



The mechanism of CO coupling reaction to form dimethyl oxalate over Pd/ α -Al₂O₃

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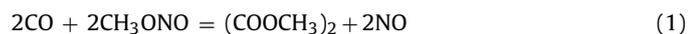
ABSTRACT

The purpose of this study is to investigate the mechanism of CO coupling reaction to form dimethyl oxalate (DMO) over Pd/ α -Al₂O₃ by using in situ infrared spectroscopy. The formation of DMO is initiated by methyl nitrite (MN) adsorption and CO adsorption over Pd/ α -Al₂O₃. Two intermediates, ON–Pd–OCH₃ and ON–Pd–COOCH₃, were identified. The formation of DMO proceeds via coupling two ON–Pd–COOCH₃ intermediates. CO adsorption generates linearly bonded CO and bridge bonded CO over Pd/ α -Al₂O₃, but only bridge bonded CO participates in the reaction. Moreover, the ratio of ON–Pd–OCH₃ to bridge bonded CO over Pd/ α -Al₂O₃ surface has significant influence on the formations of by-products (methyl formate (MF) and dimethyl carbonate (DMC)).

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1. Introduction

In the past decades, the synthesis of dimethyl oxalate (DMO) by gas-phase oxidative coupling reaction of CO and methyl nitrite (MN) over palladium catalysts has attracted great interest of researchers over the world [1–9], because one of the most interesting aspects of DMO synthesis is related to the possibility of DMO hydrogenation to ethylene glycol (EG) [10–13]. Now, the industrialization of the new EG synthesis technology is at preparatory stage in China. The present study is a part of a research program of EG synthesis from syngas in which DMO is utilized as intermediate. To continue a fundamental understanding of the catalytic reaction of CO coupling to form DMO over palladium catalyst, the mechanism of the reaction was investigated by using FTIR in present study. The oxidative coupling reaction of CO and MN is described as follows:



The mechanism of the formation of di-alkyl oxalate via oxidative coupling reaction has been studied by several research groups since 1980s [3,6,14–16]. Waller [14] proposed a speculative mechanism for the formation of di-alkyl oxalate that the oxidative addition of alkyl nitrite was followed by an intramolecular coupling reaction. They speculated that the oxidative addition of alkyl methyl (RONO) to Pd⁰ would generate an intermediate ON–Pd–OR, and CO

insertion on ON–Pd–OR would give ON–Pd–COOR. Repeating the formation of the ON–Pd–COOR leads to a Pd(COOR)₂ intermediate which yields the oxalate. Besides, they proposed that a double carbonylation pathway that a second CO insertion on ON–Pd–COOR would give ON–Pd–CO(COOR) is possible.

Subsequently, Uchiumi et al. [3] found that: (1) the catalytically active species for the formation of oxalate are Pd⁰. (2) The addition of RONO oxidizes Pd⁰ to Pd²⁺. (3) RONO dissociative adsorption provides alkoxy palladium (Pd–OR) for the DMO formation, because alcohol has no effect on the rate of the DMO formation.

Gao et al. [6] studied a coupling reaction of CO and ethyl nitrite (EN) to form diethyl oxalate by using XPS and in situ DRIRS. They identified two kinds of binding energy of Pd²⁺ in the reaction process, and inferred that the two kinds of Pd²⁺ represents two intermediates, Pd(OR)₂ generated from oxidative addition of EN and Pd(COOR)₂ generated from CO insertion, respectively.

According to these literatures, it could be concluded that: (1) the addition of alkyl nitrite causes Pd⁰ to be oxidized to Pd²⁺; (2) the alkyl nitrite adsorption generates the first intermediate, but the mode of the first intermediate (ON–Pd–OR or Pd(OR)₂) is unidentified; (3) at least two kinds of intermediates exist in the reaction process; (4) it is still uncertain that the formation of di-alkyl oxalate proceeds via coupling two acyl groups or double carbonylation.

Moreover, the role of adsorbed CO in the mechanism of the reaction was not investigated in previous studies [3,6,14–16]. Typically, there are two kinds of adsorbed CO, linearly bonded CO and bridge bonded CO, over the palladium catalysts, when CO adsorbs on Pd [17–21]. Two literatures [4,22] are referred to the influence

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of adsorbed CO on the reaction. It is reported that enhancement of CO adsorption over catalysts could promote catalysts performance. However, which kind of adsorbed CO takes part in the coupling reaction has not been reported in literatures [4,22]. In fact, verifying which kind of adsorbed CO participates in the reaction is significant to catalysts preparation; because the ratio of bridge bonded CO to linearly bonded CO could change with changing Pd cluster size [21].

To gain detailed information on the pathways of the coupling reaction of CO and MN to form DMO, the present study was performed by using in situ FTIR under unsteady state conditions.

2. Experimental

2.1. Preparation of catalysts

Pd/ α -Al₂O₃ catalysts containing 0.1 wt% Pd were prepared by impregnation of α -Al₂O₃ (BET area 16.58 m²/g) with acidified (with HNO₃, pH 1.5) aqueous solutions of Pd(NO₃)₂. Water contained in samples was gradually removed by heating at 353 K. Finally samples were calcined in static air at 773 K for 5 h. Catalysts were reduced by hydrogen (25 mol% H₂) for 5 h at 473 K before using.

2.2. FTIR experiments

In situ FTIR experiments were carried out using 10 mg of catalyst pressed in to a 12-mm diameter pellet. The pellet was placed into an in situ IR cell, and spectra were recorded by using a Nicolet Protégé 460 Fourier transmission spectrometer with a resolution of 4 cm⁻¹ and 10 scans per spectrum. Prior to adsorbate exposure, the catalysts had been heated in N₂ flow at 493 K for 14 h. In a typical experiment, the temperature was reduced to 408 K prior to the introduction of MN (MN:N₂ = 1:9) or CO (CO:N₂ = 2:8). All flow rates were approximately 30 cm³/min. Once the MN or CO adsorption equilibrium was attained, the stream was switched to a mix flow containing CO, MN, and N₂ (MN:CO:N₂ = 1:2:7) to start the coupling reaction. Once the reaction started, IR spectra were recorded with reaction time until the reaction attained steady state. All FTIR experiments were performed under the conditions of 408 K and 1 atm.

3. Results and discussion

3.1. IR spectra of DMC and MF

Dimethyl carbonate (DMC) and methyl formate (MF) are by-products of the CO coupling reaction to form DMO. Infrared spectra of DMC and MF with the presence of Pd/ α -Al₂O₃ were recorded to aid the interpretation of the spectra observed under in situ condition. Spectra of gaseous DMC and DMC with the presence of Pd/ α -Al₂O₃ at 408 K are shown in Fig. 1. Bands at 2971, 2869 and 1463 cm⁻¹ are due to the anti-symmetric stretching, symmetric stretching, and deforming C–H vibrations of the CH₃– in DMC. Moreover, bands at 1780 and 1767 cm⁻¹ are attributable to C=O stretching vibrations in DMC. Besides, a strong band at 1298 cm⁻¹ can be attributed to the C–O stretching frequencies [23].

Spectra of MF are presented in Fig. 2. Bands at 2946 and 1450 cm⁻¹ are attributed to stretching and deforming C–H vibrations of the CH₃ in MF. Three bands ranging from 1740 to 1767 cm⁻¹ are due to C=O stretching vibrations in MF. Bands from 1158 to 1221 cm⁻¹ could be attributed to C–O–C vibrations in MF. According to spectra in Figs. 1 and 2, it is discovered that spectra of gaseous by-products are the same as spectra of by-products with the presence of catalysts. Consequently, adsorptions of DMC and MF do not occur on Pd/ α -Al₂O₃ under the conditions of 408 K and 1 atm.

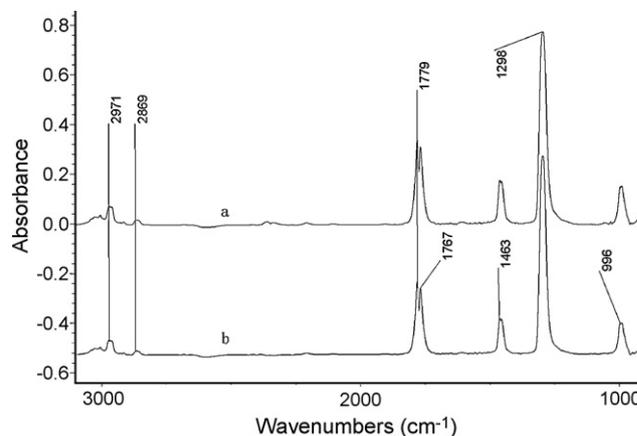


Fig. 1. Spectra of DMC (408 K, 1 atm). (a) Gaseous DMC and (b) gaseous DMC with the presence of Pd/ α -Al₂O₃ outgassed by N₂ for 10 min.

Esters have two characteristic absorbance in FTIR spectra arising from the C=O and C–O– groups [23]. According to literatures [23,24], DMO has two bands assigned to C=O vibrations at 1780 and 1752 cm⁻¹ and two bands assigned to C–O– vibrations at 1208 and 1158 cm⁻¹. Since the C=O stretching vibrations for DMC and MF are coincident with those of DMO, it is impossible to identify the presence of DMC and MF by inspection of the C=O stretching portion of the spectrum. But, the band at 1298 cm⁻¹ assigned to C–O vibration in DMC could be taken as evidence to identify the presence of DMC in the spectra of in situ experiments. Although C–O stretching vibrations for MF are partially coincident with those of DMO, bands ranging from 1158 to 1221 cm⁻¹ assigned to C–O vibration in MF could also be taken as evidence to identify the presence of MF, because the shape of bands assigned to C–O vibrations in MF is very unique from those of DMC and DMO.

3.2. IR spectra of adsorbed MN and CO

Spectra of the MN adsorption on Pd/ α -Al₂O₃ are shown in Fig. 3. For gaseous MN, as Fig. 3(a) shows, the bands at 1625 and 1680 cm⁻¹ are attributed to the N=O vibration. The bands at 2960 and 2844 cm⁻¹ are assigned to CH₃– asymmetric stretching vibrations and symmetric vibration, and the bands of the CH₃– deformation modes are at 1443 and 1388 cm⁻¹. Fig. 3(b and c) shows the MN adsorption on Pd/ α -Al₂O₃. Comparing with the spectra of gaseous MN, the bands at 1060 cm⁻¹ assigned to C–O vibration obviously increased. The bands at 1060 cm⁻¹ can be

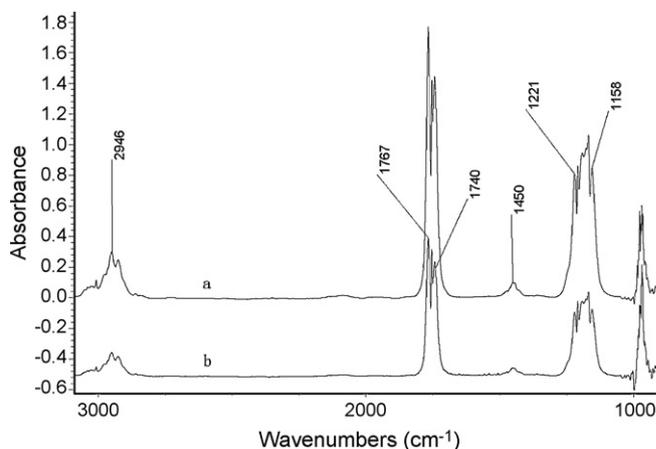


Fig. 2. Spectra of MF (408 K, 1 atm). (a) Gaseous MF and (b) gaseous MF with the presence of Pd/ α -Al₂O₃ outgassed by N₂ for 10 min.

attributed to surface methoxide species [4]. Besides, the bands at 1875 cm^{-1} assigned to gaseous NO were observed in Fig. 3(a–c), but the absorbance of the bands at 1875 cm^{-1} was fairly weak.

It is known [25,26] that when MN adsorbed on Pd/Al₂O₃, MN dissociative adsorption could occur to form surface methoxide species. Since the CH₃O–NO bond (about 42 kcal/mol in gas phase [1,27]) is weak, the cleavage of CH₃O–NO bond is believed to be the first step for the chemisorption of MN over Pd/α-Al₂O₃. Many researchers [15,16] believed that alkyl nitrite adsorption resulted in di-alkyl oxide species, RO–Pd–OR, on Pd surface. If the MN adsorption on Pd resulted in MeO–Pd–OMe species, the bands assigned to gaseous or adsorbed NO could be observed besides the bands at 1060 cm^{-1} attributed to methoxide in Fig. 3. However, adsorbed NO (1753 cm^{-1} [28]) was not observed in Fig. 3, and the bands assigned to gaseous NO were attributed to trace NO contained in feed gas (by comparing with spectra of gaseous MN). Consequently, the experimental results indicate that the adsorption of MN over Pd/α-Al₂O₃ may not occur in a pattern in which MN decomposes to form di-methoxide species and NO. Although it is lack of literatures on MN adsorption on Pd catalysts, MN adsorptions on other transition metals have been reported [26,29–33]. Gomes and Illas [33] studied MN adsorption on Au by means of density functional calculations, and they found that the most favorable adsorption geometry for MN on Au(1 1 1) is the bridge-bonded central oxygen atom. Pressley et al. [31] studied the MN adsorption on Ag(1 1 1), and they also gained similar conclusion. Considering Au, Ag, and Pd are transition metals, it is possible that the MN adsorption on Pd also generates ON–Pd–OMe as an intermediate participating in the CO coupling reaction. The further discussion on ON–Pd–OMe will be given in next section.

Fig. 4 illustrates the spectra of the CO adsorption on Pd/Al₂O₃ catalysts. Two CO adsorbed species on palladium were observed. The bands at about 1950 cm^{-1} were attributed to bridge bonded CO. And the bands at 2082 cm^{-1} assigned to linearly bonded CO were observed after removing gaseous CO by N₂ displacement, as shown in Fig. 4(b–d). Moreover, it is found that bridge bonded CO is less mobile and bonded more tightly than linearly bonded CO, because the band at 2082 cm^{-1} is weaker than the band below 1950 cm^{-1} in N₂ flow, which is in good agreement with literatures [16,20,34].

3.3. In situ IR study of CO coupling reaction

3.3.1. CO coupling reaction after MN pre-adsorption over Pd/α-Al₂O₃

The rate of CO coupling reaction to DMO is too fast to identify intermediates by simply performing in situ FTIR experiment. So, slowing down the rate of the reaction is necessary for studying the reaction mechanism by using FTIR.

It has been known that the coupling reaction is initiated by adsorptions of CO and MN. Reducing the surface concentration of reactants adsorption species could make the rate of the DMO formation slow. Consequently, conducting the CO coupling reaction over a catalysts surface which has been occupied by MN adsorption species provides an opportunity to slow down the rate of DMO synthesis.

Figs. 5 and 6 demonstrate spectra of the CO coupling reaction after MN pre-adsorption. Fig. 5(1) presents spectra of the MN pre-adsorption over Pd/α-Al₂O₃ before reaction, which is the same as the spectra in Fig. 3(b). The MN adsorption resulted in dominated surface methoxide species as the first intermediates on Pd surface because the band at 1060 cm^{-1} was obviously observed as shown in Fig. 6(1). After conducting the reaction, during the first 5 min, the bands at 1060 cm^{-1} sharply decreased, as shown in Fig. 6; moreover the bands at 2082 and 2052 cm^{-1} assigned to linearly bonded CO, the bands at 1767 , 1754 and 1742 cm^{-1} assigned to C=O vibration, the bands ranging from 1150 to 1230 cm^{-1} assigned to C–O–C

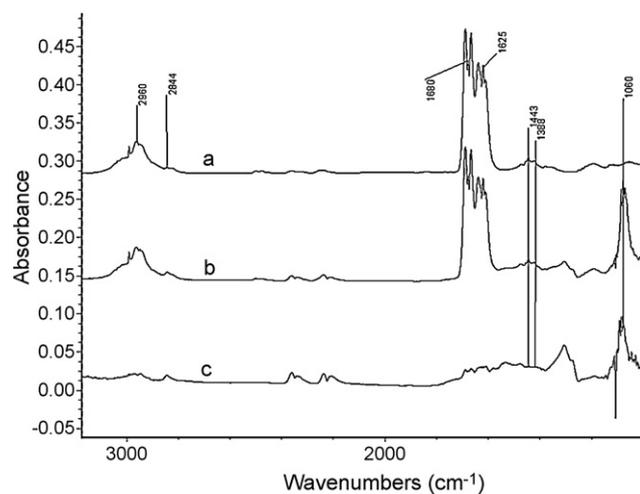


Fig. 3. Spectra of MN (408 K, 1 atm). (a) Gaseous MN, (b) MN adsorption on Pd/α-Al₂O₃ and (c) MN adsorption on Pd/α-Al₂O₃ outgassed by N₂.

vibration, and the bands at 1875 cm^{-1} attributed to gaseous NO appeared and were increasing, as shown in Figs. 5(1–4) and 7(1–4). The decreasing of the bands at 1060 cm^{-1} indicates that CO reacts with MN adsorption species to form surface acyl groups. The bands ranging from 1150 to 1230 cm^{-1} could be assigned to C–O–C vibration of surface acyl groups (–COOMe). Besides, according to spectra of MF in Fig. 2, the bands at 1767 , 1754 , 1742 and 1182 cm^{-1} are attributed to gaseous MF.

Subsequently, when bands ranging from 1150 to 1230 cm^{-1} increased to a certain level, the bands at 1767 , 1208 and 1158 cm^{-1} attributed to DMO appeared and increased, and eventually replaced the bands assigned to MF and surface acyl groups in the spectra, as shown in Fig. 5(5 and 6). Furthermore, it is discovered that the bands at 1298 cm^{-1} appeared and increased when the bands assigned to DMO appeared. Comparing with standard spectra of DMO [24] and spectra of DMC in Fig. 1, it is believed that the bands at 1298 cm^{-1} could be attributed to the C–O–C vibration of DMC. After the tenth minute, the reaction and the spectrum attained steady state. According to Fig. 5 an appearance sequence which is surface methoxide, surface acyl groups and MF, and DMC and DMO can be identified in in situ IR spectra.

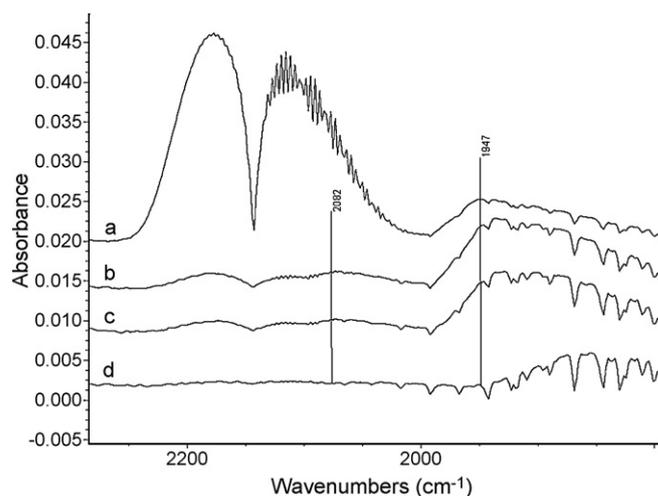


Fig. 4. Spectra of CO adsorption on Pd/α-Al₂O₃ (408 K, 1 atm). (a) CO adsorbed on catalyst, (b) outgassed by N₂ for 3 min, (c) outgassed by N₂ for 11 min and (d) outgassed by N₂ for 30 min.

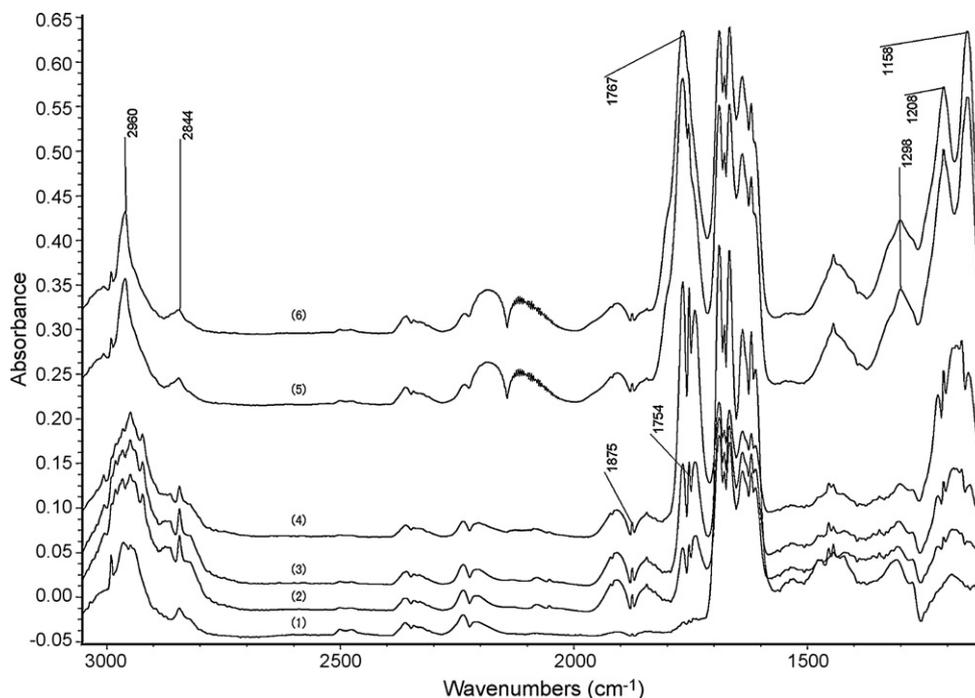


Fig. 5. Spectra of CO coupling reaction after MN pre-adsorption with reaction time, range from 1000 to 3000 cm^{-1} . (1) 0 min, (2) 1 min, (3) 3 min, (4) 5 min, (5) 6 min and (6) 10 min.

MN dissociative adsorption on Pd is the first step of the CO coupling reaction. The dissociative adsorption generates an adsorbed species of MN adsorption as the first intermediate participating in the coupling reaction. And other intermediates participating in the reaction are derived from CO insertion on the first intermediate. So, it is significant to identify the first intermediate for investigating the mechanism of the coupling reaction.

It is reported that there are two speculative modes of the surface species of MN adsorption, which are $\text{Pd}(\text{OCH}_3)_2$ [6,15,16]

and ON-Pd-OCH_3 [3,14]. If the species of MN adsorption was $\text{Pd}(\text{OCH}_3)_2$, MF could not appear in the appearance sequence. Because the reaction between $\text{Pd}(\text{OCH}_3)_2$ and adsorbed CO would generate $\text{CH}_3\text{O-Pd-COOCH}_3$ which could more probably derive DMC than MF. Consequently, considering the appearance sequence above-mentioned, IR spectra of MN adsorption in Fig. 3, and literatures [31,33] on MN adsorption on other transition metals, it is believed that the first intermediate is ON-Pd-OCH_3 .

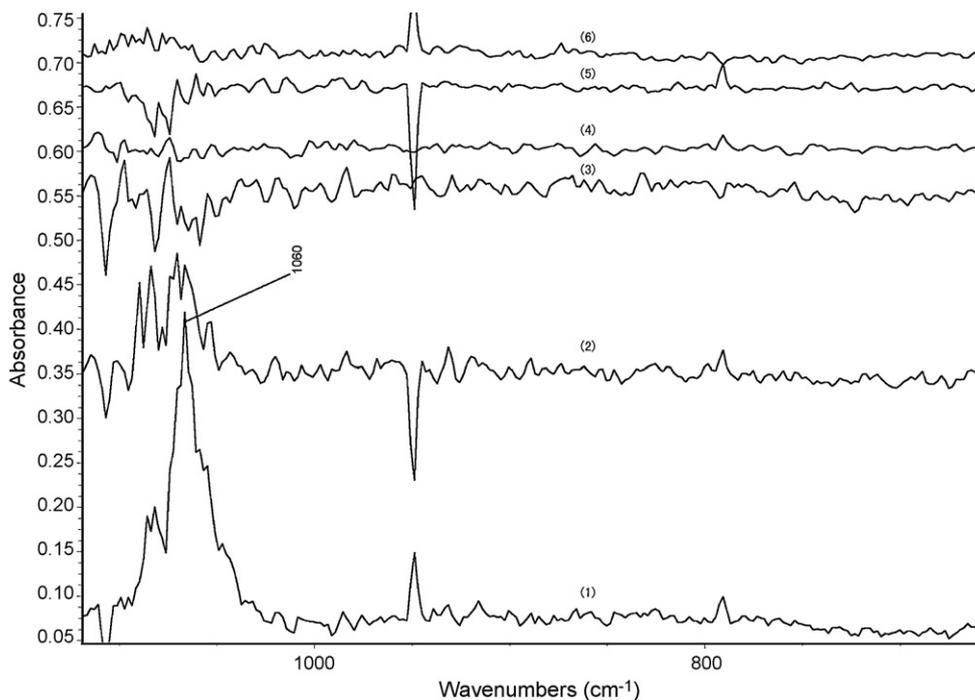


Fig. 6. Spectra of CO coupling reaction after MN pre-adsorption with reaction time, range from 700 to 1100 cm^{-1} . (1) 0 min, (2) 1 min, (3) 3 min, (4) 5 min, (5) 6 min and (6) 10 min.

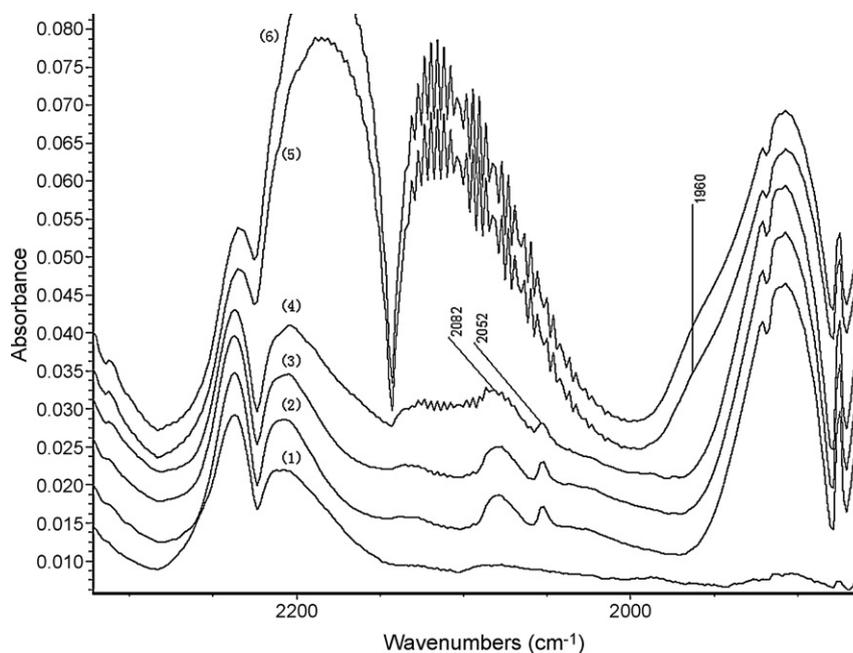


Fig. 7. CO adsorption segment of Fig. 5. (1) 0 min, (2) 1 min, (3) 3 min, (4) 5 min, (5) 6 min and (6) 10 min.

Reactions involving in Fig. 5 are described as reactions (2)–(8). Fig. 5(1–4) illustrates a process that adsorbed CO inserts on the ON-Pd-OCH₃ to form ON-Pd-COOCH₃ followed by the partial decomposition of ON-Pd-COOCH₃ to form MF and NO. The process is described as reactions (2)–(4). The proton participating in reaction (5) could be supplied from partial thermal decomposition of MN [25]:

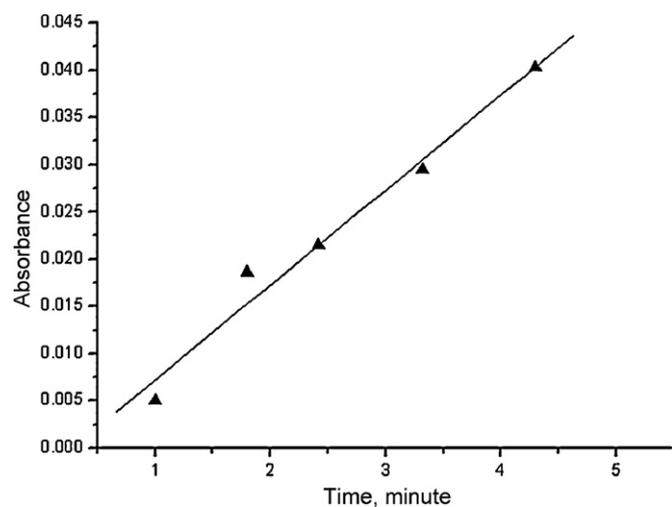
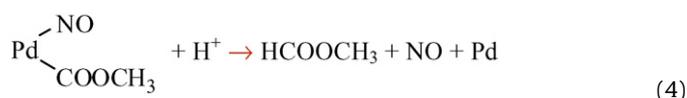
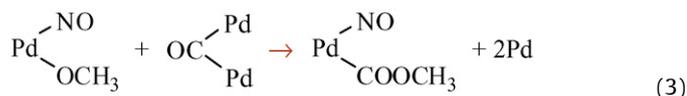
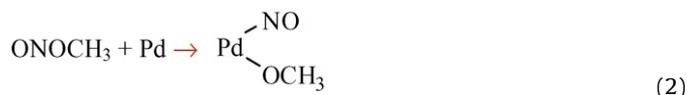
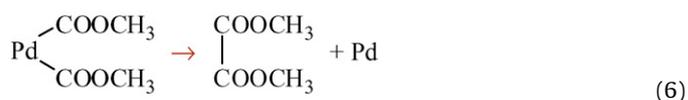
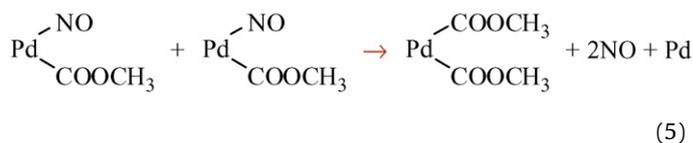
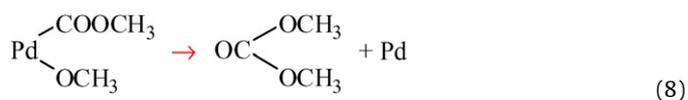
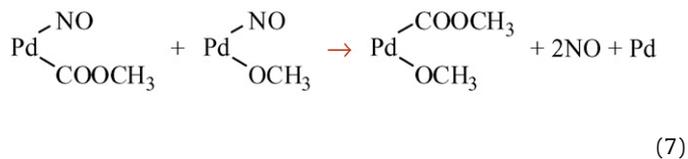


Fig. 8. Absorbance variety of the band at 2080 cm⁻¹ assigned to linearly bonded CO with reaction time.

Subsequently, as shown in Fig. 5(5 and 6), with increasing concentration of ON-Pd-COOCH₃ the rates of reactions (5) and (6) increased and bands assigned to DMO were observed in spectra. Since competition from reaction (5), reaction (4) was suppressed when the concentration of ON-Pd-COOCH₃ over catalysts surface increased to a certain level:



In Fig. 5(4–6), it is also observed the bands at 1298 cm⁻¹ attributed to the C–O–C vibration of DMC accompanying with the bands assigned to DMO. The formation of DMC is caused by the reaction between ON-Pd-OCH₃ and ON-Pd-COOCH₃. The formation is described as reactions (7) and (8). Reaction (7) is parallel to reaction (5). It has been known that DMC is the major by-product of the coupling reaction, and MF can be detected under the condition of low CO partial pressure. That is in good agreement with the IR experimental results:



A special phenomenon that linearly bonded CO appeared prior to bridge bonded CO when the coupling reaction was conducted after MN pre-adsorption is noteworthy, as shown in Figs. 5 and 7. The

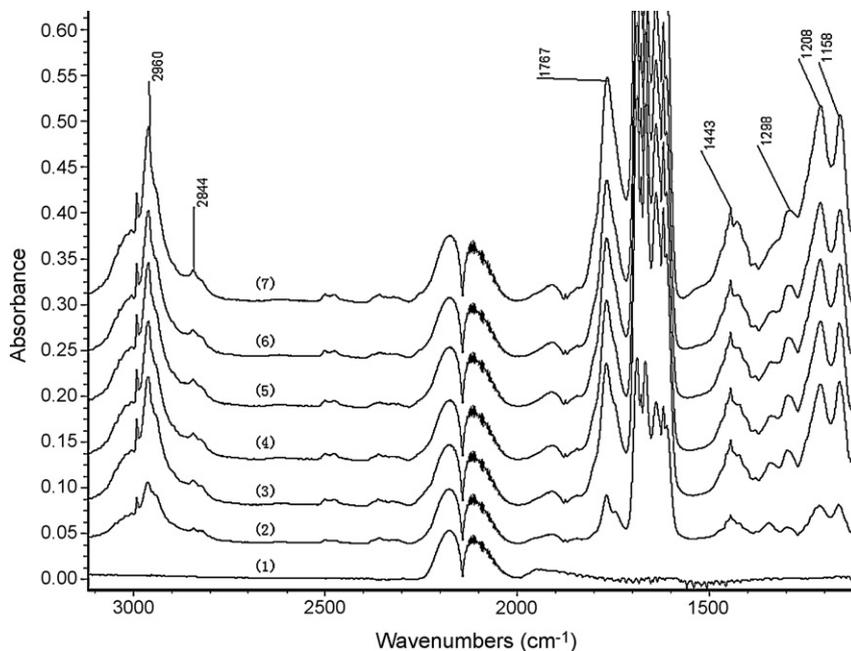


Fig. 9. Spectra of CO coupling reaction after CO pre-adsorption with reaction time. (1) 0 min, (2) 1 min, (3) 2 min, (4) 3 min, (5) 4 min, (6) 5 min and (7) 30 min.

bands at 2080 and 2050 cm^{-1} are attributed to linearly bonded CO, and the bands at 1960 cm^{-1} are attributed to bridge bonded CO in spectra. According to Figs. 5, 7 and 8, linearly bonded CO appeared prior to bridge bonded CO after the reaction occurred, and it was linearly increasing during the first 5 min. In the same time, the bands assigned to ON-Pd-COOME also increased. The bands assigned to bridge bonded CO was not observed until the time when the bands assigned to C–O–C vibration in ON-Pd-COOME disappeared and the bands assigned to C–O–C vibration in DMO appeared in the spectra.

However, it has been well known that bridge bonded CO appears prior to linearly bonded CO when CO adsorbed on Pd. In general, bridge bonded CO is less mobile and bonded more tightly than linearly bonded CO. Ladas et al. [17] studied the adsorption of CO on palladium particles supported on Al_2O_3 . They found that bridge bonded CO was filled at exposures of a few Langmuirs and it desorbed at temperatures above 400 K. Linearly bonded CO was filled at higher exposures and it desorbed already at temperatures below 400 K. Based on their work, it can be easily concluded that bridge bonded CO appears prior to linearly bonded CO when CO adsorbed

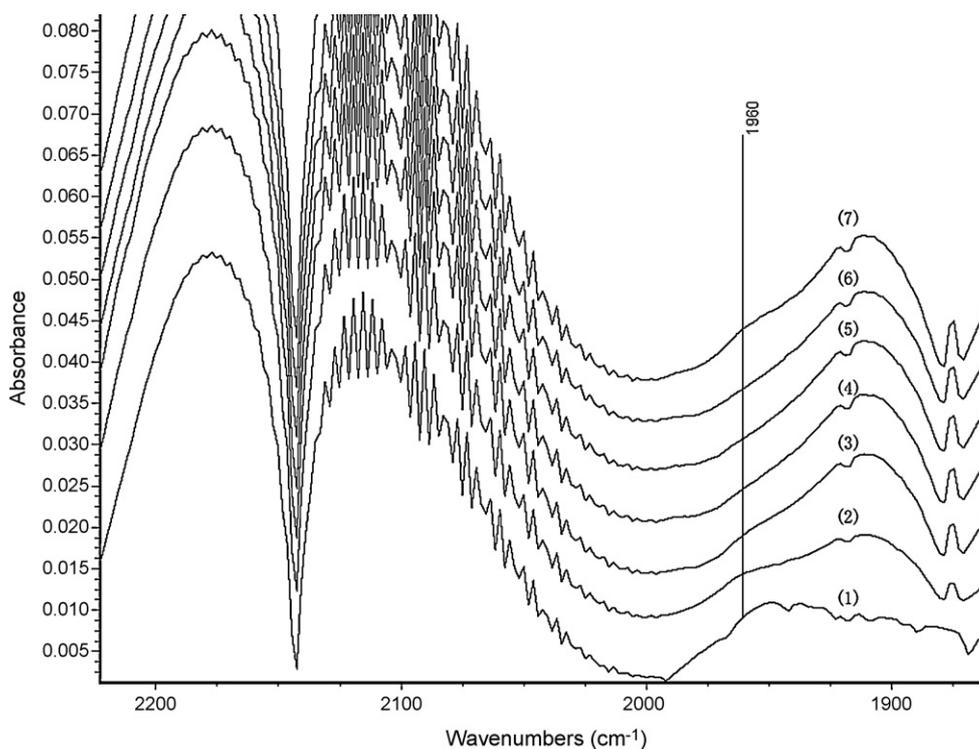


Fig. 10. CO adsorption segment of Fig. 9. (1) 0 min, (2) 1 min, (3) 2 min, (4) 3 min, (5) 4 min and (6) 5 min.

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