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A comparative DFT study of the structure and vibration spectra of the intermediate of the OCS heterogeneous reaction

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ABSTRACT

Density functional theory (DFT) calculations using the different functional of PBE1PBE, PBEPBE, LSDA, B3LYP, MPW1PW91, B3P86 and B3PW91 have been carried out to study the adsorption of HCO_3^- species on the Al_2O_3 catalyst. The geometrical structures and vibration spectra were obtained using DFT and compared with the corresponding experimental values. Theoretical calculations show that the calculated IR spectra for PBE1PBE and MPW1PW91 method are in good agreement with the experimental spectroscopic results.

1. Introduction

Carbonyl sulfide is the chemical compound with the formula OCS. It is a linear molecule consisting of a carbonyl group double bonded to a sulfur atom. OCS is the most abundant atmospheric sulfur gas in the remote troposphere [1,2]. OCS caused many researchers the long-standing interest [3–5]. Rinsland et al. [3] have investigated the multi-decade atmospheric OCS infrared measurements. Danielache et al. [4] have performed the calculations for the fractionation of sulfur isotopes in the gas-phase reaction of OCS with OH by ab initio. Yi et al. [5] have reported the exchange of OCS and dimethyl sulfide (DMS) between rice paddy fields and the atmosphere in subtropical China.

Heterogeneous reactivity of carbonyl sulfide on Al_2O_3 has been investigated by an in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) in our lab [6,7]. We fund that adsorbed OCS could be catalytically oxidized to form CO_2, SO_4^{2-} and HCO_3^- species at 298 K on the surface of Al_2O_3. HCO_3^- is the important intermediate for the heterogeneous oxidation of OCS on the surface of the Al_2O_3 catalyst. Some researchers have reported the assignment of the vibration of the surface HCO_3^- species on the surface of Al_2O_3 catalyst [8–11].

Although OCS has been studied by a lot of experimental and theoretical methods, there is still a limited understanding on the formation and configuration of intermediate involved in the heterogeneous reactions of OCS. The study on the adsorption of the intermediate of HCO_3^- species can provide useful information for exploring the OCS heterogeneous reaction mechanism on the surface of Al_2O_3 catalyst. Moreover, the performance of different DFT methods including PBE1PBE, PBEPBE, LSDA, B3LYP, MPW1PW91, B3P86 and B3PW91 has not been examined.

In this paper, we reported on studies of the structure and vibration spectra of HCO_3^- species adsorbed on Al_2O_3 catalyst using various DFT methods. The first purpose of this work is to investigate the performance of different DFT methods in predicting geometry and vibration spectrum of HCO_3^- species adsorbed on the surface of the Al_2O_3 catalyst. The second purpose of this work is to provide a wealth of theoretical data giving insights into the OCS heterogeneous reaction mechanism.

2. Calculations

All calculations were carried out using the Gaussian 09 program [12]. The structures and vibration spectra of the calculated model were determined through DFT methods including PBE1PBE [13], PBEPBE [14], LSDA [15], B3LYP [16], MPW1PW91 [17], B3P86 [18] and B3PW91 [19] at LANL2DZ [20] basis set.

PBE1PBE is the generalized-gradient-approximation exchange-correlation functional of Perdew, Burke, and Ernzerhof. PBEPBE is the 1996 functional of Perdew, Burke and Ernzerhof. LSDA (Local Spin Density Approximation) is the synonym SVWN, which requests the Slater exchange and the VWN correlation functional. B3LYP uses the non-local correlation provided by the LYP expression, and VWN functional III for local correlation (not functional V). MPW1PW91 uses modified Perdew–Wang exchange and Perdew–Wang 91 correlation. B3P86 gradient corrected functional

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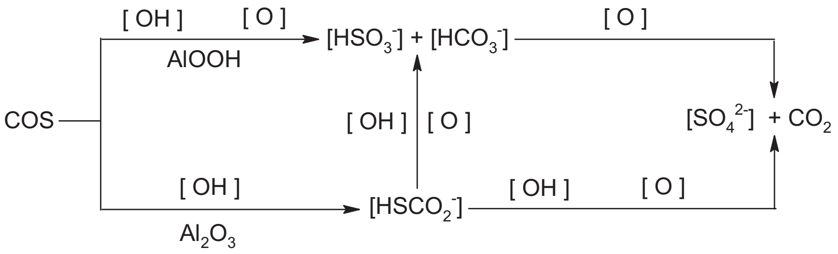

Fig. 1. Mechanism of heterogeneous oxidation of OCS on the AlOOH and Al_2O_3 samples.

is Becke's three-parameter functional with the non-local correlation provided by the Perdew 86 expressions. B3PW91 is Becke's three-parameter functional with the non-local correlation provided by the Perdew 91 expressions.

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

3. Results and discussion

3.1. Mechanism for the formation of HCO_3^- species over Al_2O_3 catalyst

A possible mechanism of the formation of HCO_3^- species over Al_2O_3 catalyst was proposed in Fig. 1 [7].

When the catalyst was exposed to a flow of OCS + O_2, OCS firstly reacted with the surface OH species to form the surface $HSCO_2^-$ species on Al_2O_3 catalyst at a room temperature, and OCS was also oxidized into the surface HCO_3^- and HSO_3^- species by oxygen and the surface OH species on the surface of catalyst at the same time. The surface $HSCO_2^-$ species was dominant surface species. It was oxidized into the surface HCO_3^- and HSO_3^- species by oxygen and the surface OH species at a room temperature. At the same time, the surface $HSCO_2^-$ species was also directly oxidized into SO_4^{2-} and CO_2 by oxygen and the surface OH species on the surface of catalyst. The surface HCO_3^- and HSO_3^- species finally were oxidized into SO_4^{2-} and CO_2. The surface HCO_3^- and HSO_3^- species are very important reaction intermediate during the heterogeneous oxidation of OCS over Al_2O_3.

3.2. Geometry optimization

The optimized structure of the calculation model was plotted in Fig. 2. A comparison of the calculated bond lengths of C–O, Al–O, O–H and the bond angles of HOC and OCO in the calculation model by different methods were presented in Table 1.

Table 1
Optimized structure parameters (bond length and bond angle) for the calculated model at PBE1PBE, PBEPBE, LSDA, B3LYP, MPW1PW91, B3P86 and B3PW91 methods.

Method	C=O (Å)	Al–O (Å)	O–H (Å)	HOC	OCO
PBE1PBE	1.2737	1.7649	0.9790	107.72	127.58
PBEPBE	1.2896	1.7814	0.9945	105.93	128.38
LSDA	1.2761	1.7675	0.9947	106.44	127.91
B3LYP	1.2789	1.7657	0.9831	107.57	127.44
MPW1PW91	1.2732	1.7638	0.9781	107.77	127.58
B3P86	1.2752	1.7641	0.9810	107.53	127.61
B3PW91	1.2760	1.7665	0.9809	107.53	127.68
HF	1.2542	1.7571	0.9541	111.30	126.01
Experiment	1.2708	1.7600	0.9318		125.17

The calculated C=O double bond lengths for the calculation model at PBE1PBE, PBEPBE, LSDA, B3LYP, MPW1PW91, B3P86, B3PW91 and HF method are 1.2737, 1.2896, 1.2761, 1.2789, 1.2732, 1.2752, 1.2760 and 1.2542 Å, respectively in Table 1. In comparison with the same experimental bond angle of 1.2708 Å [21], the error is on average about 0.0029 Å for PBE1PBE method, 0.0188 Å for PBEPBE method, 0.0053 Å for LSDA method, 0.0081 Å for B3LYP method, 0.0024 Å for MPW1PW91 method, 0.0044 Å for B3P86 method and 0.0052 Å for B3PW91 method, −0.0166 Å for HF method. The calculated C=O double bond lengths for the calculation model at PBE1PBE and MPW1PW91 method are in good agreement with the experimental value of 1.2708 Å [21].

The calculated Al–O bond lengths for the calculation model at PBE1PBE, PBEPBE, LSDA, B3LYP, MPW1PW91, B3P86 and B3PW91 method are 1.7649, 1.7814, 1.7675, 1.7657, 1.7638, 1.7641 and 1.7665 Å, respectively in Table 1. In comparison with the same experimental value of 1.76 Å [22], the error is on average about 0.0049 Å for PBE1PBE, 0.0214 Å for PBEPBE, 0.0075 Å for LSDA, 0.0057 Å for B3LYP, 0.0038 Å for MPW1PW91, 0.0041 cm^{-1} for B3P86 and 0.0065 Å for B3PW91. The calculated Al–O bond lengths for the calculation model at PBE1PBE, MPW1PW91 and B3P86 method are in good agreement with the experimental value of 1.76 Å [22].

Taking account of the effect of conjugation, our calculated values of the calculation model are in reasonable agreement with the above-mention experimental data. The HF/LANL2DZ bond lengths are slightly shorter, while the PBEPBE/LANL2DZ and LSDA/LANL2DZ bond lengths are slightly exaggerated electron correlation effect while the HF theory neglecting this effect. Compared with

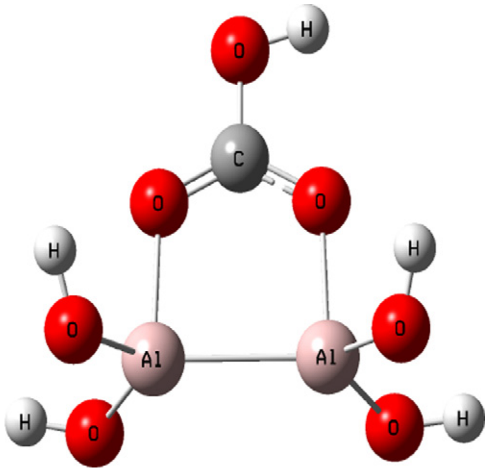

Fig. 2. The optimized structure of the calculated model for HCO_3^- species on Al_2O_3 catalyst. Red circles represent O atoms; black circles represent C atoms; white circles represent H atoms; gray circles represent Al atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)