

Conformational analysis and comparison between theoretical and experimental vibration spectra for isocyanate species on Ag/Al₂O₃ catalyst

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Abstract

Density functional theory (DFT) calculations were performed to study the structure and vibrational frequencies of the intermediate for the isocyanate (NCO) surface species on Ag/Al₂O₃ catalyst using the GAUSSIAN 98 suite of programs. Thermal decomposition of adsorbed CH₃NO₂ species leads to the formation of two types of NCO species (NCO on Ag and NCO on Al₂O₃) above 298 K. In order to investigate the reaction mechanism, we have designed the calculated models (a–g) for the NCO intermediate. Through the analysis of the vibration mode and the vibration frequency of the calculated models (a–g), we conclude that there is an excellent agreement between the calculated vibration spectrum of the model (e) containing the –Ag–NCO group or model (g) containing the –Al–NCO group and the experimental vibration spectrum.

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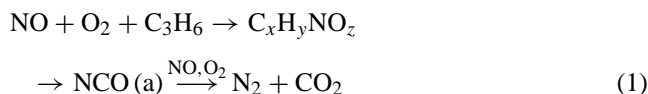
Keywords: DFT; Structure; NCO intermediate; Vibrational spectrum; DRIFTS

1. Introduction

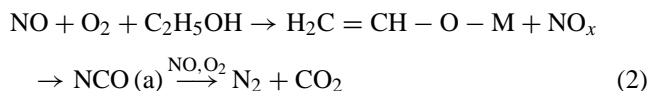
Simulating infrared spectra with ab initio, semi-empirical and density functional theory (DFT) methods are at present widely used in many fields. The simultaneous coupling of gas chromatography with Fourier transform IR spectroscopy (FT-IR) and mass spectrometry (MS) detectors is currently one of the most powerful tools for the separation and unambiguous identification of complex mixtures of organic compounds. An especially important and intriguing case is the analysis of unknown compounds. During the past years, several papers have been published exemplifying how IR simulations can assist identification of organic compounds by means of the coupled technique of gas chromatography–Fourier transform IR spectroscopy–mass spectrometry (GC–FT-IR–MS) [1–4].

The selective catalytic reduction of NO by hydrocarbons (HC-SCR of NO) is a potential method of controlling the emissions from stationary and mobile resources in which the engine operates in oxygen-rich conditions (e.g. diesel and

lean-burn engines) [5–8]. The mechanism of HC-SCR of NO in the presence of excess oxygen over Ag/Al₂O₃ has been proposed as [9–16]



and [13]



Based on our previous IR study [10,13], NCO species were detected on the Ag/Al₂O₃ surface in a vacuum system for the reaction NO + O₂ + C₃H₆ (or C₂H₅OH). Because of facile formation of C_xH_yNO_z and high reactivity of NCO species in the presence of NO and O₂, we concluded that the NCO species on the Ag/Al₂O₃ surface were the crucial intermediates of the reactions (1) and (2).

The reactivity of the intermediates containing the isocyanate group –N=C=O in catalytic chemistry has attracted

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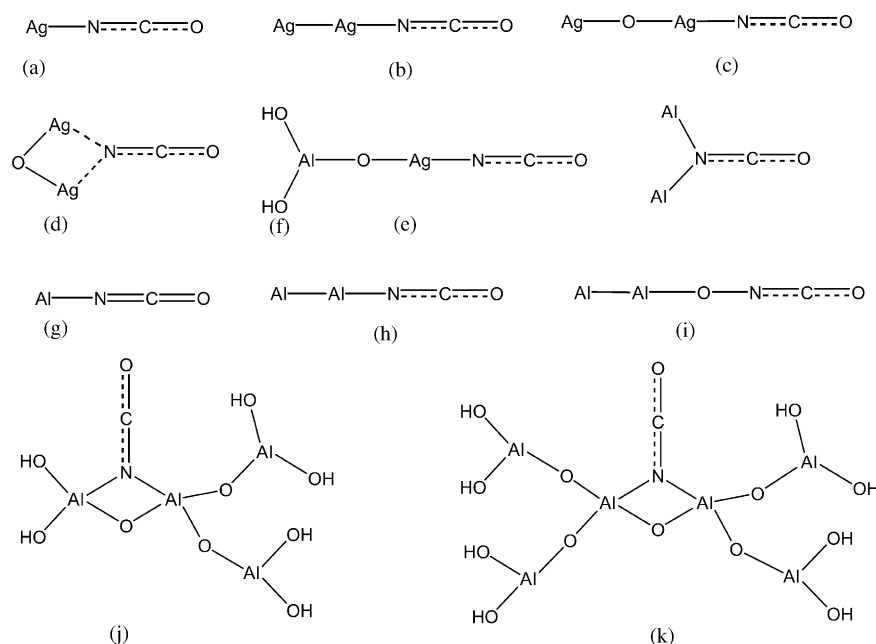
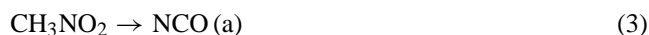


Fig. 1. Calculational models for the reaction of NCO species on Ag/Al₂O₃ catalyst.

investigations of their conformations, structure and vibrational spectra. Although the reaction mechanism on Ag/Al₂O₃ catalyst has been investigated by some researchers, there is still a limited understanding about the fundamental role of intermediate and surface chemistry involved in the de-NO_x reaction. The exact structure of the intermediates formed by the NCO species on Ag/Al₂O₃ catalyst for the selective catalytic reduction of de-NO_x is still not clear.

The objective of this work was to study the formation and surface structure of the NCO intermediates on Ag/Al₂O₃ catalyst using experimental and theoretical methods for the reaction as follows:



Because of the unknown structure of the NCO intermediates on Ag/Al₂O₃ surface, we have designed eleven calculational

models (a–k) (see Fig. 1) to investigate the structure and the vibrational frequencies of the NCO intermediate for reaction (3). The main goal of this work was to compare general views of simulated IR spectra for these calculational models with experimental spectra. A fundamental understanding of the reaction mechanism of the SCR of NO_x is believed to be essential for the development of a catalyst and improvement for its potential application.

2. Theoretical

The GAUSSIAN 98 program [17] running on an OP-TIPLEX (TM) GX260SD with Interl (R) Pentium (R) 4, 2.26 GHz Processor and 512 MB RAM was used to optimize the structures and calculate the vibrational wavenumbers for the NCO intermediate on Ag/Al₂O₃ catalyst. The 3–21G*

Table 1

Geometrical parameter, calculated vibration frequencies and intensity of the NCO antisymmetric stretching mode for the calculational models (a–k)

Model	r (N=C)	R (C=O)	R (N–M)	N–C–O	M–N–C	Va (NCO)	Intensity
a	1.20	1.21	2.03	179.88	178.90	2333	920
b	1.21	1.20	2.25	179.97	138.31	2264	857
c	1.20	1.21	2.04	179.98	179.84	2321	1103
d	1.20	1.21	2.02	179.96	179.85	2308	1500
e	1.21	1.21	2.02	179.75	177.52	2215	967
Experimental	1.23 [15]	1.146 [15]		180.00 [15]		2212	
f	1.21	1.19	1.80	179.96	179.20	2336	1152
g	1.23	1.18	2.02	180.00	137.88	2267	1228
h	1.21	1.19	1.78	179.95	179.82	2347	1989
I	1.21	1.19	1.78	179.76	175.48	2371	1262
j	1.22	1.18	1.93	176.38	135.10	2318	747
k	1.22	1.18	1.96	176.45	138.70	2317	887
Experimental	1.23 [18]	1.15 [18]		180.00 [18]		2237	

The units for bond length, bond angle, vibration frequency and intensity are angstrom, degree, cm⁻¹ and km mol⁻¹, respectively. M = Ag, Al.

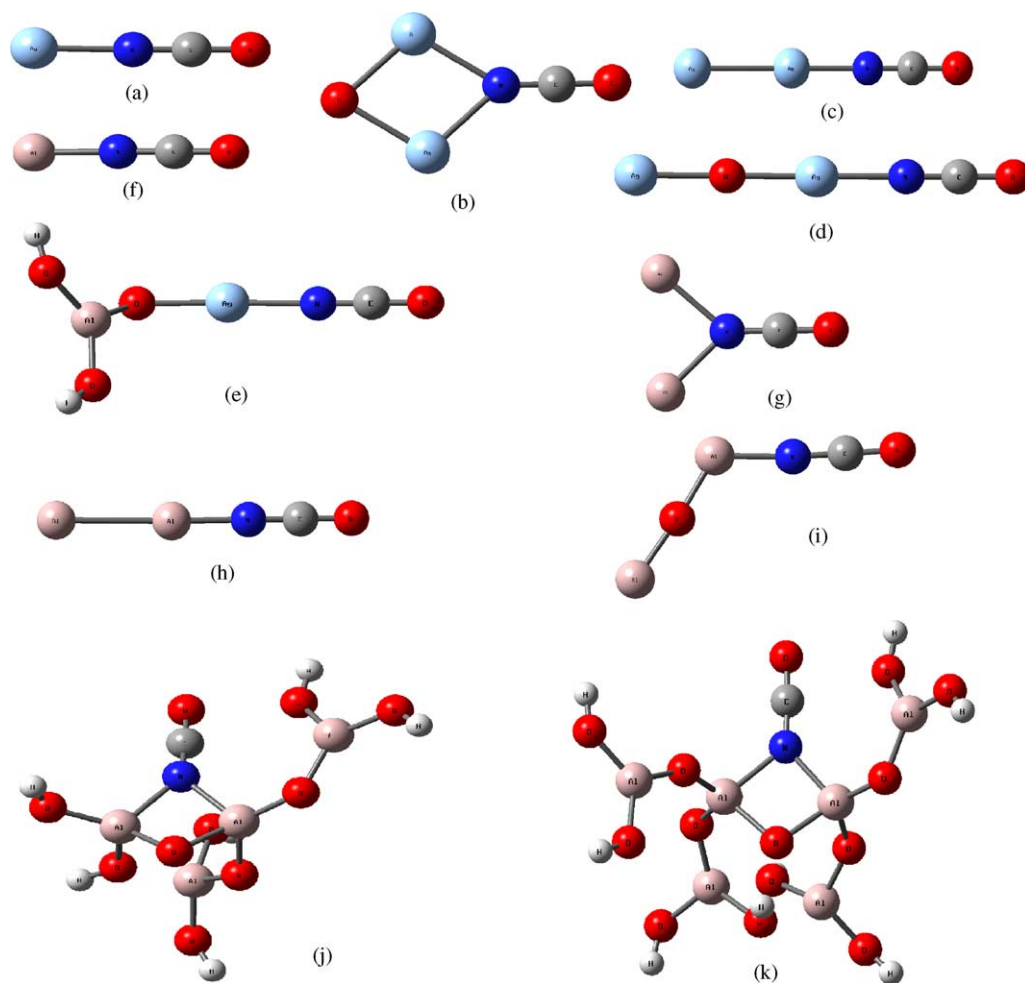


Fig. 2. The optimized structure of computational models for the adsorption of NCO with Ag/Al₂O₃ cluster. Red circles: O atoms; black circles: C atoms; blue circles: N atoms; white circles: H atoms; gray circles: Al atoms; cyan circles: Ag atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

basis set was employed to carry out the DFT-B3PW91 (Becke's three parameter functional with the non-local correlation provided by the Perdew 91 expression) calculations. The resulting vibrational frequencies and intensities were read by the HyperChemTM Version 6.0 package. We have analyzed the vibration spectrum using HyperChem program.

The HyperChem program offers many types of molecular and quantum mechanics calculations; however, the calculations for vibrational frequencies consume much time. From our experience, the calculations for a compound of more than 100 Da molecular weight normally take more than 3 days. The method in this paper combines both Gaussian 98 program and HyperChem program, thus saving a lot of computational time.

As a new quantum-chemical method, DFT has been exponentially used in inorganic and organo-metallic chemistry in the past few years with great success. Unlike the Hartree-Fock theory, DFT recovers electron correlation in the self-consistent Kohn-Sham procedure through the functions of electron density and gives good descriptions for systems, which require sophisticated treatments of electron correlation in the conventional ab initio approach. Hence,

not only is it a cost effective method, but also it is a reliable one.

3. Experimental

An Ag/Al₂O₃ catalyst (Ag loading is 5.0 wt.%) was prepared by an impregnation method as described in our earlier paper [12]. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Nexus 670 (Thermo Nicolet) FT-IR, equipped with an in situ diffuse reflection chamber and a high sensitivity MCT detector. An Ag/Al₂O₃ catalyst (ca. 30 mg) for the in situ DRIFTS studies was finely ground and placed into a ceramic crucible in the chamber. Prior to recording each DRIFTS spectrum, the sample was heated in situ in 10% O₂/He flow at 873 K for 1 h, then cooled to the desired temperature for taking a reference spectrum. At room temperature, CH₃NO₂ was introduced by He carrier. After 5 min adsorption of CH₃NO₂ on catalyst surface, all DRIFTS spectra were measured with a resolution of 4 cm⁻¹ and with an accumulation of 100 scans in the flow of He gas.

4. Results and discussion

4.1. Optimized structure

The models used in the calculation of the adsorption of NCO species on Ag/Al₂O₃ catalyst are shown in Fig. 1 (a–k). The optimized structures of the calculational models are plotted in Fig. 2. The optimized geometrical parameters are listed in Table 1. From Table 1, the calculated value of the N=C bond length in NCO for the models (a–k) is about 1.20–1.23 Å, which is within 1% of the experimental value of 1.23 Å. The C=O bond length in NCO for models (a–k) determined from DFT calculations is 1.18–1.21 Å, and the corresponding literature value at MP2/6–31G* level is 1.173 Å [15]. The optimized distance between the nitrogen atom and the aluminum atom in the models (a–e) is about 2.03–2.25 Å, while the optimized bond length for the N–Al bond in the models (f–k) is about 1.80–2.02 Å. The calculated equilibrium

∠N–C–O bond angle in NCO for the models (a–k) about 176.45–179.98° is in agreement with the corresponding experimental value of 180°.

4.2. Comparison of calculated and experimental spectra

The calculated vibration frequencies and intensity of the NCO antisymmetric stretching mode for the calculational models (a–k) and experimental values are presented in Table 1. The calculated spectra of models (a–k) and experimental spectra are plotted in Figs. 3–7.

Fig. 7 shows the in situ DRIFT spectra of Ag/Al₂O₃ in a flow of He at a temperature range of 298–673 K in steady states. Exposure of this catalyst to CH₃NO₂ at room temperature resulted in the appearance of two peaks (2237 and 2212 cm⁻¹). Based on our theoretical calculation, the peak at 2237 cm⁻¹ was assigned to ν_{as}(NCO) on Ag atom surface and the peak of 2212 cm⁻¹ was assigned to ν_{as}(NCO) on Al atom surface. These NCO species are thermally stable

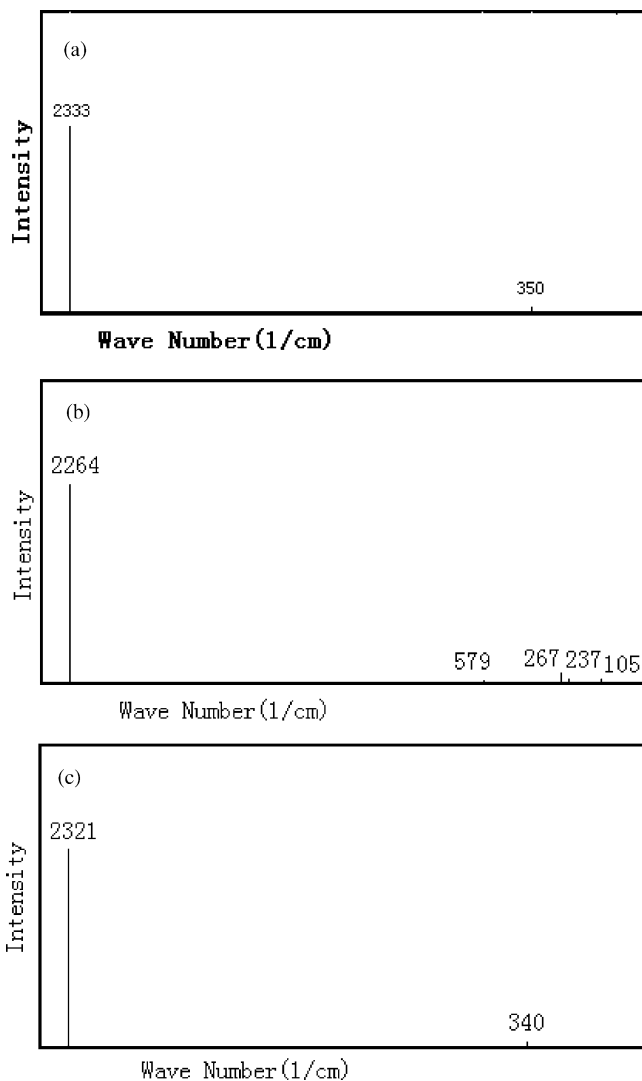


Fig. 3. Calculated spectra of models a, b and c with the spectra simulated by the methods B3PW91.

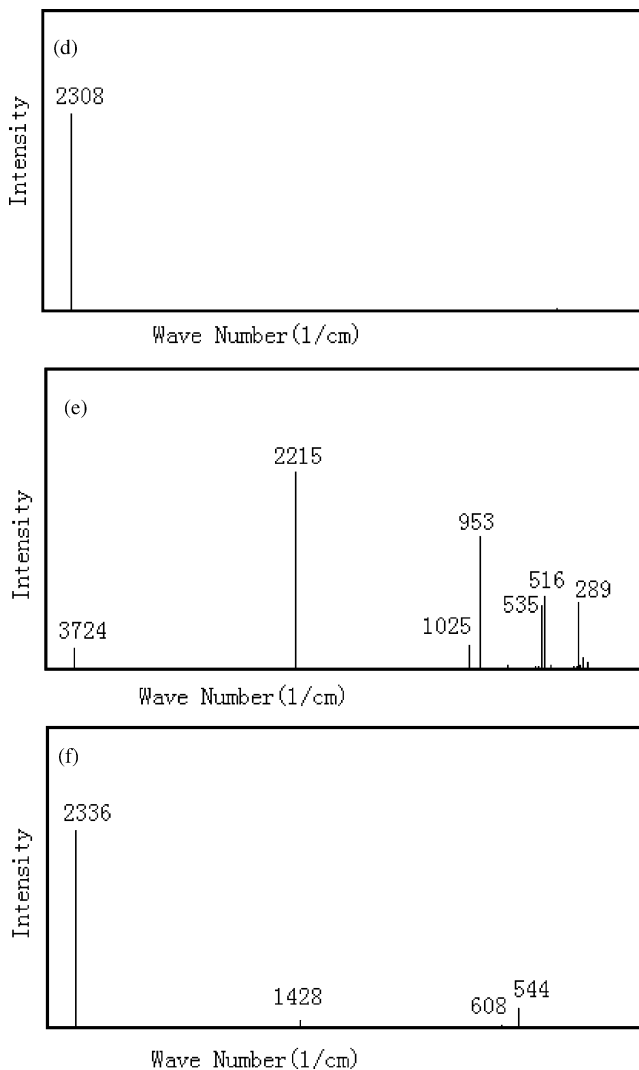


Fig. 4. Calculated spectra of models d, e and f with the spectra simulated by the methods B3PW91.

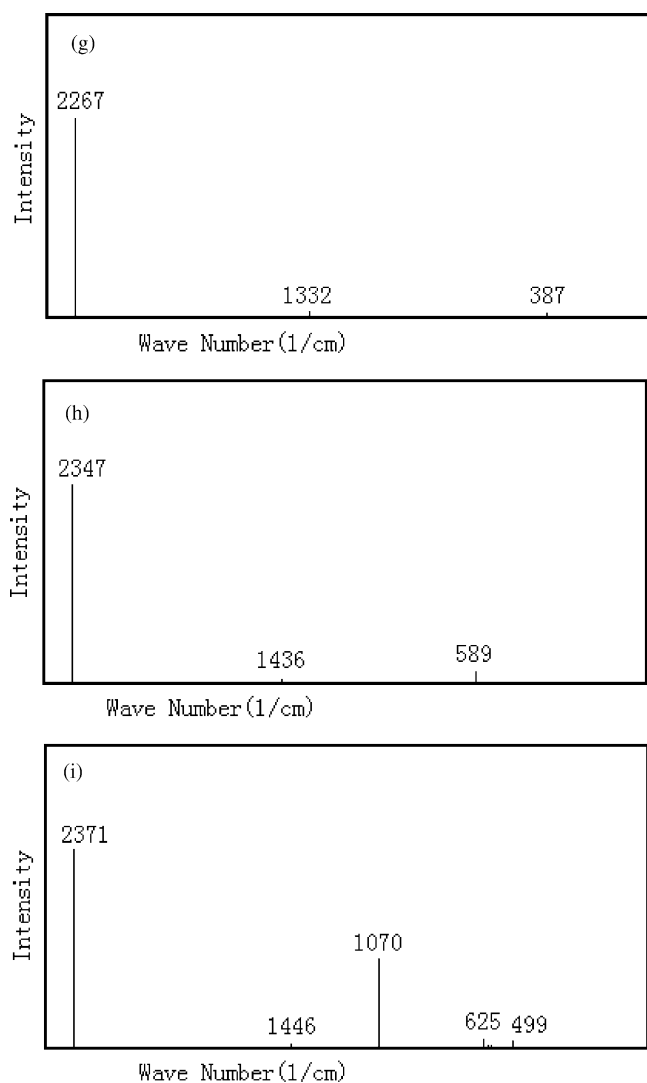


Fig. 5. Calculated spectra of models g, h and i with the spectra simulated by the methods B3PW91.

at room temperature. With increased temperature, these two peaks decreased promptly, i.e. the NCO species is very active in the catalytic surface.

The assignment of the NCO stretching fundamentals for the NCO intermediates can be made based on the DFT calculation. From the experimental FT-IR spectra (see Fig. 7), the NCO antisymmetric stretching mode for the intermediates containing the group ($-\text{Ag}-\text{NCO}$) is clearly observed as a strong absorbance at 2212 cm^{-1} ; one for the intermediate containing the group ($-\text{Al}-\text{NCO}$) is clearly observed as a strong absorbance at 2237 cm^{-1} . Because of the weak intensity, symmetric stretching mode for the surface structure containing the group ($-\text{Ag}-\text{NCO}$) or the group ($-\text{Al}-\text{NCO}$) has not been observed in the experimental FT-IR spectra. This point has been proved by the DFT calculation.

In the case of the calculated models (a–e), the calculated NCO antisymmetric stretching modes of the models (a–e) containing the group ($-\text{Ag}-\text{NCO}$) are 2333, 2264, 2321,

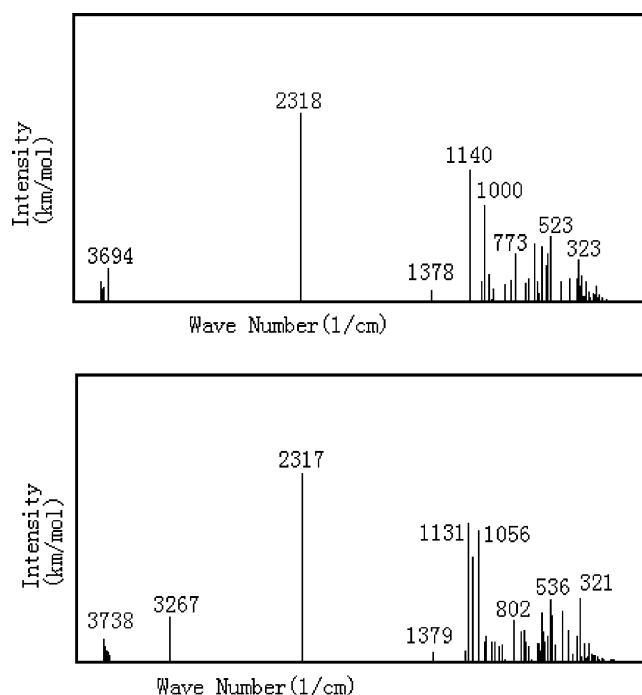


Fig. 6. Calculated spectra of models j, k with the spectra simulated by the methods B3PW91.

2308 and 2215 cm^{-1} , respectively (Figs. 3 and 4). For the same experimental frequency 2212 cm^{-1} , overestimation of experimental frequency values is on average about 5.47% for model (a), 2.35% for model (b), 4.93% for model (c), 4.34% for model (d) and 0.14% for model (e). The calculated spectrum of model (e) at 2215 cm^{-1} with 967 km mol^{-1} intensity is similar to the experimental spectrum at 2212 cm^{-1} with strong absorbance. The expressed frequency at 2215 cm^{-1} for the model (e), containing the group ($-\text{Ag}-\text{NCO}$) in Fig. 4, is a relatively good match of the most intense bands at 2212 cm^{-1} in the experimental spectrum (see Fig. 7).

In the case of the calculated models (f–k), the calculated NCO antisymmetric stretching modes $\nu_a(\text{NCO})$ containing the group ($-\text{Al}-\text{NCO}$) are 2336, 2267, 2347, 2371, 2378 and 2317 cm^{-1} , respectively (Figs. 4 and 6). For the same experimental frequency 2237 cm^{-1} , overestimation of experimental frequency values is on average about 4.43% for model (f), 1.34% for model (g), 4.92% for model (h), 5.99% for model (i), 6.30% for model (j) and 3.58% for model (k). The $\nu_a(\text{NCO})$ frequency of model (g) calculated at 2267 cm^{-1} with 1228 km mol^{-1} intensity is only 30 cm^{-1} higher than the experimental spectrum at 2237 cm^{-1} with strong transmittance within 1.34% error. The expressed frequency at 2267 cm^{-1} for model (g) containing the group ($-\text{Al}-\text{NCO}$) in Fig. 5 is a relatively good match of the most intense bands at 2237 cm^{-1} in the experimental spectrum (Fig. 7).

Comparison with the experimental data shows that the spectra of model (e) and (g) simulated by DFT-B3PW91 evidently best match the experimental counterparts for the overwhelming majority of the calculated models (a–k) considered in the present study.

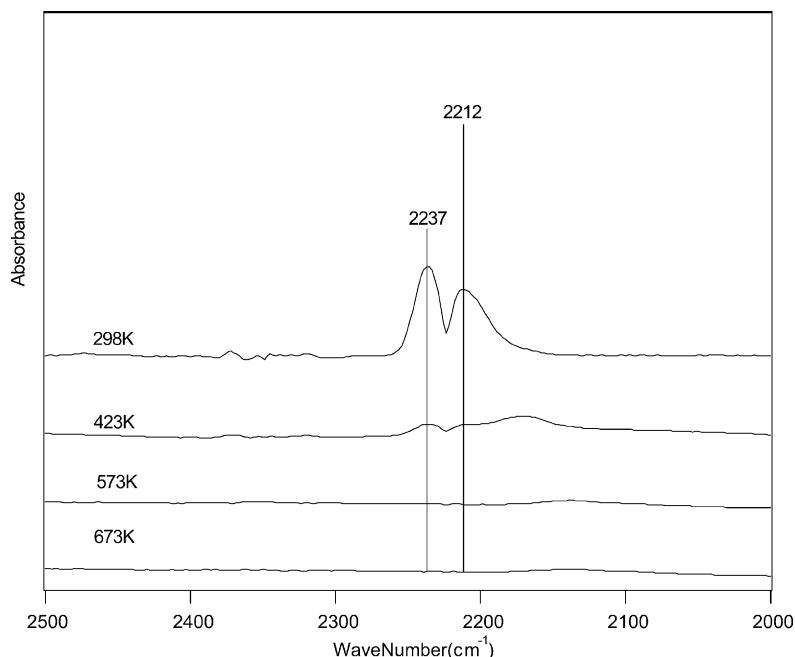


Fig. 7. In situ DRIFTS spectra of NCO adsorbed species in steady states on Ag/Al₂O₃ in the flow of He at: (a) 298 K; (b) 523 K; (c) 573 K; (d) 673 K. Conditions: CH₃NO₂ adsorbed on catalyst surface at room temperature for 5 min and the spectra were measured in the flow of He gas.

5. Conclusions

Simulating infrared spectra with DFT, quantum mechanical method can be considered as an advantageous auxiliary tool for the FT-IR identification of unambiguous compounds. The calculations show clearly that the calculated IR spectra for models (e) and (g) are in good agreement with the corresponding experimental spectra. We conclude that models (e) and (g) are the best models for the NCO intermediates containing the groups –Ag–NCO and –Al–NCO, respectively.

Acknowledgements

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