Catalysis Letters 20 (1993) 141–148

Theoretical investigation of ethylene adsorbed on Ni(100) surface by the multiple-scattering cluster method

X.S. Feng and J.C. Tang

Physics Department, Zhejiang University, Hangzhou 310027, PR China

In this paper the carbon K-edge near edge X-ray absorption fine structure spectra (NEXAFS) of adsorption system $C_2H_4/Ni(100)$ are calculated using the multiple-scattering cluster method. By a comparison between the theoretical results and experimental spectra, the chemisorption geometry of this system has been determined. The result shows that the molecule is adsorbed on the perpendicular bridge site, and the distance between the C atom and the nearest Ni atom is 1.70 Å, while the molecular plane tilting to the surface is 50°. It is found that the interaction between hydrogen atom and Ni substrate plays an important role in the formation of the adsorption structure. The above results are supported by other evidences.

Keywords: Multiple-scattering; X-ray absorption fine structure; $C_2H_4/Ni(100)$

1. Introduction

An important topic in surface science is the study of surface adsorption structure, which is the basis of understanding the mechanism of heterogeneous catalysis, in which ethylene adsorbed on a nickel surface is a typical problem.

As early as the year 1974, in order to investigate the essential of chemisorption, Rosch and Rohodin had analysed two adsorption models of ethylene on nickel by the MS-Xα method; their calculated results are compared with UPS data [1], which demonstrate that the ethylene holds its molecular configuration and the adsorption is caused by π-bond combination instead of double σ-bond combination.

Later, electron energy loss spectroscopy (EELS), thermal programmed desorption (TPD), and laser-induced desorption (LID) studies showed that at low temperature (< 150 K) ethylene is molecularly adsorbed on Ni(100); there is no rehybridization. When the species is heated to 170 K, ethylene resolves into a vinyl fragment and a hydrogen atom [2–4].

All the above studies give some adsorption characteristics, but there is no detailed structure information obtained. Recently the study of X-ray absorption fine structure, which contains more structure information, promoted the detailed understanding of the local structure of electronic states near the absorbed atom, such as the distance to neighbour atoms. Zaera et al. determined the structure of $C_2H_4/Ni(100)$ by the near-edge X-ray absorption fine structure (NEXAFS) method [5]. They demonstrated that at 90 K the molecule plane tilts about 50° to the Ni(100) surface, and the C–C bond length equals 1.45 Å. But their NEXAFS experiment cannot give further information, such as the adsorption distance, the adsorption site, etc.

In this paper we have performed a multiple-scattering cluster (MSC) analysis of the carbon K-edge NEXAFS spectra of C_2H_4/Ni(100); by a direct comparison with Zaera's experiment we have found the detailed structure information of this system. It is shown that our result is reasonable and in agreement with the experimental data.

2. MSC method

The present authors have developed the MSC method for the NEXAFS studies of molecules and adsorption surfaces [6]. We chose an atom cluster to simulate the studied species, and consider the full multiple scattering effects in the cluster, then obtain the intermediate photoelectron wave function. In MSC calculation the summation of all scattering centers is taken over all the individual atoms. Finally, the multiple-scattering effects are represented by the scattering phase shifts. We calculate the phase shifts in terms of the SCF-Xα-SW method, which demonstrates high accuracy in dealing with multiple-scattering problems [7]. In our calculation, the cluster comprises ten or twelve atoms, including one ethylene molecule. Our

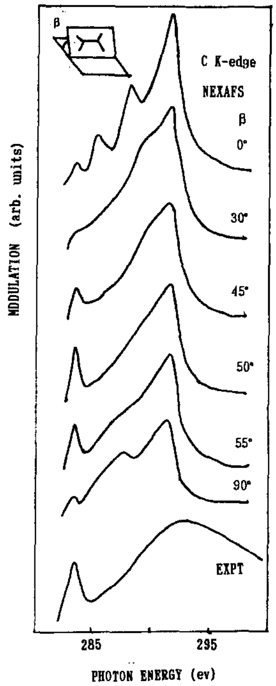

Fig. 1. The calculated carbon K-edge NEXAFS spectra of C_2H_4/Ni(100) versus the tilting angle β.

computation experience shows that more atoms in the cluster will not cause remarkable changes.

3. Results and discussion

We have studied the structure of ethylene adsorbed on Cu(100) and Ag(100) surfaces [6,8]. The results show that the molecular plane is parallel to those surfaces. But for C_2H_4/Ni(100), Zaera pointed out an ethylene plane tilting of about 50° to the Ni(100) surface [5]. It is an interesting thing which reflects the difference between those substrates, so in the first step we will determine the tilting angle (β). Fig. 1 is the plot of the calculated C K-edge spectrum versus angle β. Evidently, $\beta = 0°$ (ethylene parallel to the surface) and $\beta = 90°$ (molecule perpendicular to the surface) are not in agreement with experiment; there are four resonances appearing in the calculated spectra. The curve corresponding to $\beta = 50°$ fits with the experiment well; this supports Zaera's experimental result.

We plot the calculated C spectra versus the intramolecular bond length (L_{C-C}) in fig. 2. We change the L_{C-C} values from 1.25 to 1.50 Å. It is easy to see that the fea-

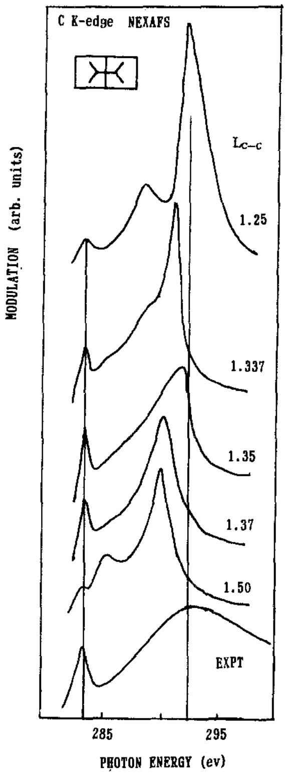

Fig. 2. Plot of C K-edge NEXAFS spectra of ethylene adsorbed on Ni(100) versus the intramolecular bond length L_{C-C}.

tures corresponding to σ resonance shift towards the low energy direction when L_{C-C} increases. This is the reflection of the correlation between the position of σ resonance and the bond length of diatomic molecules [9]. The curve with $L_{C-C} = 1.35$ Å is similar to the experimental spectrum, we judge $L_{C-C} = 1.35$ Å. This value is less than Zaera's data by 0.1 Å, and is close to the bond length of gas phase ethylene molecule (1.34 Å). The physical reason of the above fact will be discussed later.

The adsorption distance is very important for understanding the chemisorption process. It offers bonding information. We keep $L_{C-C} = 1.35$ Å and calculated the C spectra versus the adsorption height (h) from 0.7 to 1.0 Å, which is the distance of the C atom from the outmost layer of the Ni substrate. Obviously, the curves corresponding to $h = 0.7$, 0.8 and 1.0 Å do not fit with the experiment; we find that the curve with $h = 0.9$ Å fits to the experimental spectrum well. Therefore we can deduce that the length $L_{C-Ni} = 1.7$ Å, this value is the same as that in the case of CO/Ni(100) determined by LEED analysis [10] (see fig. 3).

We have used the perpendicular-bridge site model in the above calculation to optimize the L_{C-C}, β and h. Do other adsorption sites produce the similar correct spectra? The answer is no. Before optimizing the geometry in the perpendicular-bridge site model, we have calculated a lot of spectra with different models (see the inset of fig. 4) and with different L_{C-C}, h, and β values. We found that the spectra of the other five models are quite different from the spectra of the perpendi-

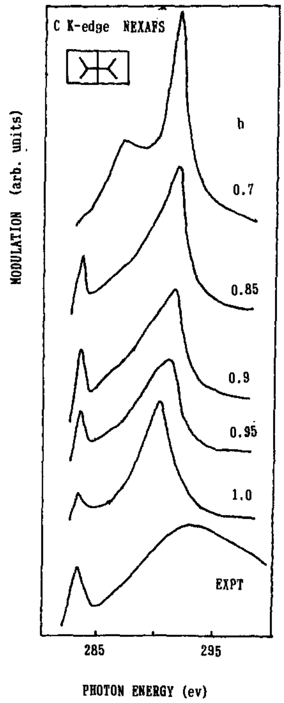

Fig. 3. Plot of the carbon K-edge NEXAFS spectra of the C_2H_4/Ni(100) versus adsorption distance (h).

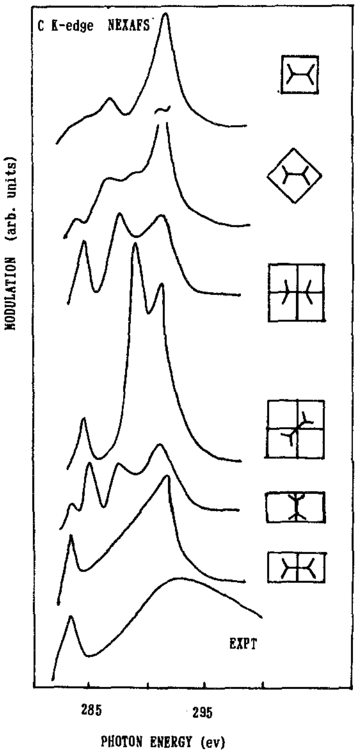

Fig. 4. Plot of the calculated C K-edge NEXAFS spectra of C_2H_4/Ni(100); the calculation is performed in six different models (see inset).

cular-bridge site model and cannot match the experiment through change of the geometry within a reasonable range. In fig. 4 we plot one typical calculated curve for every adsorption site model; we can see the difference between the perpendicular-bridge model and the other five models. So we think that the perpendicular-bridge site is the favourite adsorption site.

All the above calculated spectra are corresponding to a normal incident angle. We also calculated the spectra at different incident angles using the model and geometry determined above. Fig. 5 is the comparison between the calculated spectra and Zaera's experimental results at different incident angles. The agreement of the angular dependence between the theory and the experiment can be seen.

In order to investigate the contribution of the individual atom to the NEXAFS spectra, we construct four clusters which are (a) C-C-6Ni (two carbon atoms adsorbed on Ni substrate); (b) C-C-1-2-6Ni (add two lower hydrogen atoms upon the first cluster); (c) C-C-3-4-6Ni (add two upperhydrogen atoms upon the first cluster); (d) C-C-1-2-3-4-6Ni (the ethylene molecule adsorbed on Ni(100) surface). In fig. 6 we find that the spectrum of cluster b is similar to that of d, but the spectrum c is different from that of b; it demonstrates that the two lower hydrogen

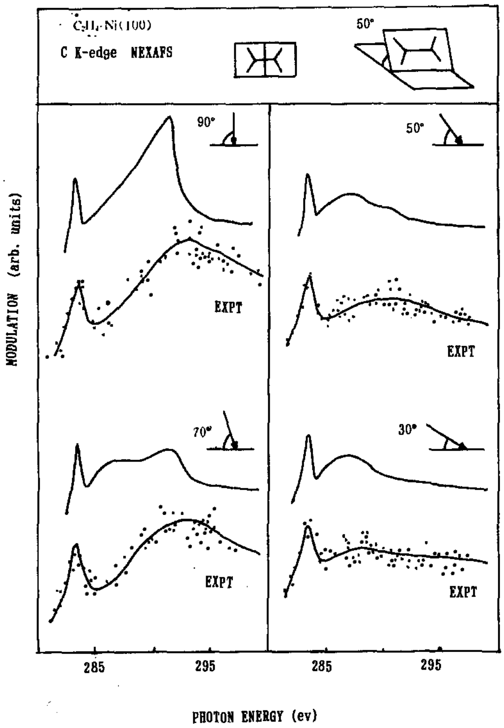

Fig. 5. Comparison of the calculated NEXAFS spectra and the experimental results at different incident angle. The geometry has been determined in figs. 1–4.

atoms play an important role in the formation of the adsorption structure, those hydrogen atoms interact with Ni substrate strongly. Of course, the remainder carbon atoms interact with Ni weakly, so the bond length L_{C-C} has a small variation (0.01 Å) when the ethylene molecule is adsorbed on Ni(100) surface.

4. Comparison between C_2H_4/Ni(100) and C_2H_4/Cu(100)

Both Ni and Cu are important transition metals for heterogeneous catalysis. In a former work we have investigated the structure of the chemisorption system of C_2H_4/Cu(100). It is interesting to make a comparison between these systems. We list the main properties of them in table 1. It is easy to see that the C–C bond length almost maintains the value in gas phase ethylene for C_2H_4/Ni(100) but it has a large elongation (0.12 Å) for the latter. Meanwhile, the C–H resonance is not excited evidently for the former, but it is excited strongly in C_2H_4/Cu(100). These properties imply that the interaction between the C and the Cu is strong, while the C–Ni interaction is weak. On the contrary, the H–Ni interaction is stronger than the H–Cu interaction.

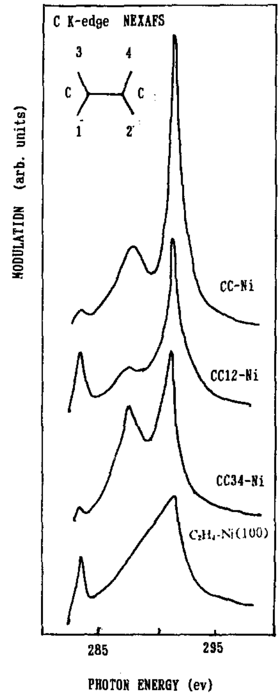

Fig. 6. The calculated NEXAFS spectra of four clusters: (a) C-C-Ni, (b) C-C-1-2-Ni, (c) C-C-3-4-Ni, (d) C-C-1-2-3-4-Ni (C_2H_4/Ni(100).

5. Conclusion

We have calculated the carbon K-edge NEXAFS spectra of C_2H_4/Ni(100) in terms of the MSC method. By a comparison between the theoretical curves and the experimental spectra we find the molecular plane tilting 50° to the substrate. This fact is in agreement with the experiment. Meanwhile we find the ethylene molecule

Table 1
Comparison between the properties of C_2H_4/Ni(100) and C_2H_4/Cu(100)

	C–C bond length (Å)	Orientation of adsorbed ethylene	Adsorption site	C–H resonance
C_2H_4/Ni(100)	1.35	molecular plane tilts 50° to Ni(100)	perpendicular bridge	disappears
C_2H_4/Cu(100)	1.46	molecular plane is parallel to Cu(100) surface	hollow	appears

adsorbed at the perpendicular-bridge-site with the bond length $L_{C-C} = 1.35$ Å. The two lower hydrogen atoms in the ethylene interact with the Ni substrate strongly, while the C–Ni interaction is rather weak. These facts imply that the H–Ni interaction plays an important role in the formation of the adsorption structure.

Acknowledgement

The authors are pleased to acknowledge the support of the National Natural Science Foundation of China and the Science Foundation of Zhejiang province.

References

[1] N. Rosch and T.N. Rhodin, Phys. Rev. Lett. 32 (1974) 1189.
[2] F. Zaera and R.B. Hall, Surf. Sci. 180 (1987) 1.
[3] F. Zaera and R.B. Hall, J. Phys. Chem. 91 (1987) 4318.
[4] R.B. Hall, S.J. Bares, A.M. DeSantolo and F. Zaera, J. Vac. Sci. Technol. A 4 (1986) 1493.
[5] F. Zaera, D.A. Fischer, R.G. Carr and J.L. Gland, J. Chem. Phys. 89 (1988) 5335.
[6] J.C. Tang, X.S. Feng, J.F. Shen, T. Fujikawa and T. Okazawa, Phys. Rev. B 44 (1991) 13018.
[7] J. Tang, in: *The Structure of Surface II*, eds. J.F. Van der Veen and M.A. Van Hove (Springer, Berlin, 1988).
[8] J.C. Tang, J.F. Shen and Y.B. Chen, Surf. Sci. Lett. 244 (1991) L125.
[9] J. Stohr, F. Sette and A.J. Johnson, Phys. Rev. Lett. 53 (1984) 1684.
[10] S.Y. Tong, A. Maldonado, C.H. Li and M.A. Van Hove, Surf. Sci. 94 (1980) 73.