



DRIFTS investigation and DFT calculation of the adsorption of CO on Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂

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ABSTRACT

Molecular structures and vibrational spectra of the CO species adsorbed on the Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂ have been investigated by means of density functional theory (DFT) calculation and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The geometrical structures and vibrational frequencies were obtained at the MPW1PW91/SDD level. Theoretical calculation shows that the calculated IR spectra were in good agreement with the experimental results. The calculated results clarify the assignment of the adsorbed CO species on the surface of Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂.

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1. Introduction

CO adsorption on the noble metals supported on oxides is an interesting subject and has been studied by many researchers [1–5]. It has been reported that CO adsorption at 300 K or lower temperatures led to the oxidative disruption of Rh, Ru and Ir crystallites supported on oxides resulting in the formation of metal carbonyl (Mⁿ⁺(CO)₂) surface species [1–3]. Berkó et al. [4,5] have studied the reconstruction of metal particles due to CO adsorption on Rh/TiO₂ (1 0 0) and Ir/TiO₂ (1 0 0) by STM method. The systems of CO/oxide-supported Pt and CO/Pt single crystal surfaces have been frequently studied by FTIR and other methods. Brandt et al. [6] have reported the adsorption of CO on Pt/SiO₂ and they observed one band at 2057 cm⁻¹ and a small shoulder at 2067 cm⁻¹, which were attributed to CO adsorbed on corner Pt atoms. Tanaka et al. [7,8] have studied the activity performance of Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂ catalysts for the selective oxidation of CO in excess of H₂. The in situ DRIFTS method was used to identify the process of CO adsorption and transformation [9]. However, the assignment of CO adsorption on the surface of catalyst in those experiments is not confirmed. Moreover, some new peaks in experiment cannot be given reasonable assignments. Therefore, theoretical calculation is needed to confirm the assignment of CO adsorption on the surface of catalyst.

Auxiliary computer simulation of IR spectra with density functional theory (DFT) quantum mechanical methods affords highly powerful and reliable tools for analytical vibration mode of CO on the surface of catalyst. Due to the use of IR simulations, impressive advances have been achieved in separation and unambiguous identification of vibration mode of CO on the surface of catalyst. DFT calculations are increasingly being applied to predict the interactions of adsorbates with catalytic sites [10]. Such DFT methods provided accurate geometries and reasonable energetics for molecules containing transition metals [11–14] are sufficient to describe the active sites in comparison of the predictions with experimental data.

The objective of this work is to study the adsorbed CO species on the Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂ catalysts using experimental and theoretical methods. This study aims to utilize in situ FTIR spectroscopy and simulatant ones toward the understanding of the formation of these active sites on the Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂ catalyst and provide theoretical evidence for the assignment of the adsorbed CO species on the Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂.

2. Theoretical

The optimized geometries and normal mode calculations were performed for 12 calculated models (A–L) with the Gaussian98 program. The properties of the calculated models were determined through the application of DFT method using the MPW1PW91 function which uses modified Perdew–Wang exchange and Perdew–Wang 91 correlation. The SDD basis set, a triple-zeta basis set and

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adopt Stuttgart/Dresden effective core potential [15] is used for all of the calculations.

3. Experimental

The samples (1 wt.% Pt/TiO₂, 1 wt.% Pt/CeO₂ and 100 wt.% FeO_x/Pt/CeO₂) were prepared by an impregnation method. 1 wt.% Pt/TiO₂ and 1 wt.% Pt/CeO₂ were prepared by immersing TiO₂ or CeO₂ in a solution of PtCl₄. Finally they were calcined at 873 K for 3 h in air. 100 wt.% FeO_x/Pt/CeO₂ was prepared by immersing the Pt/CeO₂ in a solution of Fe(NO₃)₃, and then calcined in air at 673 K for 3 h. 100 wt.% FeO_x/Pt/CeO₂ contained almost equal weight of Fe atom to the 1 wt.% Pt/CeO₂ (Fe/Pt ≈ 350). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectra were measured by a Nexus 670 (Thermo Nicolet) in situ DRIFTS spectrometer equipped with an in situ diffuse reflection chamber and a high sensitivity MCT detector. All spectra in this experiment were taken at a resolution of 4 cm⁻¹ with an accumulation of 100 scans. The sample for the in situ DRIFTS studies was finely ground and placed into a ceramic crucible in the in situ chamber. Prior to recording each DRIFTS spectrum, the sample was heated in situ in N₂ flow at 623 K for 30 min, then cooled to 313 K for taking a reference spectrum. The total gas flow rate is 240 ml/min (2.5% CO in N₂). All the spectra in the (Fig. 1) were collected after CO adsorption at 313 K for 30 min.

4. Results and discussion

4.1. Experimental results

Fig. 1 shows the in situ DRIFTS spectra of CO adsorbed on 1 wt.% Pt/TiO₂, 1 wt.% Pt/CeO₂ and 100 wt.% FeO_x/Pt/CeO₂ at 313 K. Exposure of various samples to the fed gas at 313 K resulted in the appearance of nine peaks (2172, 2119, 2116, 2073, 1857, 1809, 1786, 1743 and 1628 cm⁻¹). The peaks at 2172 and 2119 cm⁻¹ observed on all the three samples are close to the gas phase CO (P and Q branches). The CO adsorbed on the 1-wt.% Pt/TiO₂ gave two intense peaks at 2116 and 2073 cm⁻¹ and two weak peaks at 1857 and 1809 cm⁻¹. The CO adsorbed on the 100 wt.% FeO_x/Pt/CeO₂ exhibited two weak peaks at 1786 and 1743 cm⁻¹. The CO adsorbed on Pt/CeO₂ gave an intense peak at 1628 cm⁻¹. The unmarked peaks in the range of 1600–1250 cm⁻¹ could be assigned to adsorbed carbonate species as reported in the literatures [16,17].

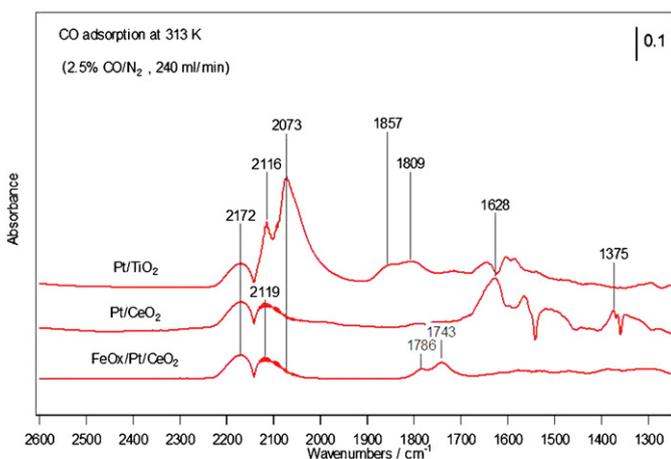


Fig. 1. In situ IR spectra of CO adsorbed on 1 wt.% Pt/TiO₂, 1 wt.% Pt/CeO₂, and 100 wt.% FeO_x/Pt/CeO₂ at 313 K.

4.2. Computational results

4.2.1. Calculation models

According to the literatures [16–20], the two peaks at 1857 and 1809 cm⁻¹ in Fig. 1 are assigned to the vibration mode of the bridge CO which may be bonded with the pair sites such as Pt–Pt and Pt–Ti. Therefore, we designed the calculated models A–C containing Pt–Pt and Pt–Ti backbone (see Fig. 2) to study the vibration mode of bridge CO adsorbed on Pt/TiO₂. The design of model D containing Pt–Ce backbone aims to identify the vibration mode of bridge CO adsorbed on Pt/CeO₂. The peaks at 1786 and 1743 cm⁻¹ were observed on the surface of FeO_x/Pt/CeO₂ in Fig. 1. We proposed that the peaks at 1786 and 1743 cm⁻¹ would be associated with the frequency of the bridge CO stretching vibration on the Pt–Fe site of FeO_x/Pt/CeO₂. Therefore, we designed the calculated models E and F containing Pt–Fe backbone (see Fig. 2) to study the vibration mode of bridge CO adsorbed on FeO_x/Pt/CeO₂.

The peak at 2073 cm⁻¹ in Fig. 1 is assigned to linearly adsorbed CO on Pt atoms in the literatures [16–20]. To confirm the assignment of CO linearly adsorbed on Pt/TiO₂, we designed the calculated models G–J (see Fig. 2) to study the vibration mode of CO linearly adsorbed on Pt/TiO₂.

The peaks at 2172 and 2119 cm⁻¹ in Fig. 1 are very close to the data of IR spectrum of gas CO in NIST Scientific and Technical Databases, therefore they should be assigned to the vibration modes of gas phase CO.

Based on the work of Takeguchi's group [16], who reported that the adsorption peak assigned to the bicarbonate species was observed at 1630 cm⁻¹ on Pt/CeO₂ catalyst, we deduce that the peak at 1628 cm⁻¹ (see Fig. 1) could be associated with $\nu(\text{OCO})$ of HCO₃⁻ on Pt/CeO₂. Therefore, we designed the calculated models K and L (see Fig. 2) to study the vibration mode of HCO₃⁻ adsorbed on Pt/CeO₂.

It must be mentioned that the overall charges of the substrates in our calculated models are neutral, which indicates two types of Pt species (Pt_n and Pt_n^{δ+}) exist in these substrates. As shown in Fig. 2, Pt_n clusters exist in Models A, C and E, and Pt_n^{δ+} clusters exist in Models B, D, F, G, H, J, K and L.

4.2.2. Vibrational frequency calculation

Optimized structures of the calculated models are plotted in Fig. 3. Calculated frequencies are listed in Table 1. Simulant spectra for the models (A–L) are shown in Figs. 4–6.

The calculated model A is to simulate the bridging adsorption of CO on the Pt–Pt site of Pt/TiO₂. The calculated stretching vibrational mode of the bridging adsorption of CO on the Pt–Pt site of Pt/TiO₂ is 1828 cm⁻¹ with 471 km/mol intensity, which is 29 cm⁻¹ lower than the experimental frequency of 1857 cm⁻¹ in Fig. 1. Underestimation of experimental frequency value is about 1.56%. The calculated model B is also to simulate the bridging adsorption of CO on the Pt–Pt site of Pt/TiO₂. The difference between models A and B is that model B considered the ambience effect of other atoms acting on Pt–Pt site. The calculated CO stretching vibrational mode of model B is 1884 cm⁻¹ with 549 km/mol intensity. In comparison with the same experimental frequency of 1857 cm⁻¹, the error is on average about 27 cm⁻¹ for model B, this overestimates the experimental value at about 1.45%. Therefore, the calculated results of model A and B are consistent with the experimental data, which indicates the CO vibration on Pt–Pt site was not significantly influenced by the ambience of other atoms. The calculated result confirmed that the peak at 1857 cm⁻¹ in Fig. 1 should be assigned to the stretching vibration mode of the bridging adsorption of CO on the Pt–Pt site of Pt/TiO₂ (Fig. 4).

The calculated model C is to simulate the bridging adsorption of CO on the Pt–Ti site of Pt/TiO₂. The calculated stretching vibrational

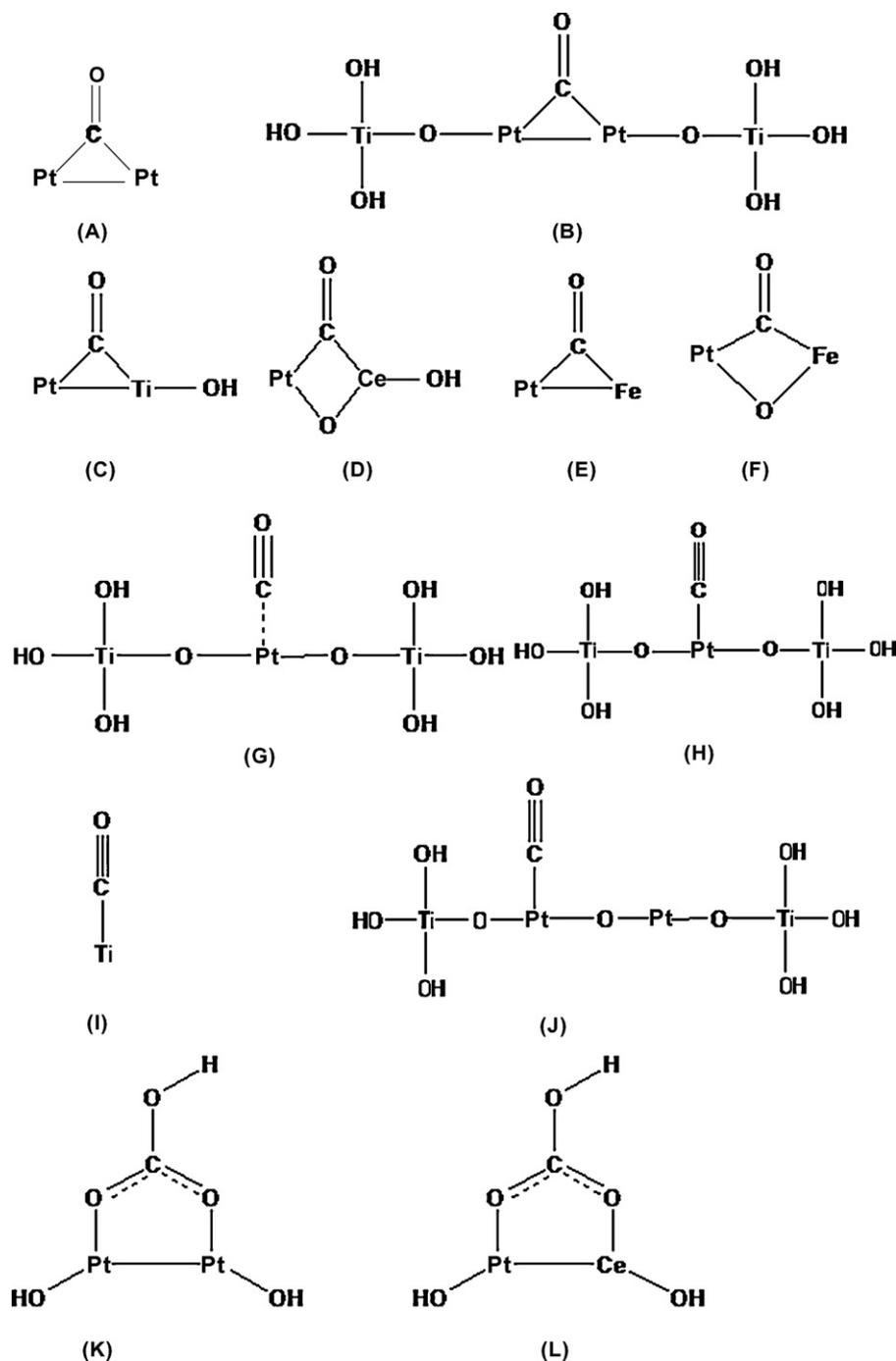


Fig. 2. Calculation models (A–L) for CO adsorbed on Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂.

mode of the bridging adsorption of CO on the Pt–Ti site of Pt/TiO₂ is 1813 cm⁻¹ with 928 km/mol intensity. Calculated frequency is 4 cm⁻¹ higher than the experimental one of 1809 cm⁻¹. Overestimation of experimental frequency values is about 0.22%. Therefore, the calculated value is very close to the experimental value. The calculated result confirmed that the peak at 1809 cm⁻¹ in Fig. 1 should be assigned to the stretching vibration mode of the bridging adsorption of CO on the Pt–Ti site of Pt/TiO₂.

The calculated model D is to simulate the bridging adsorption of CO on the Pt–O–Ce site of Pt/CeO₂ and FeO_x/Pt/CeO₂. The calculated stretching vibrational mode of the bridging adsorption of CO on the Pt–O–Ce site is 1637 cm⁻¹ with 430 km/mol intensity.

The calculated value is 9 cm⁻¹ higher than the experimental data of 1628 cm⁻¹, and overestimation of experimental frequency values is about 0.55%. The calculated model K is to simulate the adsorption of HCO₃⁻ on the Pt–Pt site of Pt/CeO₂. The calculated antisymmetric stretching vibration mode of HCO₃⁻ adsorption on the Pt–Pt site of Pt/CeO₂ is 1654 cm⁻¹ with 258 km/mol intensity. Calculated frequency is 26 cm⁻¹ higher than the experimental one of 1628 cm⁻¹, and overestimation of experimental frequency values is about 1.60%. The symmetric stretching vibration mode calculated at 1393 cm⁻¹ with 567 km/mol intensity is 18 cm⁻¹ higher than the experimental one at 1375 cm⁻¹ within 1.30% error. The calculated model L is to simulate the adsorption of HCO₃⁻ on

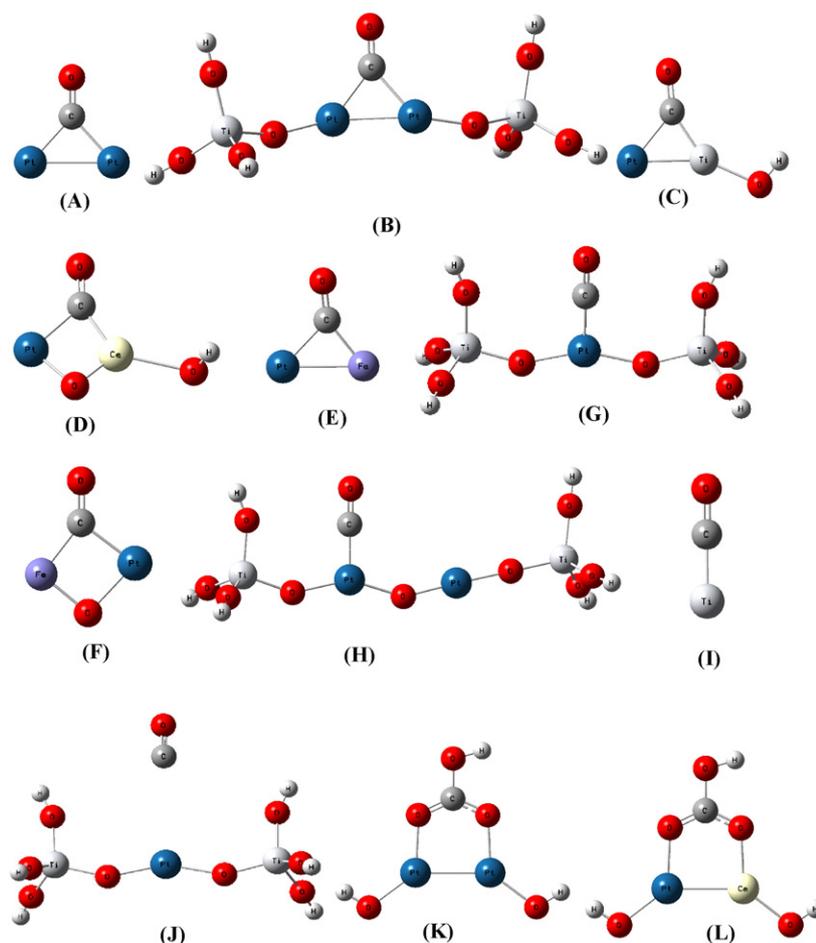


Fig. 3. Optimized configuration of calculation models (A–L) for CO adsorbed on Pt/TiO₂, Pt/CeO₂ and FeO_x/Pt/CeO₂ and models K and L for HCO₃[−] adsorbed on Pt/CeO₂.

the Pt–Ce site of Pt/CeO₂. The calculated antisymmetric stretching vibration mode of HCO₃[−] adsorption on the Pt–Ce site of Pt/CeO₂ is 1606 cm^{−1} with 1746 km/mol intensity. Calculated frequency is 22 cm^{−1} lower than the experimental one of 1628 cm^{−1}, and underestimation of experimental frequency values is about 1.35%. The symmetric stretching vibration mode calculated at 1293 cm^{−1} with 1611 km/mol intensity is 82 cm^{−1} lower than the experimental one at 1375 cm^{−1} within 5.96% error. Comparing model D, K and L, we can conclude that model D is not consistent with the corresponding experimental spectra because it cannot explain the peak appeared at 1375 cm^{−1}. For model L, there is big error between the calculated value and experimental value for symmetric stretching vibration mode of the adsorbed HCO₃[−] species. So the calculation

results indicate that the peak at 1628 cm^{−1} should be assigned to the antisymmetric stretching vibration mode of HCO₃[−] adsorption on the Pt–Pt site of Pt/CeO₂. Considering the different IR spectra observed on Pt/CeO₂ and FeO_x/Pt/CeO₂, the physical overlay FeO_x may influence the interaction between Pt and Ce.

The calculated model E is to simulate the bridging adsorption of CO on the Pt–Fe site of FeO_x/Pt/CeO₂. The calculated stretching vibrational mode of the bridging adsorption of CO on the Pt–Fe site of FeO_x/Pt/CeO₂ is 1794 cm^{−1} with 616 km/mol intensity, which is very close to the peak at 1786 cm^{−1} in Fig. 1. The calculated value of 1794 cm^{−1} is 8 cm^{−1} higher than the experimental frequency of 1786 cm^{−1}, which overestimate the experimental frequency at about 0.45%. The calculated result confirmed that the

Table 1
Calculated vibrational frequencies (cm^{−1}) at MPW1PW91/SDD level for the 10 calculated models (A–L)

Model	Frequency (cm ^{−1})	Intensity (km/mol)	experiment (cm ^{−1})	Vibration mode
A	1828	471	1857	Bridge CO str.
B	1884	549	1857	Bridge CO str.
C	1813	928	1809	Bridge CO str.
D	1637	430	1628	Bridge CO str.
E	1794	616	1786	Bridge CO str.
F	1764	614	1743	Bridge CO str.
G	2090	539	2073	Linearly CO str.
H	2080	586	2073	Linearly CO str.
I	1714	932	2073	Linearly CO str.
J	2108	128	2116	Linearly CO str.
K	1654	258	1628	<i>v</i> _{as} (OCO) of HCO ₃ [−]
L	1606	1746	1628	<i>v</i> _{as} (OCO) of HCO ₃ [−]

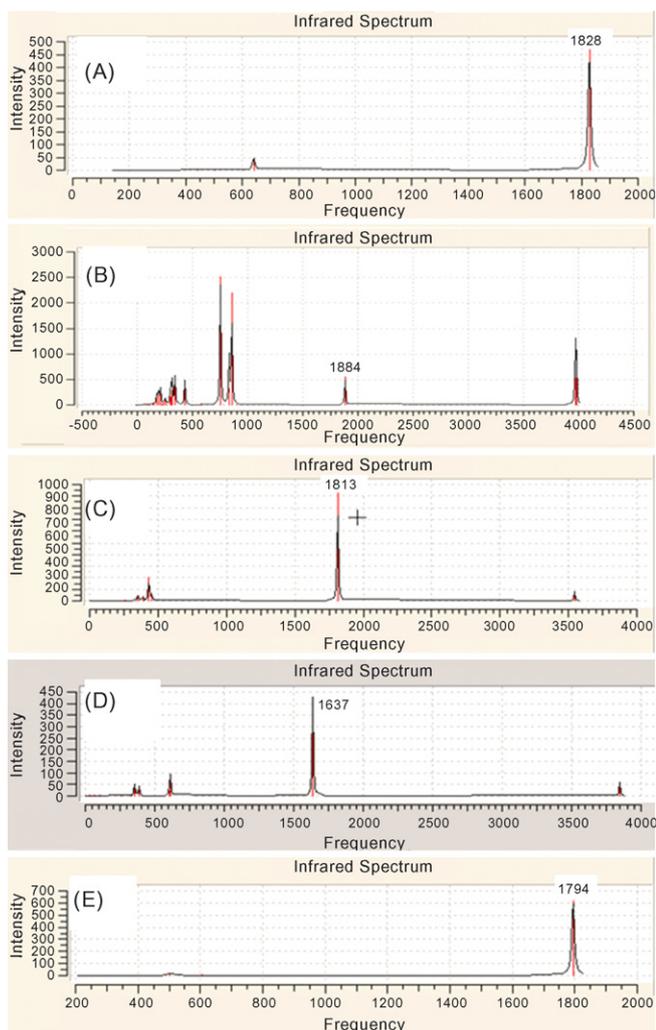


Fig. 4. Calculated vibrational IR spectra for the models (A–E) at DFT-MPW1PW91/SDD level.

peak at 1786 cm^{-1} in Fig. 1 should be assigned to the stretching vibration mode of the bridging adsorption of CO on the $-\text{Pt}-\text{Fe}-$ site of $\text{FeO}_x/\text{Pt}/\text{CeO}_2$. The calculated model F is to simulate the bridging adsorption of CO on the $-\text{Pt}-\text{O}-\text{Fe}-$ site of $\text{FeO}_x/\text{Pt}/\text{CeO}_2$. The calculated stretching vibrational mode of the bridging adsorption of CO on the $-\text{Pt}-\text{O}-\text{Fe}-$ site of $\text{FeO}_x/\text{Pt}/\text{CeO}_2$ is 1764 cm^{-1} with 614 kJ/mol intensity, which is 21 cm^{-1} higher than the peak at 1743 cm^{-1} in Fig. 1. The calculated value overestimates the experimental frequency at about 1.20%. The calculated result confirmed that the peak at 1743 cm^{-1} in Fig. 1 should be assigned to the stretching vibration mode of the bridging adsorption of CO on the $-\text{Pt}-\text{O}-\text{Fe}-$ site of $\text{FeO}_x/\text{Pt}/\text{CeO}_2$.

The calculated model G is to simulate the linear adsorption of CO on the $-\text{Pt}-$ site of Pt/TiO_2 . The calculated stretching vibrational mode of CO linearly adsorbed on the surface of Pt/TiO_2 for model G is 2090 cm^{-1} with 539 kJ/mol intensity. In comparison with the experimental frequency of 2073 cm^{-1} , the error is on average about 17 cm^{-1} for model G, which overestimate the experimental value at about 0.82%. The calculated model H is to simulate the linear adsorption of CO on the $-\text{Pt}-\text{O}-\text{Pt}-$ site of Pt/TiO_2 . The calculated stretching vibrational mode of CO linear adsorption is 2080 cm^{-1} with 586 kJ/mol intensity, which is 7 cm^{-1} higher than the experimental frequency of 2073 cm^{-1} . The calculated value overestimates the experimental one at about 0.33%. The calculated value is very

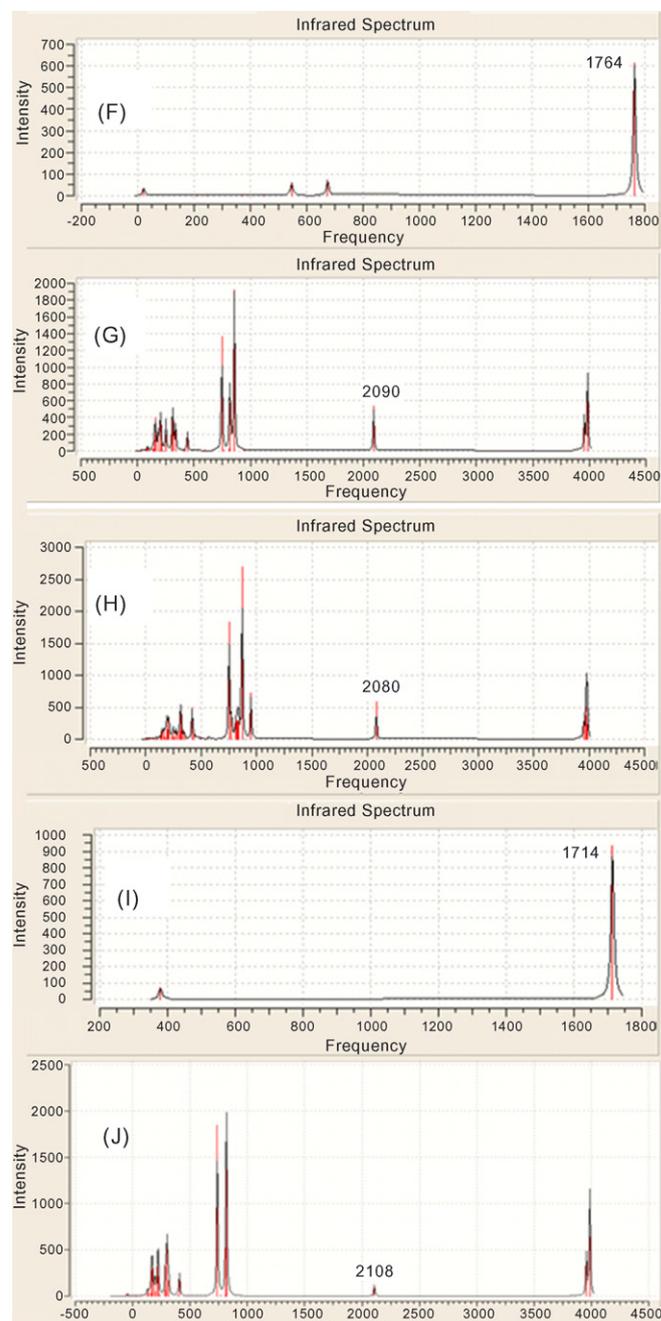


Fig. 5. Calculated vibrational IR spectra for the models (F–J) at DFT-MPW1PW91/SDD level.

close the experimental one. The calculated model I is to simulate the linear adsorption of CO on the $-\text{Ti}-$ site of Pt/TiO_2 . The calculated stretching vibrational mode of CO linear adsorption is 1714 cm^{-1} with 932 kJ/mol intensity, which does not appear in experimental spectra in Fig. 1. The result indicates that it is not possible for CO adsorbed on $-\text{Ti}-$ site of Pt/TiO_2 . Comparing models G–I, models G and H are in good agreement with the corresponding experimental spectra. The calculated result confirmed that the peak at 2073 cm^{-1} in Fig. 1 should be assigned to the stretching vibration mode of the linear adsorption of CO on the Pt site of Pt/TiO_2 .

The calculated model J is to simulate the linear physical adsorption of CO on the $-\text{Pt}-$ site of Pt/TiO_2 . The optimized distance between C atom and Pt atom is 4.00 \AA which is much longer than 1.97 \AA of normal C–Pt bond length. This phenomenon indicates

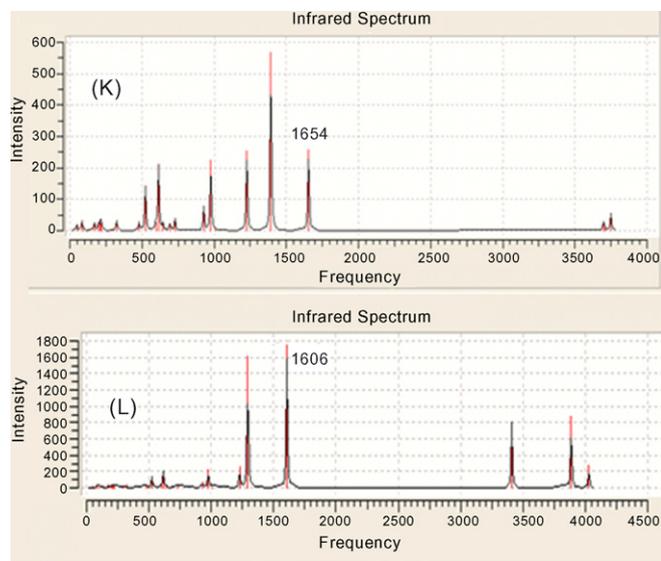


Fig. 6. Calculated vibrational IR spectra for the models (K and L) at DFT-MPW1PW91/SDD level.

that there is very weak interaction between CO and $-Pt-$ site in model J. The calculated stretching vibrational mode of the linear physical adsorption of CO on the $-Pt-$ site of Pt/TiO₂ is 2108 cm⁻¹ with 128 kJ/mol intensity, which is 8 cm⁻¹ lower than the peak at 2116 cm⁻¹ in Fig. 1. The calculated value underestimates the experimental frequency at only about 0.37%. The calculated result confirmed that the peak at 2116 cm⁻¹ in Fig. 1 should be assigned to the stretching vibration mode of the linear physical adsorption of CO on the $-Pt-$ site of Pt/TiO₂.

5. Conclusions

The calculations show clearly that the calculated IR spectra for models A–C, E–H, J and K are in good agreement with the corresponding experimental ones. The peaks at 1857 and 1809 cm⁻¹ in Fig. 1 should be assigned to the stretching vibration mode of the bridging adsorption of CO on the Pt–Pt and Pt–Ti site of Pt/TiO₂, respectively. The peaks at 1786 and 1743 cm⁻¹

in Fig. 1 should be assigned to the stretching vibration mode of the bridging adsorption of CO on the Pt–Fe and Pt–O–Fe site of FeO_x/Pt/CeO₂, respectively. The peak at 1628 cm⁻¹ could be ascribed to the antisymmetric stretching vibration mode of HCO₃⁻ adsorption on the Pt–Pt site of Pt/CeO₂. The peaks at 2073 and 2116 cm⁻¹ in Fig. 1 should be assigned to the stretching vibration mode of the linear adsorption and linear physical adsorption of CO on the Pt site of Pt/TiO₂, respectively. The peak at 2172 and 2119 cm⁻¹ in Fig. 1 should be assigned to the vibration mode of gas phase CO.

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