

Theoretical and experiment studies on the adsorption of formate species on the surface of catalyst

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ABSTRACT

Density functional theory (DFT) calculations and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were performed to study the formation and adsorption of formate species over the Cu–Al₂O₃ catalyst. The geometrical structures and vibration spectra of calculated models were obtained at the PBE1PBE level of DFT and compared with the corresponding experimental values. Theoretical calculations show that the calculated IR spectra are in good agreement with the experimental spectroscopic results. The mechanism of the catalyst deactivation and regeneration was also discussed during the process of the removal of HCHO on the Cu–Al₂O₃ catalyst at the room temperature.

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1. Introduction

Formaldehyde (HCHO) is the dominating volatile organic compound (VOC) in the indoor environment [1]. Moreover, HCHO is very bad for health. It can cause the nasal tumors, respiratory tract, eye membranes irritation and skin irritation [2].

Catalytic oxidation is an effective method for removing VOC because VOC can be oxidized into CO over catalyst at much lower temperature than those of thermal oxidation [3–5]. However, catalytic oxidation is still very difficult to eliminate HCHO at the room temperature.

Using adsorbents can effectively remove the HCHO at the room temperature. This method has been studied by many researchers [6–8]. Eriksson et al. [6] have reported the study about the removal of gaseous HCHO using potassium permanganate, activated carbon and aluminum oxide and so on. Arthur [7] found that HCHO concentration was dropped from 1.3–1.8 to 0.2–0.3 ppm within a few hours but returned to its initial level after 1–5 days through filter beds of potassium permanganate in a mobile house with active airflow. Sekine and Nishimura [8] have reported that copper oxides could react with HCHO with the high reactivity at the room temperature. Recently, Sekine and Nishimura [8] have found that activated carbon particles and manganese oxides not only reduced indoor HCHO concentration from 0.21 to 0.04 ppm for more than

7 months, but also enhanced the loss of HCHO gas from building material in apartments.

Although using adsorbents is effective method to remove HCHO at the room temperature, there is still a limited understanding on the formation and configuration of intermediate involved in the reaction. The mechanism of catalyst deactivation and regeneration is also still not clear.

In this paper, we reported on studies of the formation and adsorption of formate species over the Cu–Al₂O₃ catalyst using experimental and theoretical methods. The study aims to utilize in situ DRIFTS and stimulant spectrum toward the understanding of the mechanism of the catalyst deactivation and regeneration during the process of the removal of HCHO on the Cu–Al₂O₃ catalyst at the room temperature.

2. Experimental

2.1. Catalyst preparation

Utilized Al₂O₃ (gamma type) has a total BET surface area of 250 m²/g as supporter of Cu–Al₂O₃ (Cu metal loading: 10 wt.%) catalyst, which was prepared by an impregnation method with an aqueous solution of copper nitrate, followed by evaporation to dryness in a rotary evaporator under a reduced pressure at 333 K. The wet sample obtained was dried at 393 K for 12 h, and then calcined in air at 873 K for 3 h. Before the catalytic tests, the catalysts were sieved into 40–60 meshes.

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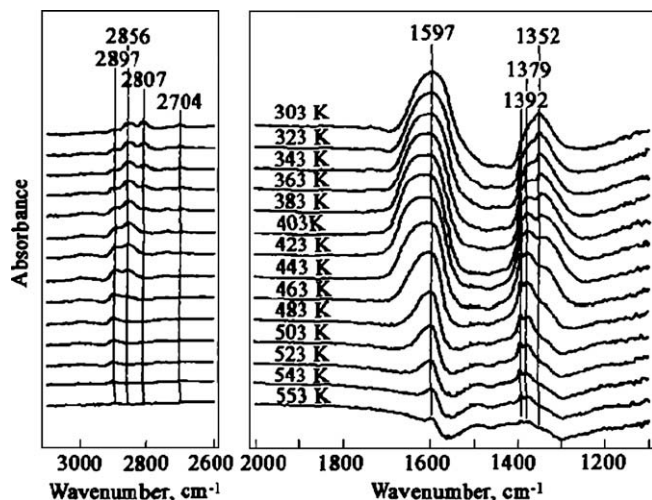
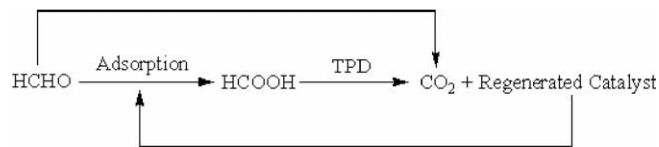


Fig. 1. In situ DRIFT spectra of Cu-Al₂O₃ catalyst in a flow of N₂ mixture at various temperatures (303–553 K) after HCHO + O₂ adsorption for 600 min on the Cu-Al₂O₃ catalyst.

2.2. DRIFTS

DRIFT and in situ DRIFT spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N₂ cooled MCT



Scheme 1. The process of the HCHO elimination over Cu-Al₂O₃.

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 measured with a resolution of 4 cm⁻¹ and accumulating 100 scans. A background spectrum was subtracted from each spectrum, respectively.

2.3. Theoretical section

All calculations were performed using the Gaussian98 program [9]. The properties of the calculated models were determined through the application of density functional theory (DFT) using the PBE1PBE [10] function and LANL2DZ [11] basis set. PBE1PBE is the generalized-gradient-approximation exchange-correlation functional of Perdew, Burke, and Ernzerhof. The LANL2DZ effective core potential basis set was used for all of the calculations. The LANL2DZ basis replaces the 1s through 2p electrons of the heavy atoms with a potential field for a considerable computational savings. A double- ζ quality dunning basis was used for the light atoms

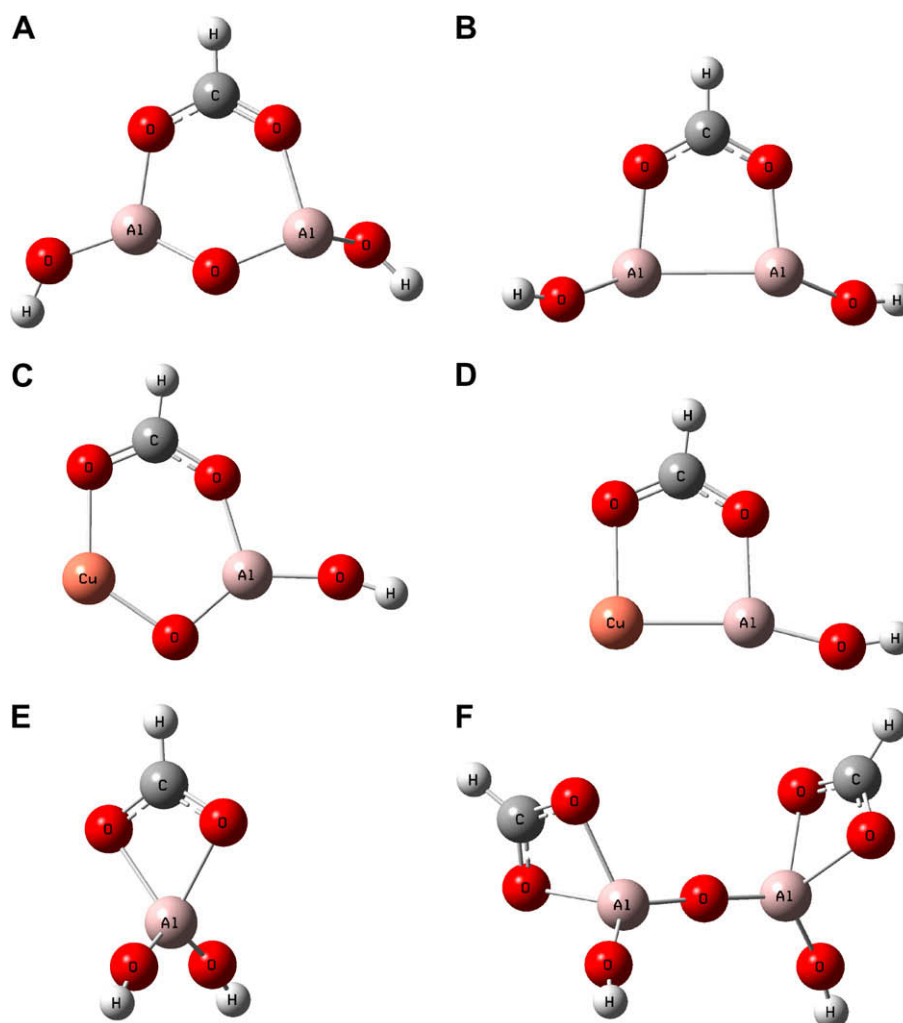


Fig. 2. Optimized configuration of calculation models for formate species adsorption on the Cu-Al₂O₃ catalyst.

and the remaining heavy atom electrons. Stability calculations confirmed the ground-state configuration of all the wave functions.

3. Results and discussion

3.1. Experimental spectra

Fig. 1 shows the in situ DRIFT spectra of the Cu–Al₂O₃ catalyst in a flow of N₂ at various temperatures (303–553 K) after HCHO + O₂ adsorption for 600 min on the Cu–Al₂O₃. Exposure of this catalyst to the fed gas resulted in the appearance of eight peaks (2897, 2856, 2807, 2704, 1597, 1392, 1379 and 1352 cm⁻¹). According to previous studies, two strong bands at 1597 and 1352 cm⁻¹ were

ascribed to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ [12–15], the small and shoulder bands at 2897, 2856, 2807 and 2704 cm⁻¹ were assigned to $\nu(\text{C-H})$ [13–15], and the peaks at 1392 and 1379 cm were assigned to $\delta(\text{C-H})$ [13–15]. No peak of the adsorbed HCHO could be observed, even at room temperature. The findings showed that a large amount of HCOOH was formed over the Cu/Al₂O₃ surface.

3.2. Mechanism for the formation of adsorbed formate species over Cu–Al₂O₃ catalyst

On the basis of our previous results, we propose Scheme 1 for the process of the HCHO elimination over Cu–Al₂O₃.

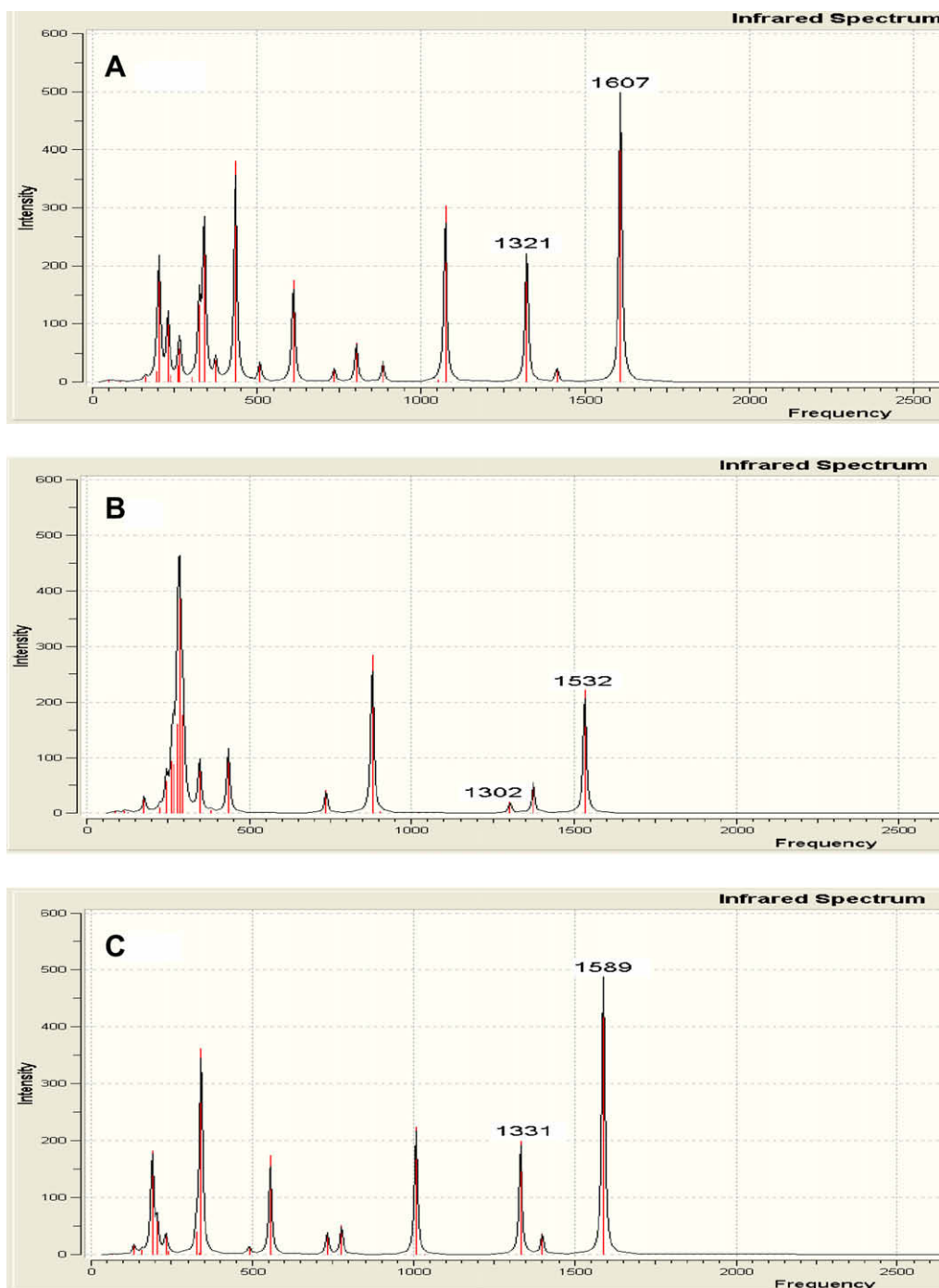


Fig. 3. Calculated vibration IR spectra for the models (A–C) at DFT-PBE1PBE/LANL2DZ level.

When the catalyst was exposed to HCHO + O₂ mixture for 600 min, the deactivated Cu–Al₂O₃ catalyst was heated to 773 K in a flow of 40 cm³/min helium. HCHO firstly adsorbed on the Cu–Al₂O₃ catalyst surface, and then was oxidized into HCOOH at the room temperature. The results of the in situ DRIFTS, Density functional theory calculations and temperature programmed desorption (TPD) showed that HCHO was completely oxidized into HCOOH over Cu–Al₂O₃ at the room temperature. With increasing the temperature in a flow of helium, HCOOH was completely decomposed into CO₂ over the catalyst surface, and the deactivated Cu–Al₂O₃ is regenerated at the same time. In addition, although Cu

had no obvious influence on the adsorption of HCHO on Al₂O₃, Cu dramatically lowered the decomposition temperature of HCOOH into CO₂. It was shown that the Cu–Al₂O₃ catalyst had a good ability for the removal of HCHO, and appeared to be promising for its application in destroying HCHO at the room temperature.

3.3. Optimized structure

In order to investigate the structure of the adsorption of formate species on the Cu–Al₂O₃ catalyst, we designed six calculated models (A–F). The optimized structures of these calculation models are

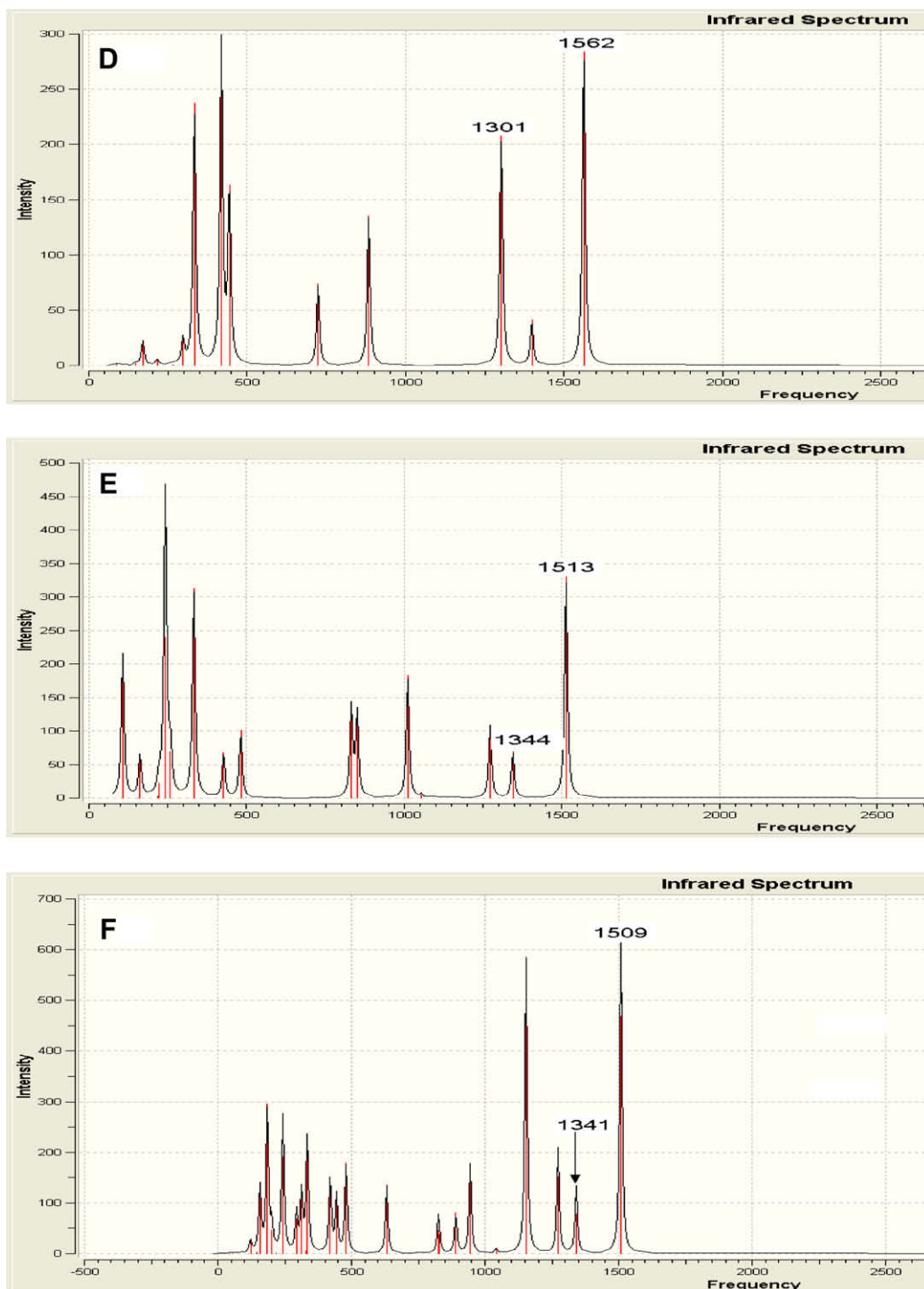


Fig. 4. Calculated vibration IR spectra for the models (D–F) at DFT-PBE1PBE/LANL2DZ level.

Table 1

Calculated vibration frequencies (in cm^{-1}) and IR intensity (in km/mol) for the calculated model at PBE1PBE/LANL2DZ level, and corresponding frequencies in the experimental gas-phase spectra

Model	Frequency (cm^{-1})	Intensity (km/mol)	Vibration mode
A	1607	510	$\nu_{\text{as}}(\text{COO})$
	1321	237	$\nu_{\text{s}}(\text{COO})$
B	1532	226	$\nu_{\text{as}}(\text{COO})$
	1302	55	$\nu_{\text{s}}(\text{COO})$
C	1589	515	$\nu_{\text{as}}(\text{COO})$
	1331	203	$\nu_{\text{s}}(\text{COO})$
D	1562	290	$\nu_{\text{as}}(\text{COO})$
	1301	208	$\nu_{\text{s}}(\text{COO})$
E	1513	332	$\nu_{\text{as}}(\text{COO})$
	1344	69	$\nu_{\text{s}}(\text{COO})$
F	1509	468	$\nu_{\text{as}}(\text{COO})$
	1341	79	$\nu_{\text{s}}(\text{COO})$
Experiment (cm^{-1})	1597		$\nu_{\text{as}}(\text{COO})$
	1352		$\nu_{\text{s}}(\text{COO})$

plotted in Fig. 2. The optimized C=O bond length in formate species for the models (A–F) is about 1.23–1.24 Å, which is within 2% error of the experimental value of 1.22 Å. The C–H bond length in formate species for the models (A–F) is about 1.09 Å, which is in good agreement with experimental value of 1.09 Å.

3.4. Comparison of simulated and experimental spectra

The optimized geometries were taken as the basis for the calculation of IR frequencies by a normal coordinate analysis. Simulation spectra of Cu–Al₂O₃ are depicted in Figs. 3 and 4. Calculated vibration frequencies (in cm^{-1}) and IR intensity (in km/mol) and corresponding frequencies in the experimental gas-phase spectra are listed in Table 1.

The calculated antisymmetric stretching vibration modes of the adsorbed formate species for the models (A–F) are 1607, 1532, 1589, 1562, 1513 and 1509 cm^{-1} , respectively (Figs. 3 and 4). In comparison with the same experimental frequency of 1597 cm^{-1} , the error is on average about 10 cm^{-1} for model (A), –65 cm^{-1} for model (B), –8 cm^{-1} for model (C), –35 cm^{-1} for model (D), –84 cm^{-1} for model (E) and –88 cm^{-1} for model (F). For the same experimental frequency of 1597 cm^{-1} , overestimation of experimental frequency values is about 0.62% for model (A); underestimation of experimental frequency values is about 4.07% for model (B), 0.50% for model (C), 2.19% for model (D), 5.25% for model (E) and 5.51% for model (F). The calculated frequencies of model (A) at 1607 cm^{-1} with 510 km/mol intensity is relatively good matches of the most intense bands at 1597 cm^{-1} in the experimental spectrum (Fig. 1). The calculated frequencies of model (C) at 1589 cm^{-1} with 515 km/mol intensity is also in good agreement with the experimental value of 1597 cm^{-1} (Fig. 1).

The calculated symmetric stretching vibration modes of the adsorbed formate species for the models (A–F) are 1341, 1302, 1331, 1301, 1344 and 1321 cm^{-1} , respectively (Fig. 3 and Fig. 4). In comparison with the same experimental frequency of 1352 cm^{-1} , the error is on average about –31 cm^{-1} for model (A), –50 cm^{-1} for model (B), –21 cm^{-1} for model (C), –51 cm^{-1} for model (D), –8 cm^{-1} for model (E) and –11 cm^{-1} for model (F). For the same

experimental frequency of 1352 cm^{-1} , underestimation of experimental frequency values is about 2.29% for model (A), 3.69% for model (B), 1.55% for model (C), 3.77% for model (D), 0.59% for model (E) and 0.81% for model (F). The calculated frequency of model (E) at 1344 cm^{-1} with 69 km/mol intensity is relatively good matches of the peak at 1352 cm^{-1} in the experimental spectrum (Fig. 1).

Although the calculated symmetric stretching vibration mode of the adsorbed formate species of model (E) is better than that of model A, there is big error between the calculated and experimental antisymmetric stretching vibration modes of the adsorbed formate species for model (E). Therefore, the spectra of model (A) simulated by DFT-PBE1PBE evidently best match the experimental counterparts for overwhelming majority of the calculated models (A–F) considered in the present study.

4. Conclusion

The calculated IR spectrum for the model (A) is of reasonable similarity to the corresponding experimental spectrum. Furthermore, calculated antisymmetric and symmetric stretching vibration modes of the adsorbed acetate species for the model (A) are in good agreement with experimental data. The calculations show clearly that simulating infrared spectra with density functional theory (DFT) quantum mechanical method can be considered as the advantageous auxiliary tool for analyzing the mechanism of the formate species adsorption over the Cu–Al₂O₃ catalyst.

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