



Combined XPS and in situ DRIRS study of mechanism of Pd–Fe/ α -Al₂O₃ catalyzed CO coupling reaction to diethyl oxalate

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Abstract

The mechanism for the reaction of CO coupling to diethyl oxalate (DEO) over Pd–Fe/ α -Al₂O₃ in gaseous phase at normal pressure was studied by X-ray photoelectron spectroscopy (XPS) and in situ diffuse reflectance infrared spectroscopy (DRIRS) techniques. The adsorption of two reactants, carbon monoxide and ethyl nitrite, on the catalyst was observed, respectively with in situ DRIRS as well as the catalysts after ethyl nitrite adsorption and after in situ reaction were also characterized by XPS measurement. These observational results show that (1) The ethyl nitrite on the catalyst surface has a dissociative chemisorption which leads to the oxidation of Pd⁰ to Pd²⁺ (active component on the catalyst). So the reaction is a redox process; (2) Two intermediates, palladium complexes, in the reaction process are involved. From this, the mechanism steps of the reaction were proposed and the two intermediates were inferred.

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1. Introduction

In the past decades, a new environmentally benign chemical process to synthesize diethyl oxalate (DEO) by catalytic coupling reaction of CO in gaseous phase at normal pressure has attracted great interest of many researchers in the world. Some studies on the catalyst preparation, reaction conditions and kinetics for CO coupling to diethyl oxalate at normal pressure have been reported in the literature [1–5].

In our previous work [4,5], the Pd–Fe/ α -Al₂O₃ catalyst prepared for CO coupling reaction to DEO at 393 K at normal pressure exhibited high catalytic activity, high selectivity and fair stability, applicable to industrial production. Now, the industrialization of this new synthesis technology is at preparatory stage in China. To continue a fundamental understanding of the surface catalytic reaction of CO coupling to DEO over group VIII metal catalyst, the mechanism

of Pd–Fe/ α -Al₂O₃ catalyzed reaction of CO coupling was studied by X-ray photoelectron spectroscopy (XPS) and in situ diffuse reflectance infrared spectroscopy (DRIRS) techniques. In this paper, the types of the surface catalytic reaction and the reaction mechanism were not only determined but the pathways and two intermediates involved in this process were also proposed. The observational experimental results in the adsorption of two reactants, CO and ethyl nitrite, respectively on Pd–Fe/ α -Al₂O₃ show that the catalyst is capable of adsorbing two reactants, respectively and the active component, Pd⁰, on the catalyst undergoes redox process during the reaction.

As well known, IR spectroscopy techniques have been widely applied to the study on the surface catalytic reaction to obtain various surface information for half a century. In most investigations on catalytic reaction, transmission IR technique was employed, but it can suffer potential problem [6] such as the complicated sample preparation and the provided weak absorption signals due to the addition of considerable quantity of inert substance, KBr or Al₂O₃ in the

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sample containing components to be of poor transmission of light. So, in recent decades, Diffuse Reflectance IR technique has been developed [7], having the potential of yielding more accurate and more detailed information without introducing KBr or other inert substances to the catalyst sample. Thus, it is a very effective method for in situ study of surface catalytic reaction. In present work, DRIRS technique was used because palladium on the catalyst transmits light poorly, and combined with XPS measurements to observe the pathways of CO coupling reaction to DEO. A combined measurements of XPS and in situ DRIRS provide various surface information on the adsorption of two reactants, the redox process of the active component, Pd⁰, and the intermediates involved in the reaction.

2. Experimental

The Pd–Fe/ α -Al₂O₃ catalyst were prepared as described in detail previously [5]. The α -Al₂O₃ support was retreated so as to meet the needs of catalyst preparation. Then it was impregnated with a aqueous solution of PdCl₂ and FeCl₃ for 12 h, dried at 393 K for 12 h and calcined in air at 673 K for 12 h. Before the prepared catalyst was used, it must be reduced in hydrogen at 773 K for 8 h.

Data of XPS for the catalyst sample were recorded with P-E PHI-1600 ESCA using a Mg K α source (1253.6 eV). The catalyst sample was fixed on a sample stage and was evacuated to 2×10^{-7} Pa for the measurement. The binding energies were corrected by using the value of 74.0 eV for the Al2p peak for the catalyst.

Infrared spectra were measured using a BRUKER VECTOR 22 diffuse reflectance infrared spectrometer with a solution of 2 cm⁻¹, equipped with a stainless steel in situ IR flow cell. The powder sample was placed into the cell, which had been evacuated at 473 K and had been in N₂ flow for 30 min at 473 K. Then, it was pretreated for 30 min at 423 K in N₂. After cooling down to the desired temperature, the reactants were introduced in constant flowing and the IR spectra were recorded. The reactants used were carbon monoxide (purity 99.9%) and ethyl nitrite (C₂H₅ONO) obtained by

dropping H₂SO₄ into an ethanol solution of sodium nitrite (purity 95%).

3. Results and discussion

3.1. Adsorption of carbon monoxide

Fig. 1a, b, c shows the infrared spectra of CO on the Pd–Fe/ α -Al₂O₃ catalyst at 298, 363 and 393 K. In general [8,9], the bands above 2000 and below 2000 cm⁻¹ are assigned to linearly-bound CO and bridge-bound CO, respectively. So the bands at about 2079 and 1970 cm⁻¹ in Fig. 1 represent that there are both the linearly adsorbed CO and the bridge adsorbed CO on the catalyst at 298, 363 and 393 K though the band at about 2079 cm⁻¹ is close to the band at about 2116 cm⁻¹ assigned to CO in gaseous phase. Moreover, from Fig. 1a₂, b₂, c₂, the linearly adsorbed CO is found to be weaker than the bridge adsorbed CO when they were in N₂ flow, especially, that at 393 K, because the peaks at 2079 cm⁻¹ are smaller than that at 1970 cm⁻¹.

3.2. Dissociative adsorption of ethyl nitrite (reactant) and oxidation of Pd⁰ to Pd²⁺

Figs. 2 and 3, respectively show the IR spectra of ethyl nitrite without the catalyst in the in situ IR cell at 393, 423 and 473 K and that on the catalyst in the cell at 298, 363 and 393 K. The bands at 1617 and 1668 cm⁻¹ in Figs. 2 and 3 are attributed to the N=O vibration of ethyl nitrite [10], accompanied at the bands in 3319 and 3209 cm⁻¹. The bands at 2994, 2958 and 2902 cm⁻¹ are assigned to CH₃– and CH₂– asymmetric stretching vibrations and symmetric vibration, the bands of the CH₃– and CH₂– deformation modes being at 1453, 1389 and 1312 cm⁻¹.

From Figs. 2 and 3, the decomposition reaction of ethyl nitrite without the catalyst is found to take place at 473 K, whereas, the ethyl nitrite on the catalyst still decomposes at 363 K because additional bands appear at about 1759 and 1727 cm⁻¹ assigned to carbonyl group [10].

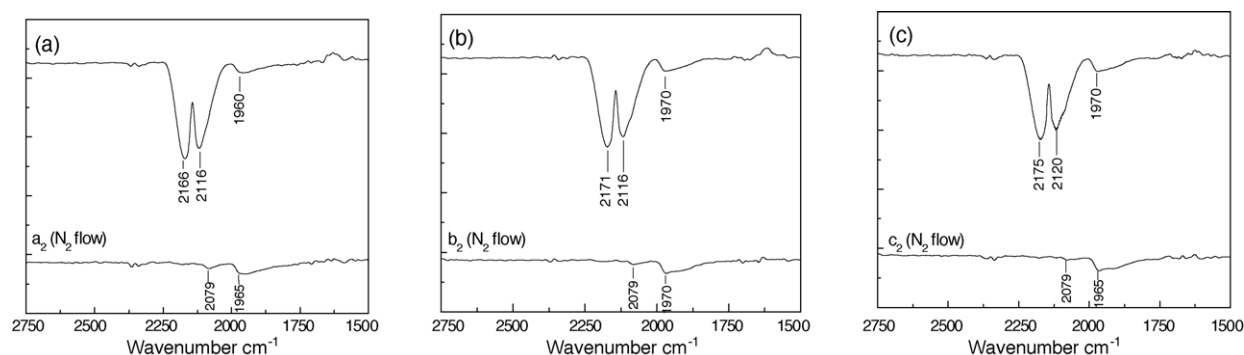


Fig. 1. IR spectra of adsorbed CO on Pd system catalyst at different temperatures (a) 298 K, (b) 363 K and (c) 393 K.

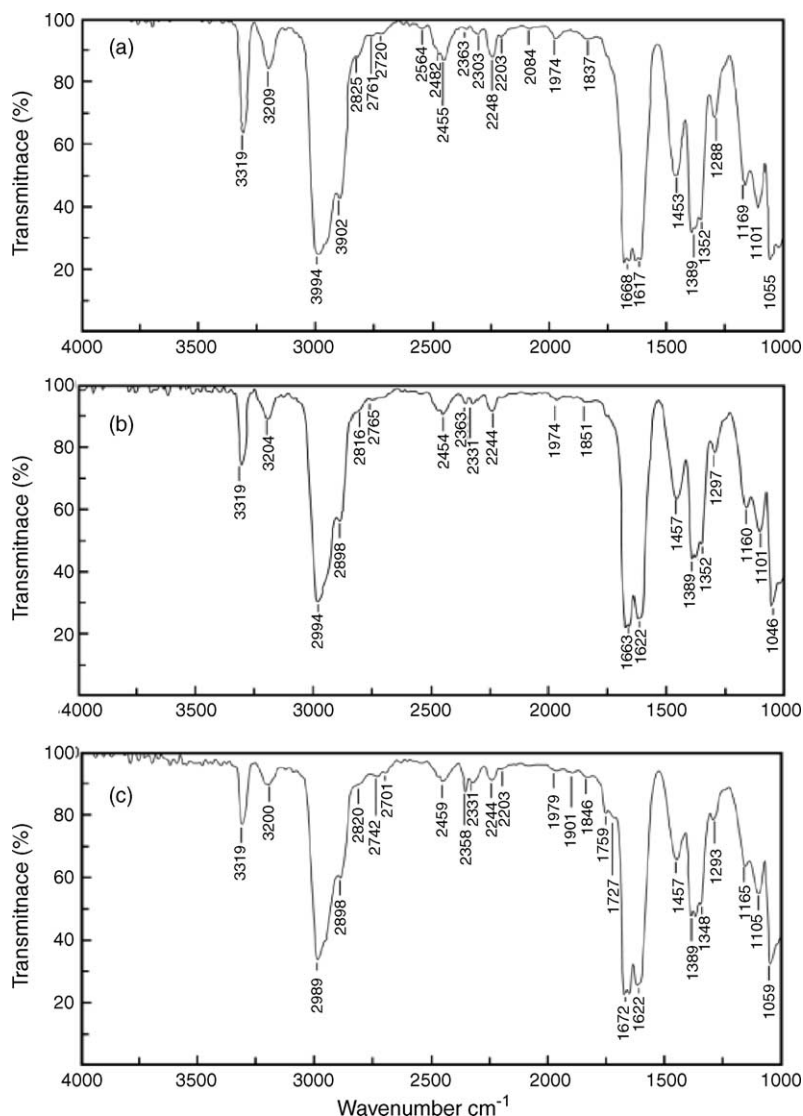


Fig. 2. IR spectra of C_2H_5ONO without catalyst at different temperatures (a) 393 K, (b) 423 K and (c) 473 K.

This indicates that the reactant, ethyl nitrite, can be not only adsorbed on the catalyst surface but the catalytic adsorption of ethyl nitrite also accelerates its decomposition. So, a dissociative adsorption of ethyl nitrite on the catalyst surface was confirmed.

Subsequently, the catalyst used in the experiment of dissociative adsorption of ethyl nitrite was taken from the in situ cell and immediately put into a sealed small bottle, ready for its XPS characterization. XPS patterns of the catalysts before and after the ethyl nitrite adsorption are displayed in Fig. 4.

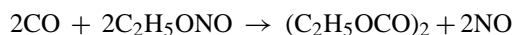
Fig. 4 shows that the Pd element on the surface of the fresh catalyst before the ethyl nitrite adsorption was in Pd^0 state, whereas that on the catalyst after the ethyl nitrite adsorption was in both Pd^0 and Pd^{2+} because the Pd peaks at 335.1 and 340.3 eV are assigned to Pd^0 , and these at 337.2 and 342.1 eV are assigned to Pd^{2+} [11]. It is evident that the

dissociative adsorption of ethyl nitrite on the catalyst surface causes Pd^0 to be oxidized to Pd^{2+} . Meanwhile, it is inferred that ethyloxypalladium complex ($Pd^{2+}(C_2H_5O^-)_2$) on the catalyst surface is formed as first intermediate involved in the CO coupling reaction.

3.3. Reaction of carbon monoxide and ethyl nitrite to diethyl oxalate

3.3.1. In situ IR spectra of the reaction

The chemical equation of CO coupling reaction is



IR spectra of the reaction of CO and C_2H_5ONO on the catalyst at 353, 363 and 383 K are presented in Fig. 5.

We know that the bands at about 1181 and 1160 cm^{-1} are assigned to the C–O stretching vibrations of the prod-

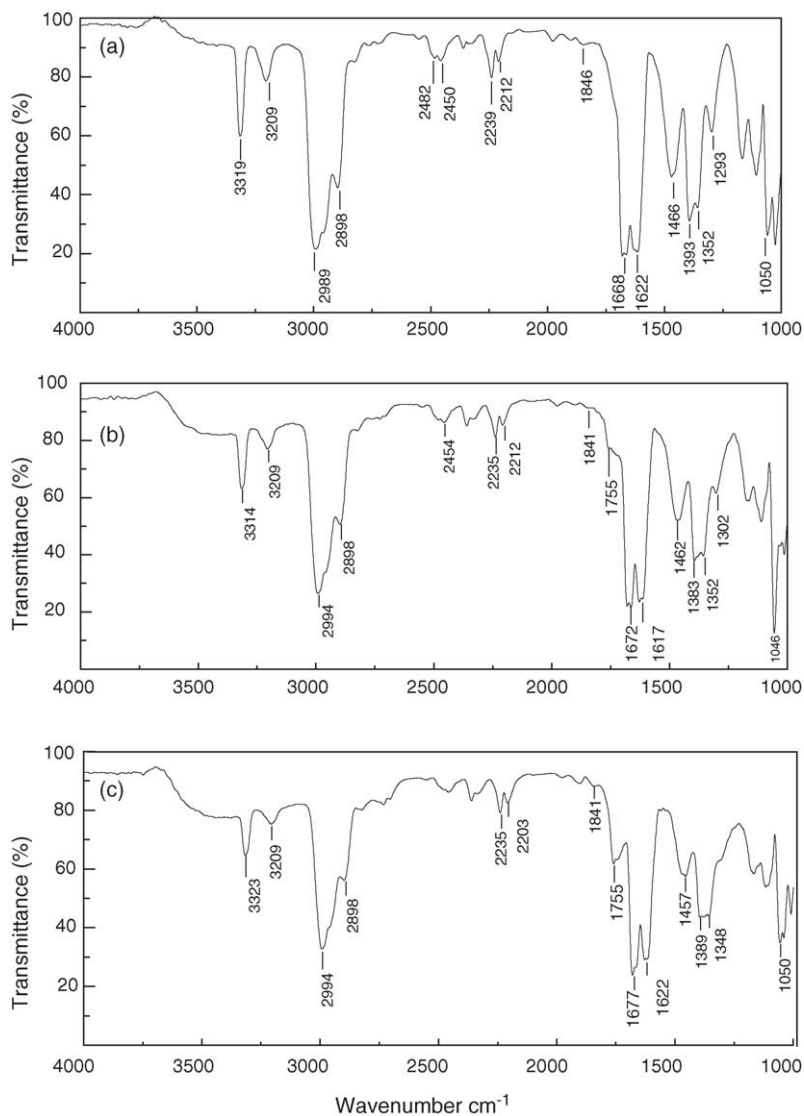


Fig. 3. IR spectra of C_2H_5ONO adsorption on Pd-Fe/ $\alpha-Al_2O_3$ catalyst at different temperatures (a) 298 K, (b) 363 K and (c) 393 K.

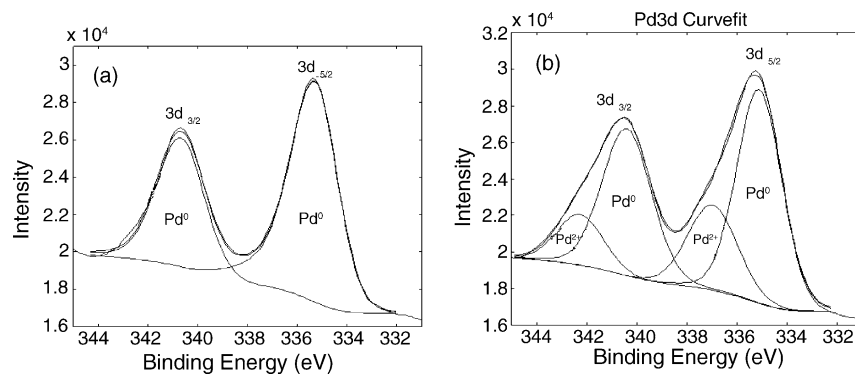


Fig. 4. Curvefit of Pd for XPS profiles of Pd-Fe/ $\alpha-Al_2O_3$ catalyst (a) fresh catalyst and (b) catalyst after C_2H_5ONO adsorption.

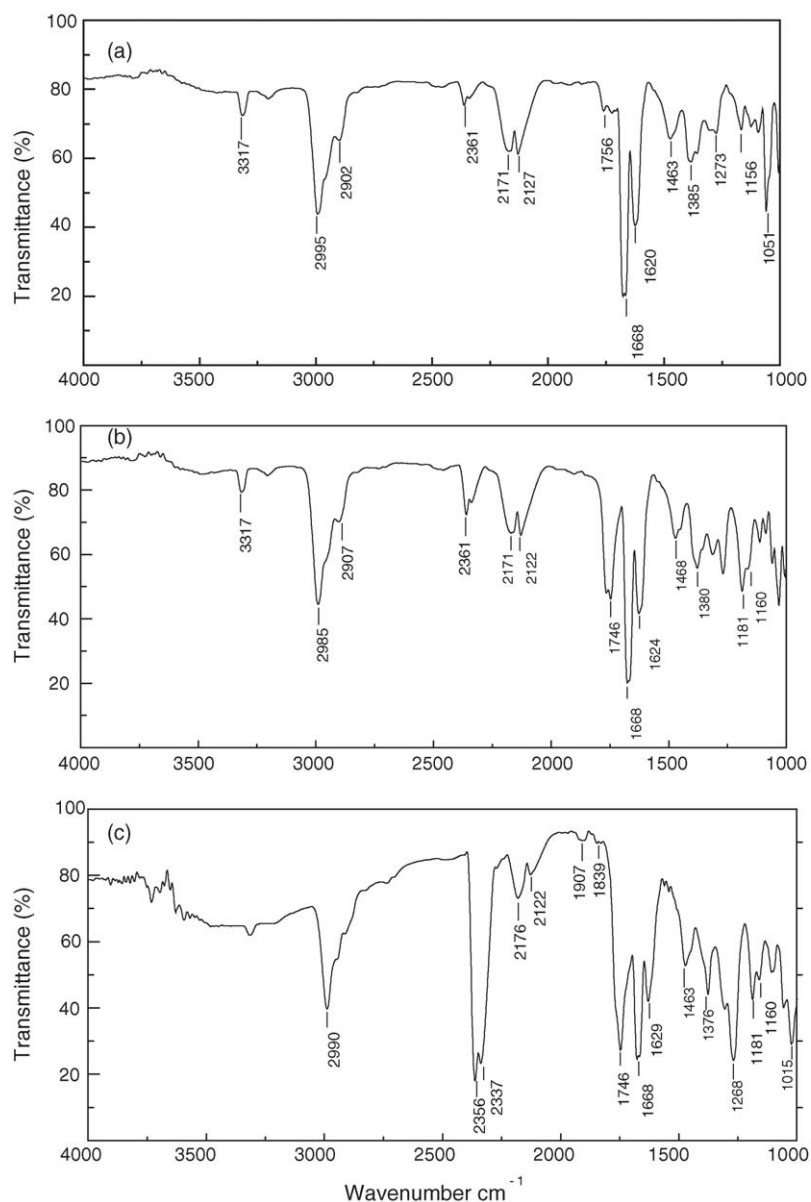


Fig. 5. IR spectra of CO coupling reaction to DEO on Pd-Fe/ α -Al₂O₃ catalyst at different temperatures (a) 353 K, (b) 363 K and (c) 383 K.

uct, diethyl oxalate (DEO) and the bands at about 1759 and 1742 cm⁻¹ are assigned to the C=O stretching vibrations of product, DEO, or intermediate produced by ethyl nitrite decomposition mentioned in Section 3.2. Therefore, Fig. 5 reveals that a considerable quantity of product, diethyl oxalate, is formed at 363 and 383 K but a small quantity of intermediate is formed at 353 K due to the peaks at 1181 and 1160 cm⁻¹ being not obvious. Moreover, according to the datum line of IR spectra measurement, both the peaks (about 1759 and 1742 cm⁻¹) in C=O stretching vibration region and that (about 1181 and 1161 cm⁻¹) in C–O stretching vibration region are found to increase in intensity between 363 and 383 K, but the former does more evidently than the latter. This may be because reaction rate of ethyl nitrite decomposition increases more remarkably with increasing temperature from

363 to 383 K than that of producing diethyl oxalate (DEO) with a lower activated energy.

3.3.2. XPS characterization of the catalyst after the reaction

Since IR spectra results didn't provide detailed information on the kinds of intermediate involved in the pathways of the reaction, we attempted to make use of XPS measurement of the catalyst after the reaction so as to obtain some information on the intermediate. The catalyst in the in situ cell was taken out after the reaction of CO and C₂H₅ONO in the cell stopped suddenly for retaining intermediates. Then it was characterized by XPS measurements. The above-mentioned experiments were done for several times. The one of XPS results obtained is displayed in Fig. 6 while most of XPS re-

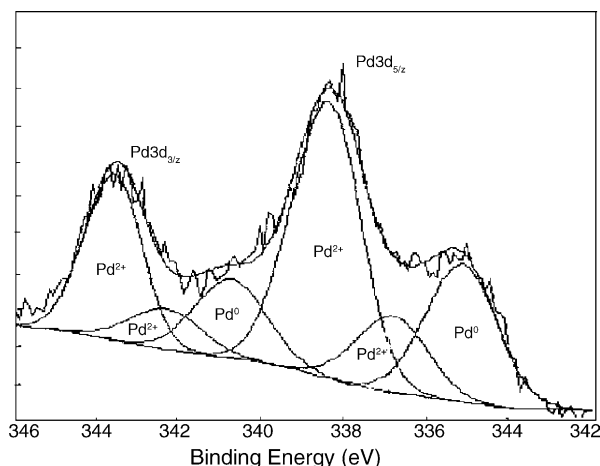


Fig. 6. Curvefit of Pd for XPS profiles of catalyst after CO coupling reaction without N_2 flowing.

sults were just as Fig. 4. Fig. 6 provides valuable information on the kinds of the intermediates for us.

In Fig. 6, two kinds of binding energy of Pd^{2+} were found. The one kind of binding energy is at 337.2 and 341.2 eV, just as that in Fig. 4 and the other kind is at 338.2 and 343.5 eV.

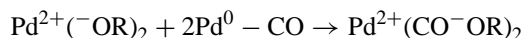
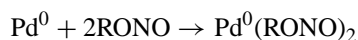
The micro information suggests the existence of two kinds of Pd^{2+} in different chemical situations in the reaction process. That is to say, two kinds of intermediates, palladium complex, were involved in the pathways of the reaction. The one corresponding to binding energy of 337.2 and 341.2 eV is ethoxy palladium complex just as mentioned in Section 3.2. The other corresponding to binding energy of 338.2 and 343.5 eV should be carboethoxypalladium complex whose existence was identified in the literature [12]. It was inferred that the second kind of intermediates, carboethoxypalladium $Pd^{2+}(CO^-OC_2H_5)_2$, was produced by adsorbed CO insertion into metal ion (Pd^{2+})—alkoxy ion ($C_2H_5O^-$) bond. The binding energy of 338.2 eV of Pd^{2+} in the second kind of intermediate is larger than that of 337.2 eV in the first kind, which is benefit to the reduction–elimination reaction of the second kind of intermediate producing the diethyl oxalate by carbonyl coupling. So the second kind of intermediate is more unstable and harder to remain than the first one.

3.4. Mechanism of palladium-catalyzed CO coupling reaction

Based on the observational results in situ IR and XPS measurements, the mechanism for CO coupling reaction to diethyl oxalate over Pd–Fe/ α - Al_2O_3 catalyst can be proposed. The first step in the catalytic reaction is a dissociative chemisorption of the reactant, ethyl nitrite, over the Pd–Fe/ α - Al_2O_3 catalyst, accompanying the oxidation of Pd^0 to Pd^{2+} and the formation of the first intermediate, ethoxy-palladium complex. Subsequently, the weak linearly adsorbed CO molecule inserts metal ion–alkoxy ion bond, and the second intermediate, carboethoxy-palladium complex, is formed. Consequently, the reduction–elimination re-

action of the second intermediate takes place rapidly, producing diethyl oxalate by carbonyl coupling, because the carboethoxy-palladium complex is extremely unstable.

The steps in the mechanism are expressed as follows



The mechanism of the surface catalytic reaction shows palladium active component on the catalyst surface to undergo redox cycle in the reaction process. It is similar to the process of oxidative addition and reductive elimination in catalytic reaction from organometallic chemistry [13].

The ethyl nitrite in the mechanism of CO coupling reaction plays a role in oxidizing Pd^0 to Pd^{2+} and providing negative alkoxy ion. Since adsorption of CO on Pd^{2+} is stronger than that on Pd^0 due to Pd^{2+} being of more unoccupied d orbit than Pd^0 , the linearly adsorbed CO, being easier to blow away in N_2 than the bridge adsorbed CO on Pd^0 , inserts metal ion–alkoxy ion bond in the first intermediate.

In addition, the role of Fe in this catalytic system had been investigated in our previous study [14]. The iron element was found to be in Fe^{2+} state on the surface of Pd–Fe/ α - Al_2O_3 catalyst and to be preferentially dispersed on the support while the active component, palladium, locates on the FeO layer due to the differences in the interactions of two substances among the active component, the promoter and the support. Therefore, Fe as the promoter plays a role in maintaining the stability of the active component Pd on the surface of the catalyst.

4. Conclusion

CO coupling reaction to diethyl oxalate over Pd–Fe/ α - Al_2O_3 in the presence of ethyl nitrite was confirmed to be a redox process in which palladium, active component on the catalyst surface, undergoes a cycle of oxidation of Pd^0 to Pd^{2+} and reduction of Pd^{2+} to Pd^0 by XPS and in situ IR measurements. Two reactants, carbon monoxide and ethyl nitrite, can be adsorbed, respectively on the catalyst surface. The dissociative chemisorption of ethyl nitrite leads to the oxidation of Pd^0 to Pd^{2+} . Based on all the observational results of in situ IR and XPS measurements, the mechanism for CO coupling reaction to DEO was proposed. Two intermediates in the mechanism are involved. The first one is inferred to be ethoxy palladium complex and the second one to be carboethoxypalladium complex, which is more unstable than the first one.

The oxidative addition and reductive elimination from organometallic chemistry can be used to describe the formation of the first intermediate and the process from the

second intermediate to the product, DEO, in the mechanism steps.

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