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A comparative study of TiO_2 supported noble metal catalysts for the oxidation of formaldehyde at room temperature

Changbin Zhang, Hong He *

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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Abstract

The TiO_2 supported noble metal (Au, Rh, Pd and Pt) catalysts were prepared by impregnation method and characterized by means of X-ray diffraction (XRD) and BET. These catalysts were tested for the catalytic oxidation of formaldehyde (HCHO). It was found that the order of activity was $Pt/TiO_2 \gg Rh/TiO_2 > Pd/TiO_2 > Au/TiO_2 \gg TiO_2$. HCHO could be completely oxidized into CO_2 and H_2O over Pt/TiO_2 in a gas hourly space velocity (GHSV) of 50,000 h^{-1} even at room temperature. In contrast, the other catalysts were much less effective for HCHO oxidation at the same reaction conditions. HCHO conversion to CO_2 was only 20% over the Rh/TiO_2 at 20 °C. The Pd/TiO_2 and Au/TiO_2 showed no activities for HCHO oxidation at 20 °C. The different activities of the noble metals for HCHO oxidation were studied with respect to the behavior of adsorbed species on the catalysts surface at room temperature using in situ DRIFTS. The results show that the activities of the TiO_2 supported Pt, Rh, Pd and Au catalysts for HCHO oxidation are closely related to their capacities for the formation of formate species and the formate decomposition into CO species. Based on in situ DRIFTS studies, a simplified reaction scheme of HCHO oxidation was also proposed.

Keywords: Formaldehyde; Noble metal; TiO_2; Formate species; In situ DRIFTS

1. Introduction

Formaldehyde (HCHO) emitted from building/furnishing materials and consumer products is known to cause nasal tumors, irritation of the mucous membranes of the eyes, respiratory tract and skin [1,2], and considered as a major indoor air pollutant in air-tight houses. Due to the increasing concern about HCHO emission, the abatement of its emission is of significant practical interest at low temperature, especially at room temperature.

A number of studies, related to the removal of HCHO by adsorbents, have been carried out both in the lab and in the field [3–5]. However, the effectiveness of the removal materials was limited for a short period due to their removal capacities.

Catalytic oxidation is one of the most promising technologies for the abatement of VOCs emission because VOCs can be oxidized into CO_2 over catalysts at much lower temperature than that of thermal oxidation [6]. The supported noble metal catalysts or metal oxides (Ag, Cu, Cr and Mn) are the conventional catalysts for catalytic oxidation reaction [7–20]. Among them, the oxidized films of Ni, Pd and Al, silver–cerium composite oxide and Pd/Al_2O_3 catalysts were found to be effective for HCHO oxidation [14–16]. Because these reported catalysts generally have the activities for HCHO decomposition into CO_2 at a high temperature (>60 °C), they are not convenient for the removal of indoor HCHO without thermal and photon sources. Sekine [20] found manganese oxide could react with HCHO and release CO_2 in a static reaction vessel even at room temperature, suggesting that this metal oxide can be used as an active component for HCHO removal in indoor air. However, the manganese oxide still showed very low removal efficiency for HCHO at room temperature, so it is limited for the indoor HCHO removal. In addition, Álvarez et al. [16] reported that the Al_2O_3 supported manganese oxide catalysts showed activity for HCHO oxidation to CO_2 at above 150 °C. Generally, little other studies was reported on catalytic oxidation of HCHO at room temperature. Therefore the development of a total oxidation catalyst for HCHO decomposition at room temperature is still strongly needed.

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62923563.
E-mail address: honghe@rcees.ac.cn (H. He).

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Recently, we reported a perfect Pt/TiO_2 catalyst over which HCHO can be completely oxidized into CO_2 and H_2O at room temperature [21]. It suggests that TiO_2 is a favorable support for low temperature oxidation of HCHO. On the basis of these results, we reported a comparative study on HCHO oxidation over the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts in the present work. The different activities of the noble metals on HCHO oxidation were studied with respect to the behavior of adsorbed species on the catalyst surface using in situ DRIFTS at room temperature.

2. Experimental

2.1. Catalyst preparation

The TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts were prepared by an impregnation method with an anatase type TiO_2 (Wako Pure Chemicals) and an aqueous solution of $AuCl_4$, $RhCl_3$, $Pd(NO_3)_2$ and H_2PtCl_6, respectively. After impregnation, the excessive water was removed in a rotary evaporator at 80 °C. The samples were dried at 110 °C for 12 h and then calcined at 400 °C for 2 h. The loading of noble metal was 1 wt.%. Pretreatments of TiO_2 supported noble metal catalysts are needed to get a steady-going catalytic performance.

2.2. Activity test of catalysts

The activity tests for the catalytic oxidation of HCHO over catalysts were performed with a fixed-bed quartz flow reactor by passing a gas mixture of $HCHO/O_2/He$ = 100 ppm/20 vol%/ balance at a total flow rate of 50 $cm^3\ min^{-1}$ (gas hourly space velocities (GHSV): 50,000 h^{-1}). HCHO standard gas was constantly introduced from a gas-generator system [5]. The HCHO, CO and CO_2 were analyzed using a gas chromatograph (GC) equipped with hydrogen flame ionization detector (FID) and Ni catalyst convertor which was used for converting the carbon oxides quantitatively into methane in the presence of hydrogen before the detector. Separations were carried out using two columns: a carbon molecular sieve column for permanent gases (CO and CO_2) and a GDX-403 column for the HCHO. The operating parameters were as follows: temperature of the detector, 180 °C; temperature of the column, 50 °C; carrier gas, helium 30 ml/min; volume of the analyzed sample, 1 ml.

2.3. Characterization of catalyst

The nitrogen adsorption–desorption isotherms were obtained at −196 °C over the whole range of relative pressures, using a Micromeritics ASAP2000 automatic equipment on samples degassed at 220 °C. Specific areas were computed from these isotherms by applying the BET method and taking a value of 0.162 nm^2 for the cross-section of the physically adsorbed nitrogen molecule. The fresh catalysts were characterized by X-ray diffractometry using a computerized Rigaku D/max-RB X-Ray Diffractometer (Japan, Cu Kα radiation, 0.154056 nm).

2.4. In situ DRIFTS

In situ DRIFT spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N_2 cooled MCT detector. The sample (about 30 mg) for study was finely grounded and placed in a ceramic crucible. A flow of feed gas mixture was controlled by mass flow meters. All spectra were recorded with a resolution of 4 cm^{-1} and accumulating 100 scans. A background spectrum was subtracted from each spectrum, respectively.

3. Results and discussion

3.1. Catalytic test

The catalytic activities of pure TiO_2 and the TiO_2 supported 1 wt.% noble metal (Pt, Rh, Pd and Au) catalysts were evaluated for HCHO oxidation as shown in Fig. 1. It is evident that the most effective catalyst for HCHO oxidation was the Pt/TiO_2, while the worst active catalyst was pure TiO_2. The order of activity observed was $Pt/TiO_2 \gg Rh/TiO_2 > Pd/TiO_2 > Au/TiO_2 \gg TiO_2$. In the case of Pt/TiO_2, HCHO could be completely oxidized into CO_2 and H_2O in a GHSV of 50,000 h^{-1} even at room temperature. However, the other catalysts were much less effective under the same reaction conditions. HCHO conversion to CO_2 was only 20% over the Rh/TiO_2 at 20 °C. The Pd/TiO_2 and Au/TiO_2 showed no activities for HCHO oxidation at 20 °C. It is worthwhile to point out that pure TiO_2 has no activity for HCHO oxidation to CO_2 in the temperature range investigated (20–120 °C). These findings show that the most appropriate active sites for HCHO oxidation are surface noble metal sides [27], and the different activities of the TiO_2 supported noble metal catalysts are related to the different capacities of noble metals on HCHO oxidation.

3.2. Characterization of catalysts

BET surface areas of TiO_2 and the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts are shown in Table 1. All

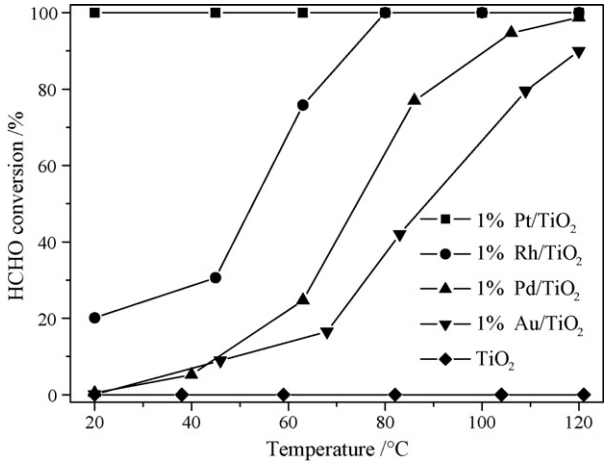

Fig. 1. HCHO conversions over TiO_2 (◆); Pt/TiO_2 (■); Rh/TiO_2 (●); Pd/TiO_2 (▲); Au/TiO_2 (▼) catalysts at various temperature. Reaction conditions: HCHO 100 ppm, O_2 20 vol%, He balance, total flow rate: 50 $cm^3\ min^{-1}$, GHSVs: 50,000 h^{-1}.

Table 1
BET surface areas of TiO_2 and the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts

Sample	BET area (m^2/g)
TiO_2	49.6
Pt/TiO_2	47.4
Rh/TiO_2	48.4
Pd/TiO_2	46.3
Au/TiO_2	43.9

catalysts presented very similar surface area values. With respect to the bare TiO_2, surface areas of the noble metal loaded catalysts slightly decreased. Deposit of small particles of noble metals on TiO_2 may account for the drop of BET area.

Catalyst structures were revealed by XRD. As shown in Fig. 2, XRD patterns of the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts were essentially the same as that of the pure TiO_2 sample (anatase type). The introduction of noble metals did not induce the appearances of the peaks of polycrystalline noble metals, which indicates that the noble metals are in very high dispersion degree on catalysts. High-resolution TEM images also suggested a smaller typical particle size of noble metals than 1 nm (data not shown).

3.3. In situ DRIFTS study of HCHO oxidation

In the following experiments, the different activities of the noble metals on HCHO oxidation were studied with respect to the behavior of adsorbed species on the catalyst surface at room temperature using in situ DRIFTS.

Fig. 3 shows the dynamic changes in the DRIFTS spectra of the Pt/TiO_2 as a function of time in a flow of O_2 + HCHO + He at room temperature. After exposing the catalyst to O_2 + HCHO + He mixture gas at room temperature, four bands appeared at 2062, 1657, 1570 and 1359 cm^{-1}. With time increasing, the bands intensities increased and reached a steady level after 60 min. According to previous studies, two strong bands at 1570 and 1359 cm^{-1} were ascribed to ν_{as}(COO) and

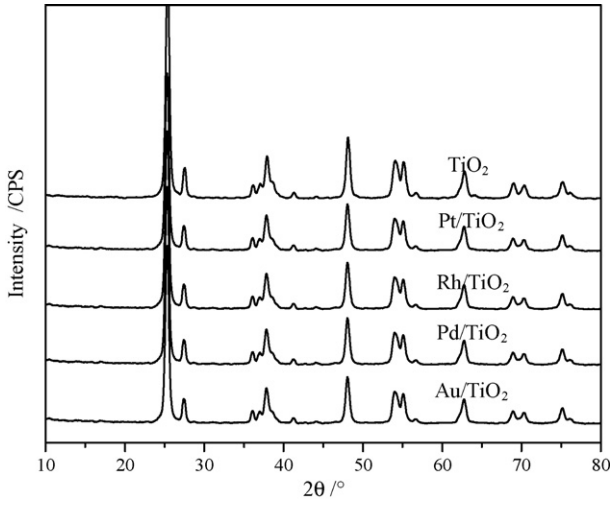

Fig. 2. X-ray diffraction patterns of TiO_2 and the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts.

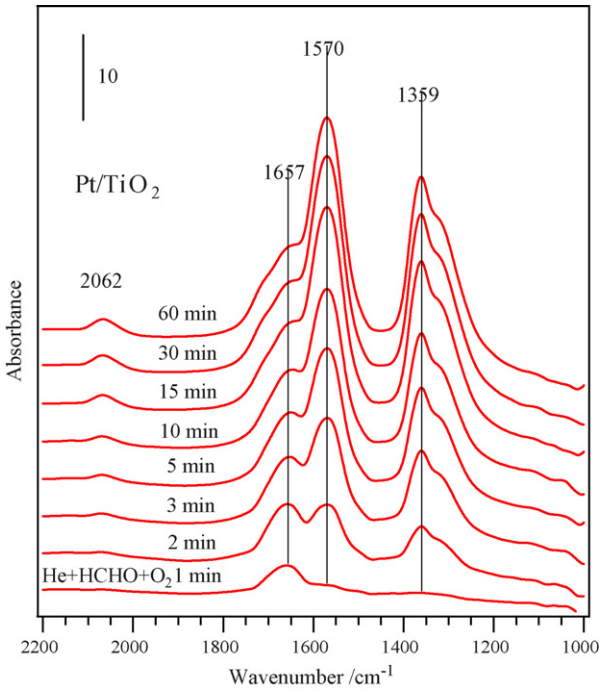

Fig. 3. Dynamic changes of in situ DRIFTS spectra of the Pt/TiO_2 catalyst as a function of time in a flow of O_2 + HCHO + He at room temperature.

ν_s(COO) on TiO_2 sites [22–27]. This shows that the adsorbed HCHO rapidly convert into formate species on the Pt/TiO_2. A very weak band appeared at 2062 cm^{-1} was assignable to linear CO adsorbed on Pt [26,27], and the band at 1657 cm^{-1} was due to water adsorbed on the catalyst (originated from the water in reactant gases). However, no peaks due to molecularly adsorbed HCOOH and HCHO were observed on the catalyst in the flow of O_2 + HCHO + He at room temperature [26–28].

After the catalysts were exposed to a flow of O_2 + HCHO + He for 60 min (Fig. 3), the flow of O_2 + HCHO was stopped and the sample was purged by helium. The dynamic changes in the DRIFTS spectra of Pt/TiO_2 catalyst are shown in Fig. 4A. The integrated peak areas of surface formate and CO in Fig. 4A are displayed as a function of time in Fig. 4B. The bands of formate species at 1570 and 1359 cm^{-1} gradually decreased, and almost disappeared after about 15 min. Meanwhile, two strong bands appeared at 2062 and 1757 cm^{-1}, which could be assigned to linearly adsorbed CO (2062 cm^{-1}) and bridge adsorbed CO (1757 cm^{-1}) on Pt metal particles [26–28], and their intensities reached a steady level within 15 min. This indicates that surface formate species on Pt/TiO_2 can decompose into adsorbed CO species in the absence of O_2 at room temperature.

The Pt/TiO_2 catalyst was then purged for 60 min by O_2. The dynamic changes of in situ DRIFTS of the Pt/TiO_2 as a function of time in a flow of O_2 were shown in Fig. 5. The adsorbed CO bands rapidly decreased and completely disappeared in 5 min, which shows that the adsorbed CO species were extremely reactive toward O_2 on the Pt/TiO_2 even at room temperature. It is worthwhile to point out that CO consuming rate should be faster than its forming rate under the reaction conditions because little adsorbed CO

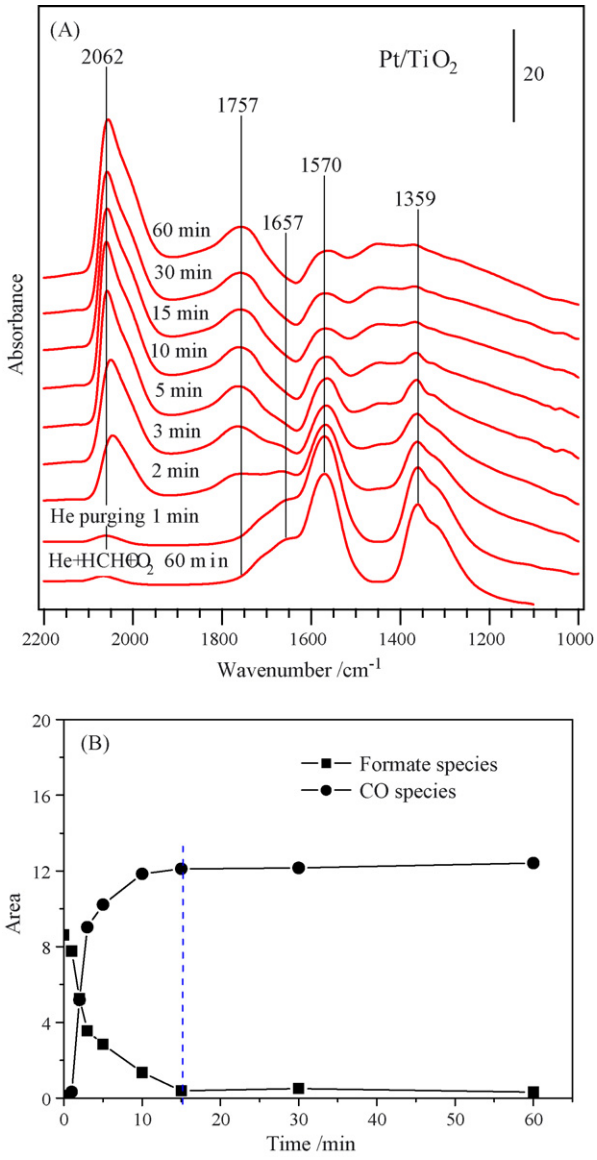

Fig. 4. (A) Dynamic changes of in situ DRIFTS spectra of the Pt/TiO_2 catalyst as a function of time in a flow of helium at room temperature after exposed catalyst to a flow of O_2 + HCHO + He for 60 min (shown in Fig. 3). (B) Time dependence of the integrated areas of the peak in the range of 1407–1240 cm^{-1} (■, formate species), 1930–2096 cm^{-1} (●, CO species).

species was observed on Pt/TiO_2 catalyst in the flow of O_2 + HCHO + He as shown in Fig. 3.

The same sets of experiments were also performed on the Rh/TiO_2, Pd/TiO_2 and Au/TiO_2 at room temperature. The DRIFTS spectra of Rh/TiO_2, Pd/TiO_2 and Au/TiO_2 are showed and compared with those of Pt/TiO_2 in Figs. 6–8.

As shown in Fig. 6, the formate species at 1570, 1359 cm^{-1} formed on all of catalysts after the catalysts were exposed to a flow of O_2 + HCHO + He for 60 min. The formate species are dominant surface species (1359, 1570 cm^{-1}) on the Pt/TiO_2 and Rh/TiO_2, accompanied with trace adsorbed CO species (2062 cm^{-1}) on Pt/TiO_2. Beside the formate species, two strong bands attributed to dioxymethylene species at 1414 and 1107 cm^{-1} appeared and dominated on the Pd/TiO_2 and Au/TiO_2 [27]. Raskó and co-workers [27] have reported that

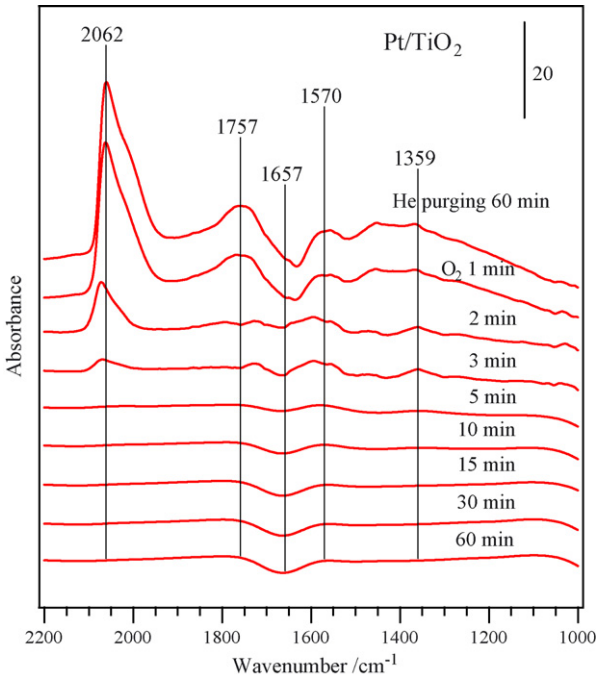

Fig. 5. Dynamic changes of in situ DRIFTS spectra of the Pt/TiO_2 as a function of time in a flow of O_2 at room temperature after the sample was purged by helium for 60 min (shown in Fig. 4).

hydrogen transfer inside the dioxymethylene species could lead to the formation of formic acid, and the dissociation of formic acid will cause the appearance of the formate species. Taking into account the information above, we concluded that surface dioxymethylene and formate species are the main intermediates for HCHO oxidation. The activities of catalysts for the

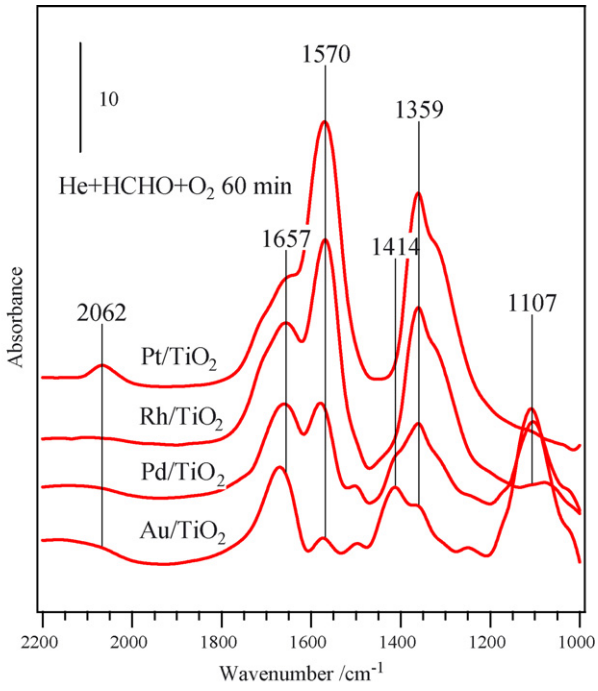

Fig. 6. DRIFTS spectra of the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts in a flow of HCHO + He + O_2 for 60 min at room temperature.

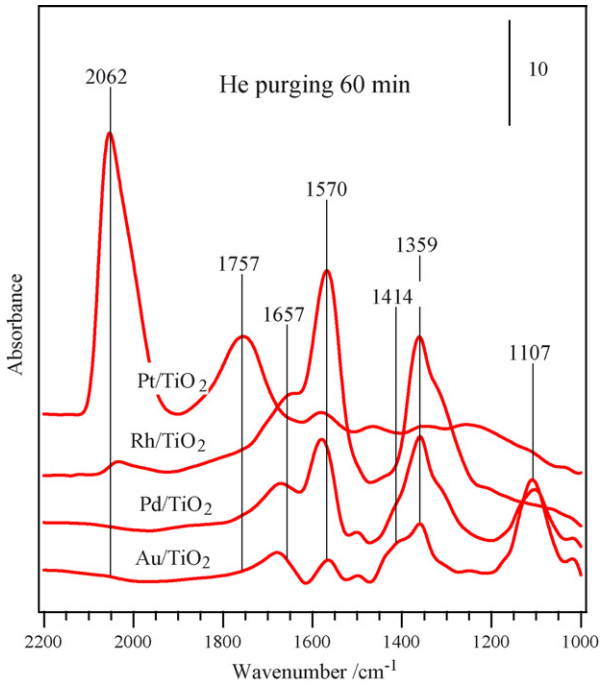

Fig. 7. DRIFTS spectra of the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts in a flow of helium for 60 min after exposed catalysts to a flow of O_2 + HCHO + He for 60 min (shown in Fig. 6).

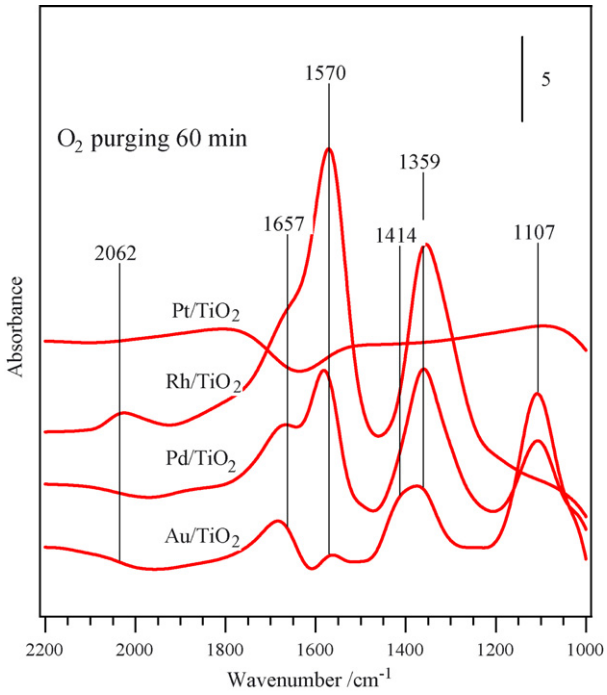

Fig. 8. DRIFTS spectra of the TiO_2 supported noble metal (Pt, Rh, Pd and Au) catalysts in a flow of O_2 for 60 min after the samples were purged by helium for 60 min (shown in Fig. 7).

formation of surface formate species are in the order of Pt/TiO_2 > Rh/TiO_2 ≫ Pd/TiO_2 > Au/TiO_2, which is harmony with the results of activity test. It must be reminded that neither the formate nor dioxymethylene species was detected on pure TiO_2 at the same conditions (not shown). We suppose that the appearances of the formate and dioxymethylene species on the TiO_2 supported noble metal catalysts are ascribed to the increase of the numbers of surface sites capable of oxidizing HCHO with the introduction of noble metal onto TiO_2 [26]. With the different oxidation capacities of the noble metals, either the formate or dioxymethylene species can dominate over the catalyst surfaces.

As shown in Fig. 7, after the samples were purged by helium for 60 min, linear CO (2062 cm^{-1}) and bridge CO (1757 cm^{-1}) became dominant surface species on Pt/TiO_2 surface. However, only a trace amount of the adsorbed CO species formed on the Rh/TiO_2 with a slight decrease of the formate species. The spectra of the Pd/TiO_2 and Au/TiO_2 were not obviously different from the spectra before purged by helium (Fig. 6). The findings show that surface formate species cannot easily decompose into the CO species on the TiO_2 supported Rh, Pd and Au catalysts. As shown in Fig. 8, the spectra of the Rh/TiO_2, Pd/TiO_2 and Au/TiO_2 did not change during O_2 purging for 60 min.

On the basis of the results, a simplified reaction scheme for the catalytic oxidation of HCHO on the TiO_2 supported Pt, Rh, Pd and Au catalysts was proposed and shown in Fig. 9. The dioxymethylene, formate and adsorbed CO species are the important reaction intermediates for HCHO oxidation. HCHO is oxidized into surface dioxymethylene species followed by formate species. The surface formate species decompose into adsorbed CO species and H_2O, and then CO species react with O_2 to produce gas phase CO_2. The conversion of surface formate species to adsorbed CO on the catalysts is the rate-determining step for the catalytic oxidation of HCHO. In the case of Pt/TiO_2, the formate species can quickly form and decompose into adsorbed CO on the catalyst surface without the presence of O_2, and then be oxidized into CO_2 in the presence of O_2 even at room temperature. Therefore, the Pt/TiO_2 shows a very high activity for HCHO oxidation. In the case of Rh/TiO_2, the formate species can also form, but not easily decompose into adsorbed CO on the catalyst surface, so that Rh/TiO_2 is much less effective than

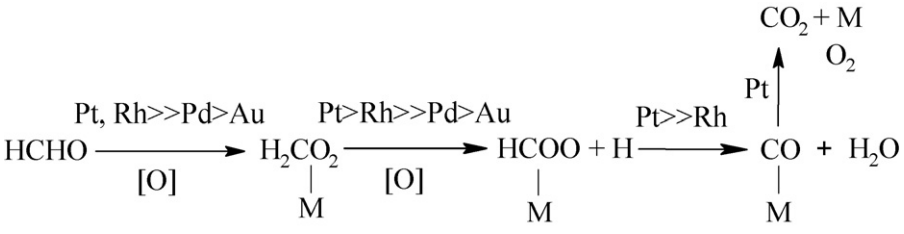

Fig. 9. Reaction scheme of the catalytic oxidation of HCHO on the TiO_2 supported Pt, Rh, Pd and Au catalysts.

Pt/TiO_2 for HCHO oxidation. In contrast, the Pd/TiO_2 and Au/TiO_2 are not effective for both the formation of formate species and its decomposition into CO, so their activities are much lower than that of Rh/TiO_2.

4. Conclusions

The Pt/TiO_2 is the most active catalyst for HCHO oxidation among the TiO_2 supported 1 wt.% noble metal (Pt, Rh, Pd and Au) catalysts. HCHO can be completely oxidized into CO_2 in a GHSV of 50,000 h^{-1} over the Pt/TiO_2 even at room temperature. Dioxymethylene, formate and CO species are the important reaction intermediates, and the conversion of surface formate species into adsorbed CO is the rate-determining step for the catalytic oxidation of HCHO. The formate species can be easily formed and decomposed into adsorbed CO on Pt/TiO_2 surface, and then be oxidized to CO_2 by O_2, so the Pt/TiO_2 shows a very high activity for HCHO oxidation. TiO_2 supported Rh, Pd and Au catalysts are much less effective for either the formation of formate species or the formate decomposition into CO species, so their activities for HCHO oxidation are very low.

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