particles with the elevation of reduction temperature from 200 to 450 °C. Combined with the results from EPR, it is reasonably concluded that the rapidly decreasing of CO chemisorption for both 0.075% Pd/TiO₂ (A) and 0.075% Pd/TiO₂ (R) with the elevation of reduction temperature from 200 to 450 °C is not caused by the sintering of small 0.075% Pd particles, but mainly by the covering of the surface of Pd particles by TiO_{2-x} migrated from titania support.

3.3. CO-IR

As IR signal of CO for low loaded supported palladium catalyst (0.075% Pd/TiO₂ or Al₂O₃) is very weak, we prepared higher loaded supported palladium catalysts, e.g. 1.5% Pd/TiO₂ (A), 1.5% Pd/TiO₂ (R) and 1.5% Pd/Al₂O₃ and made an investigation on these catalysts by CO-FTIR to elucidate the SMSI on these catalysts. Figs. 5 and 6 compare the IR spectra of CO absorbed on 1.5% Pd/TiO₂ (A), 1.5% Pd/TiO₂ (R) and 1.5% Pd/Al₂O₃ under

Table 1
The properties of catalysts and the CO adsorption

Catalyst	Temperature of reduction by H ₂	Surface area (m ² g ⁻¹)	Average crystal size of support by XRD (nm)	CO/Pd (molar ratio)
0.075% Pd/TiO ₂ (R)	200	22	62	0.33
0.075% Pd/TiO ₂ (A)	200	45	33	0.57
0.15% Pd/TiO ₂ (A)	200	45	33	0.47
0.075% Pd/TiO ₂ (R)	450	22	62	0.15
0.075% Pd/TiO ₂ (A)	450	45	33	0.16

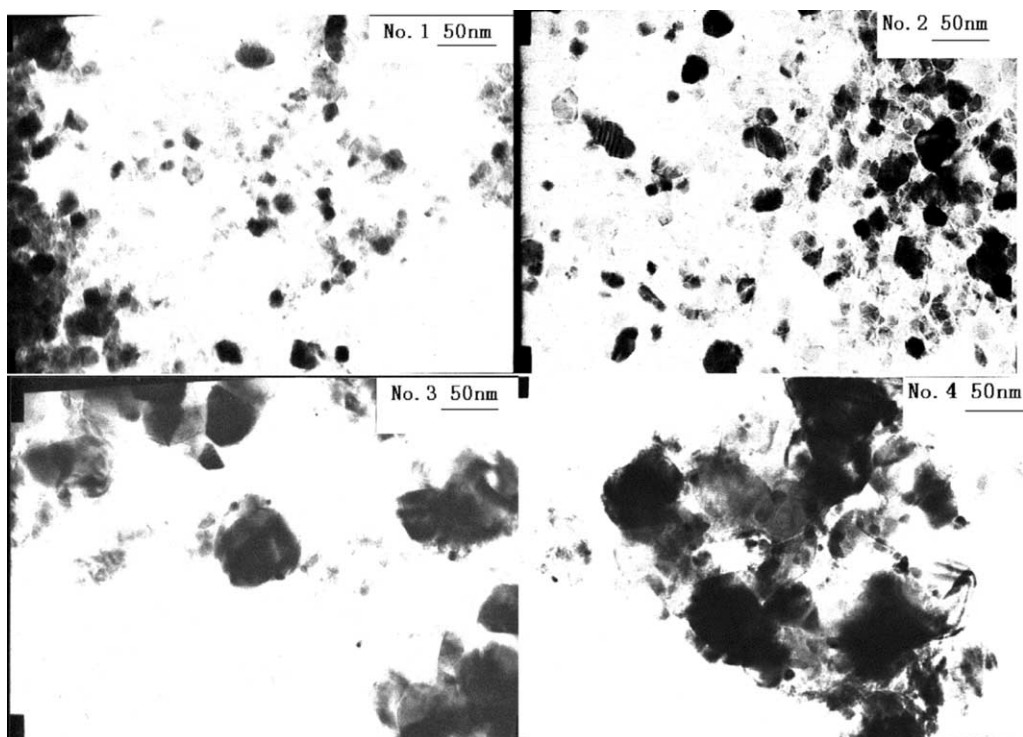


Fig. 4. Morphology of as-prepared 1.5% Pd/TiO₂ catalysts pre-reduced by H₂ at different temperature (°C): (1) 1.5% Pd/TiO₂ (A)-200, (2) 1.5% Pd/TiO₂ (A)-450, (3) 1.5% Pd/TiO₂ (R)-200, (4) 1.5% Pd/TiO₂ (R)-450.

different CO pressure. The IR bands of CO absorbed on Pd are divided into four modes depending on their locations: linear (2050–2160 cm⁻¹), compressed-bridged (1995–1975 cm⁻¹), isolated-bridged (1960–1925 cm⁻¹), and tri-coordinated (1890–1870 cm⁻¹) modes [24]. The intense band at 2100 cm⁻¹ for 1.5% Pd/TiO₂ (A) and 1.5% Pd/TiO₂ (R) is assigned to the linear absorbed CO on Pd.

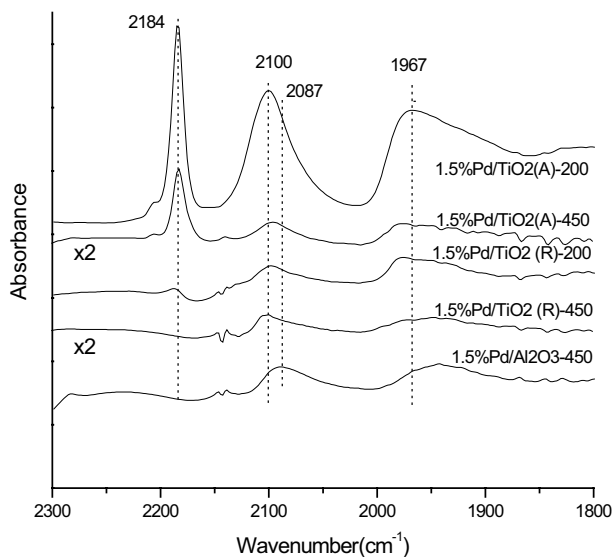


Fig. 5. IR spectra of CO (200 Torr) adsorbed on the as-synthesized catalysts.

Upon decreasing the CO pressure from 200 to 0.5 Torr, the IR band of linearly absorbed CO on Pd diminished markedly, but the IR band of multiply absorbed CO on Pd remained virtually unaltered, which proves that the intensity of linearly absorbed CO on Pd are much more weak than one of multiply absorbed CO.

Compared to IR spectra of CO adsorbed on 1.5% Pd/Al₂O₃, 1.5% Pd/TiO₂ (A) catalyst reduced at 200 and 450 °C has a new IR band of CO at 2180 cm⁻¹, which is assigned to CO adsorbed on Ti³⁺ sites [25]. However,

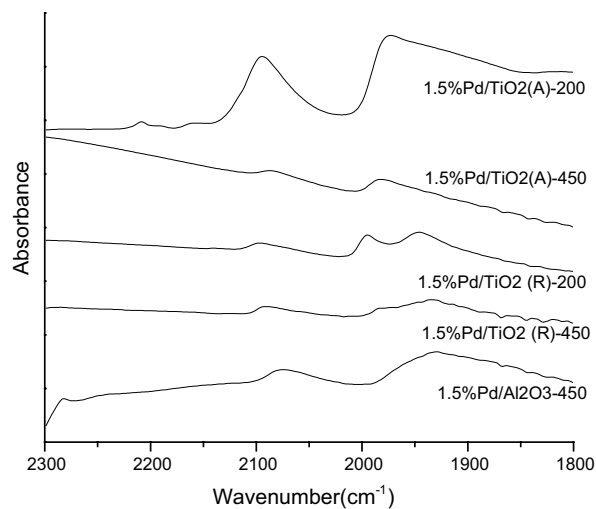


Fig. 6. IR spectra of CO (0.5 Torr) adsorbed on as-synthesized catalysts.

there is only a very small IR band of CO at 2180 cm^{-1} for 1.5% Pd/TiO₂ (R) reduced at 200 °C. These results further confirm the conclusion by EPR that the produced Ti³⁺ in Pd/TiO₂ (R) reduced at 200 °C is unstable in the presence of CO because of oxidation of Ti³⁺ by CO, and the produced Ti³⁺ in Pd/TiO₂ (A) reduced at 200 °C is stable in the presence of CO because of SMSI between Pd and Ti³⁺. This linearly absorbed CO on Ti³⁺ is very weakly absorbed as the IR band of linearly absorbed CO on Ti³⁺ diminished markedly with the decrease of CO pressure, and is not detectable under 0.5 Torr. The results of EPR show that there is SMSI between Pd and Ti³⁺ both for Pd/TiO₂ (A) and Pd/TiO₂ (R) reduced at 450 °C which could stabilize Ti³⁺, but only Pd/TiO₂ (A) reduced at 450 °C has a small IR signal of CO adsorbed on Ti³⁺ sites, which is partly attributed to low CO chemisorption for Pd/TiO₂ reduced at 450 °C (seen in Table 1). It could be reasonably inferred that CO adsorbed on Ti³⁺ sites for Pd/TiO₂ (R) reduced at 450 °C is more weak than one for Pd/TiO₂ (A) reduced at 450 °C so that no IR signal of CO adsorbed on Ti³⁺ sites is observed for Pd/TiO₂ (R) reduced at 450 °C.

3.4. Catalytic performance

The conversion and selectivity of as-synthesized catalysts were summarized in Table 2. From Table 2, it can be seen that industry used 0.3% Pd/Al₂O₃ catalyst, which has similar Pd loading per surface area to 0.075% Pd/TiO₂ (A), has only 48.7% conversion of alkadienes and 27.0% selectivity of alkenes at 100 °C, 14 atm, 8.33 ml g⁻¹ catalyst h⁻¹ and H₂/alkadienes (molar ratio) = 1.28. The use of rutile and anatase titania as the support of supported palladium catalyst instead of γ -Al₂O₃ results in the elevation of both conversion of alkadienes and selectivity of alkenes. For titania supported palladium catalysts, the anatase titania supported palladium catalyst 0.075% Pd/TiO₂ (A) has higher conversion of alkadienes (72.6%) and selectivity of alkenes (72.4%) than the rutile titania supported palladium catalyst 0.075% Pd/TiO₂ (R). The difference of catalytic properties of 0.075% Pd/TiO₂ (A) and 0.075% Pd/TiO₂ (R) maybe have some relationship to their difference of Pd loading per surface area of titania support. It can be seen from Tables 1 and 2 that 0.15% Pd/TiO₂ (A) has same Pd loading per surface area of titania support with 0.075% Pd/TiO₂ (R), but the

former catalyst still has higher selectivity of alkenes (55.0%) than the later catalyst (34.7%). No matter how the reaction conditions (e.g. reaction temperature, pressure, liquid space velocity, etc.) were changed, the trends of Pd/TiO₂ (A) catalyst pre-reduced at lower temperature showing better selectivity of alkenes than Pd/TiO₂ (R) and Pd/Al₂O₃ kept unchanged. Obviously, the structure and properties of support play important role in the catalytic performance of supported palladium catalysts. With the elevation of reduction temperature of catalyst from 200 to 450 °C, there is a sharp change of catalytic properties, especially for selectivity of alkenes, on titania (rutile or anatase) supported palladium catalysts.

The consideration of the surface and catalytic properties of titania supported noble metals is associated with strong metal-support interaction, which is one of the most interesting and most studied effects in catalysis. There have been many interpretations for the SMSI effect. The main interpretations are the morphological and the electronic effects. The morphological effects could reasonably explain our results: titania from catalyst is partly reduced and suboxide phase migrates onto the metal particle. Thus, the part of metal surface partially covered by TiO_x is blocked [26,27], which results in the moderating of dissociative processes leading to the formation of carbonaceous deposits, carbene species or self-hydrogenation reaction that are claimed to be responsible for the decrease of selectivity [28,29], due to the limited availability of contiguous adsorption of Pd sites. Under lower reduction temperature, the reduction of Ti⁴⁺ and the migration of the produced Ti³⁺ in the surface lattice of rutile TiO₂ is more difficult than in one of anatase TiO₂, which results in the more weak role of dilution effect of covered suboxide TiO_x on palladium for rutile TiO₂ supported palladium catalyst than for anatase TiO₂ supported palladium catalyst; however, under higher pre-reduction temperature, the dilution effect of covered suboxide TiO_x on palladium become much stronger for both anatase and rutile TiO₂ supported palladium catalyst. This is reason why the anatase titania supported palladium catalyst has higher selectivity of alkenes than rutile titania supported palladium catalysts under lower pre-reduction temperature, and but both anatase and rutile TiO₂ supported palladium catalyst all have higher selectivity under higher pre-reduction temperature.

Table 2
Activity and selectivity of catalysts at 100 °C, 14 atm, 8.33 ml g⁻¹ catalyst h⁻¹ and H₂/alkadienes (molar ratio) = 1.28

Catalyst	Temperature of reduction by H ₂ (°C)	Conversion of alkadienes (mol.%)	Selectivity of alkenes (mol.%)	Yield of alkenes (mol.%)
0.075% Pd/TiO ₂ (R)	200	62.6	34.7	21.7
0.075% Pd/TiO ₂ (A)	200	72.6	72.4	52.7
0.15% Pd/TiO ₂ (A)	200	49.4	55.0	27.2
0.075% Pd/TiO ₂ (R)	450	69.5	86.4	55.3
0.075% Pd/TiO ₂ (A)	450	60.5	89.5	54.1
0.3% Pd/Al ₂ O ₃	200	48.6	27.0	13.1

4. Conclusion

In conclusion, in situ EPR and IR investigation by using CO as probe molecules show that even pre-reduced by H₂ at lower temperature results in SMSI for anatase titania supported palladium catalyst, but not for rutile titania supported palladium catalyst. This difference is attributed that the Ti³⁺ ions produced by reduction of Ti⁴⁺ are fixed in the surface lattice of TiO₂, as rutile titania is more thermodynamically and structurally stable than anatase titania so that the Ti³⁺ ions fixed in the surface lattice of anatase TiO₂ is easier to diffuse to surface of palladium particle than one in the surface lattice of rutile TiO₂. The reason why the pre-reduction of both anatase and rutile supported palladium catalyst at higher temperature results in SMSI between Ti³⁺ and Pd is attributed that the thermal diffusion of produced Ti³⁺ ion at higher temperature is much easier than at lower temperature so that it could overcome the binding of surface lattice of both anatase and rutile titania to move to the surface or surrounding of palladium particle. The anatase titania supported palladium catalyst 0.075% Pd/TiO₂ (A) reduced at lower temperature has higher selectivity of alkenes than rutile titania supported palladium catalysts 0.075% Pd/TiO₂ (R). For titania (rutile or anatase) supported palladium catalysts, the elevation of pre-reduction temperature from 200 to 450 °C gives rise to sharp change of catalytic properties, especially for selectivity of alkenes. The very different catalytic properties between 0.075% Pd/TiO₂ (R) and 0.075% Pd/TiO₂ (A) catalyst pre-reduced at lower temperature, and the rapid change of conversion and selectivity of 0.075% Pd/TiO₂ (A) and 0.075% Pd/TiO₂ (R) with the elevation of pre-reduction temperature are reasonably explained by the presence of SMSI both for anatase titania supported palladium catalyst pre-reduced at lower temperature, and titania (rutile and anatase) supported palladium catalyst pre-reduced at higher temperature.

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