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XPS Studies of CO Adsorption on Polycrystalline Nickel Surface

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The chemisorption of CO molecules on polycrystalline nickel surface has been studied by investigating the resulting chemisorbed species with the X-ray photoelectron spectroscopy at temperatures between 300K through 433K. It is found that the adsorbed CO molecules are dissociated by the simple C-O bond cleavage as well as by the disproportionation reaction at temperatures above 373K. The former type dissociation is more favored at low coverages and at elevated temperatures. The isotherms of CO chemisorption are obtained from the xps intensities of C 1s peaks, and then the activation energy of the dissociative adsorption is estimated as a function of the CO exposure. These activation energies are extrapolated to zero coverage to obtain the activation energy of chemisorption in which thermal C-O bond cleavage takes place. The value obtained is 38.1 kJ/mol.

Introduction

The chemisorption of carbon monoxide on transition metal surfaces has been extensively studied in connection with many catalysis, such as the Fischer-Tropsch synthesis and the exhaust gas purification.[1-3] It is generally accepted that elements to the left of a line connecting Co and W on the periodic table display dissociative adsorption while elements of the other side display molecular adsorption.[4-7] Nickel is, however, found to be exceptional in that it adsorbs CO molecule dissociatively at moderately high temperatures (T> 500K),[8-14] while it adsorbs CO undissociatively at low temperatures (T≤300K).[15-20]

Benziger et al.[18] reported the result of molecularly adsorbed CO on the on-top site as well as on the bridged-site of nickel surface in the temperature range of 190K through 280K with the temperature programmed reflection absorption infra-red spectroscopy. Blyholder[21] proposed a molecular or-

bital model for the CO chemisorption bond in order to explain their IR spectra. Barber et al.[19] also observed the similar type of molecular adsorption with SIMS in the temperature range of 77K through 390K, and partial dissociation of adsorbed CO molecules when the temperature is raised above 390K. According to thermal desorption measurements, however, the molecularly adsorbed CO is stable up to ca 450K.[8,16,20] For example, Ertl et al.[20] observed a single non-dissociative TDS peak at 440K from Ni(111) surface when the CO coverage is less than 0.33, and an extra shoulder on the lower temperature side of this single peak when the coverage exceeds 0.33; Wedler et al.[16] observed a similar result with three non-dissociative peaks at 170K, 310-360K, and 460-490K, respectively.

The adsorbed CO molecule becomes unstable and dissociates to leave atomic carbon and oxygen species on the substrate surface if temperature is elevated. The dissociation is known to take place by a disproportionation reaction and/

or by a simple thermal dissociation with C-O bond cleavage. The former reaction can be confirmed by the detection of CO_2 formed.[1,2,22-24] Baker *et al.*[22] observed the disproportionation reaction at 460K, while Gravelle *et al.*[23] observed it at 350K. There are, of course, many other experimental reports which support the disproportionation reaction, though the temperature ranges reported vary with the reporters.[25-28] There are, on the other hand, no less amount of reports which support the thermal dissociation of C-O bond cleavage.[13,14,19,29,30] According to Rosei *et al.*[29] CO molecules adsorbed on Ni(110) surface undergo thermal dissociation at $470K < T < 620K$ and $10^{-6} < P_{CO} < 3 \times 10^{-5}$ torr with the activation energy of 23 kcal/mol. The resulting atomic oxygen species may combine with CO to form CO_2. Tracy *et al.*[8] obtained a more direct evidence for the thermal dissociation of adsorbed CO molecules at 475K, and above. Joyner *et al.*[13] and Eastman *et al.*[14] also reported evidences for the thermal dissociation. The dissociation may take place also by an interaction of electron beams.[12,31,32] This possibility should be taken into account especially when the dissociation is studied with instruments which utilize electron beams. It is really confusing to understand the nature of the CO dissociation.

In this work, various chemical species resulting from CO chemisorption on polycrystalline nickel surface are assayed systematically by investigating xps spectra of carbon, oxygen, and nickel at various temperatures between 300K through 433K and at various CO exposures. The concentration of these species are, then, determined from the respective xps peak area. The dissociation mechanism of CO molecules on the nickel surface, as well as the conditions under which the dissociation takes place are studied. The activation energy for the dissociation is also determined.

Experimental

The ultra high vacuum xps system (ESCA 750, Shimadzu Co., Japan) is used to obtain xps spectra of Ni-CO adsorption system. The pressure of the ESCA chamber is monitored with a BA ionization gauge, and the composition of the gas in the chamber is determined with a quadrupole mass spectrometer (VG. Ltd., Masstorr FX., England). The temperature of the adsorbent is raised, if required, at the rate of about 1K/sec, which is monitored with a chromel-alumel thermocouple.

Polycrystalline nickel of purity 99.95% (Fruchi Chem. Co., Japan) is used as the adsorbent, and carbon monoxide of purity 99.95% (Seitetsu Chem. Co., Japan) as the adsorbate. The adsorbent treatment and the calibration of binding energy spectra are carried out quite similarly as described in the earlier paper.[33]

Results and Discussion

A. XPS Spectra

In the present work, polycrystalline nickel surface is exposed to carbon monoxide gas at $7 \times 10^{-9} - 5 \times 10^{-6}$ torr after the necessary surface treatment. The length of exposing time is controlled to give desired exposures. The xps spectra of the resulting nickel surface have been studied for O 1s, C 1s, and Ni $2p_{3/2}$ as well as Ni valence band at various temperatures between 300K through 433K.

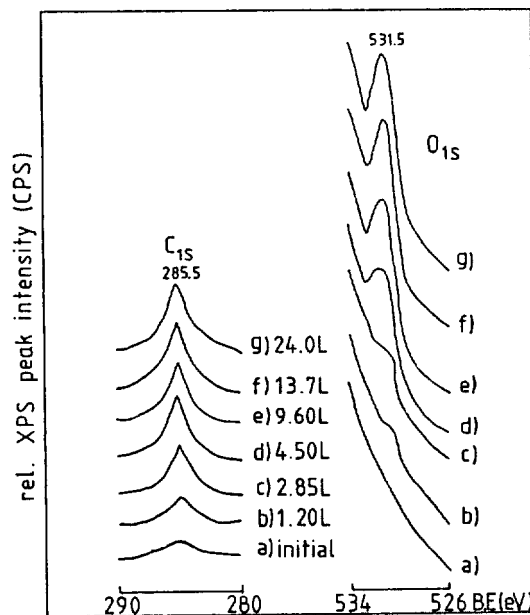**1. The spectra at 300K** The spectra of O 1s and C 1s obtained at 300K with varying CO exposure are shown in

Figure 1. The xps spectra of O 1s and C 1s at 300K with varying CO exposure.
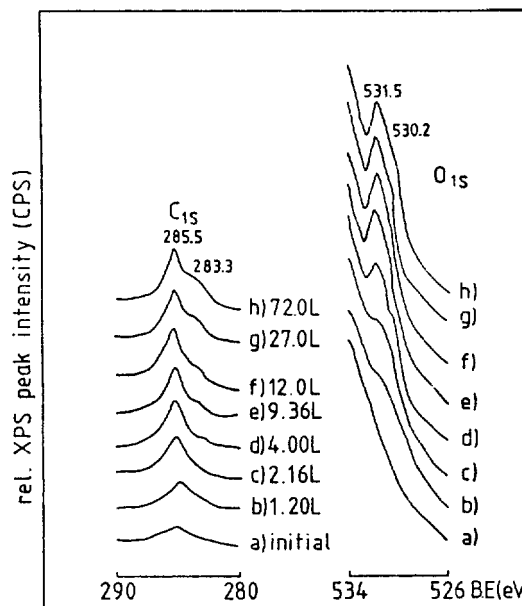

Figure 2. The xps spectra of C 1s and O 1s at 325K with varying CO exposure.

Figure 1. The C 1s and O 1s peaks at 285.5eV and 531.5eV, respectively, are known to be due to the molecularly adsorbed CO. Their intensities increase with the CO exposure until they are saturated at ca 4.5L (1L = 1×10^{-6} torr sec). Ertl *et al.*[9,20] obtained a similar result previously. The Ni $2p_{3/2}$ peak at 852.8eV is also investigated at this temperature, and it is found that the intensity decreases without any binding energy shift with the increase in CO exposure. The valence band spectrum of nickel at 0.5eV shows a similar feature. However, three shoulders are gradually developed on this valence band peak at 7.8, 10.6, and 13.1eV, respectively, with the increase in exposure. These shoulders are due to 5σ, 1π, and 4σ of adsorbed CO molecules, respectively.[13,34] All of the above observations indicate that the nickel surface ad-
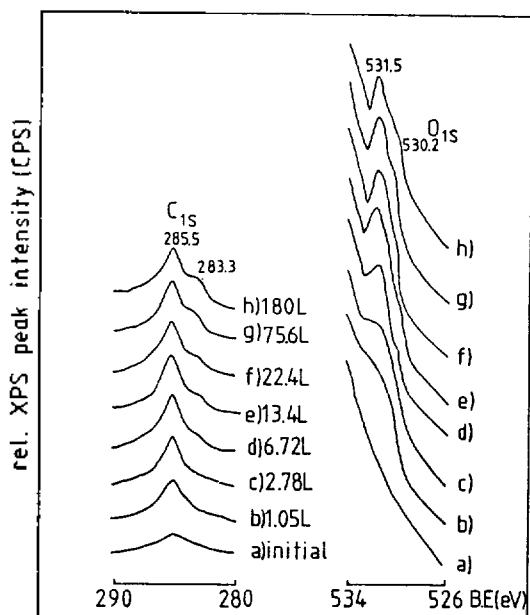
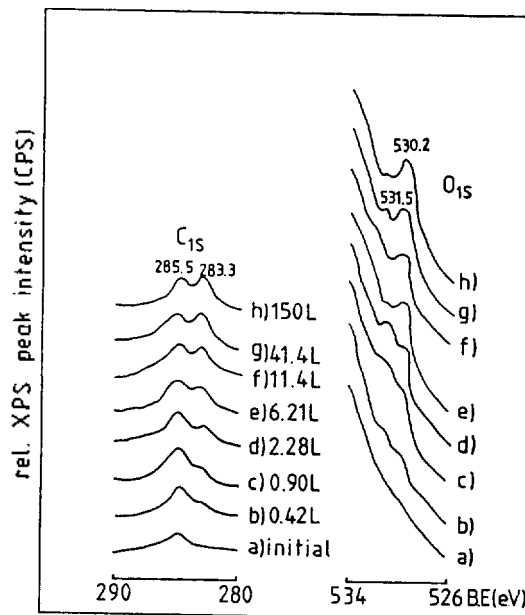**Figure 3.** The xps spectra of C 1s and O 1s at 350K with varying CO exposure.

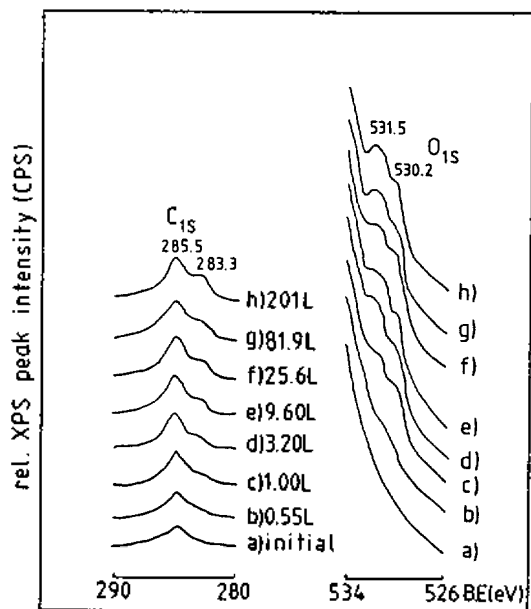**Figure 5.** The xps spectra of C 1s and O 1s at 383K with varying CO exposure.

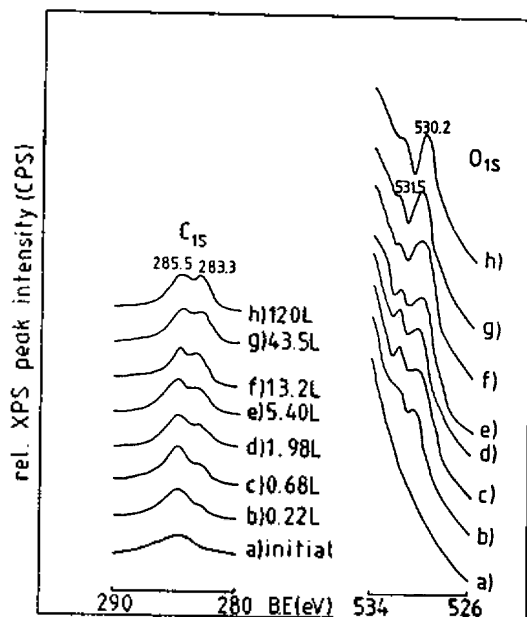**Figure 4.** The xps spectra of C 1s and O 1s at 373K with varying CO exposure.

Figure 6. The xps spectra of C 1s and O 1s at 393K with varying CO exposure.

sorbs CO molecularly at this temperature.

2. The spectra at 325, 350, and 373K The spectra at these three temperatures are much similar to each other as shown in Figures 2,3, and 4. Molecularly adsorbed CO maintains intense peaks of C 1s and O 1s at 285.5eV and 531.5eV, respectively. However, it can be seen that shoulders develope steadily with the increase in exposure as temperature is raised. These shoulders are due to atomic (carbidic) carbon and atomic oxygen species, respectively. These species may result from either the dissociation of the CO molecules or the diffusion out of the adsorbent bulk. For the clarification, the adsorbent is exposed to CO for 4.50L at 350K, and then the intensities of C 1s and O 1s peaks are monitored for the following 3 hours. There was little change. It is certain that

both the atomic species result from the dissociation of CO molecules, and that the dissociation does not take place at the initial stage of exposure. When the adsorbent was further exposed to CO gas at an increased pressure, the shoulder peaks developed further and a marked increase in partial pressure of CO_2 was observed in the gas phase. It is concluded that the dissociation take place disproportionately if the gas pressure is increased at this temperature. The exposure at which the dissociation take place decreases with the increase in temperature; 9.36L at 325K: 6.72L at 350K: and 3.2L at 373K.

3. The spectra at 383K and 393K The spectra of C 1s and O 1s at 383K and 393K are shown in Figures 5 and 6. It can be seen that the peaks due to the dissociated species
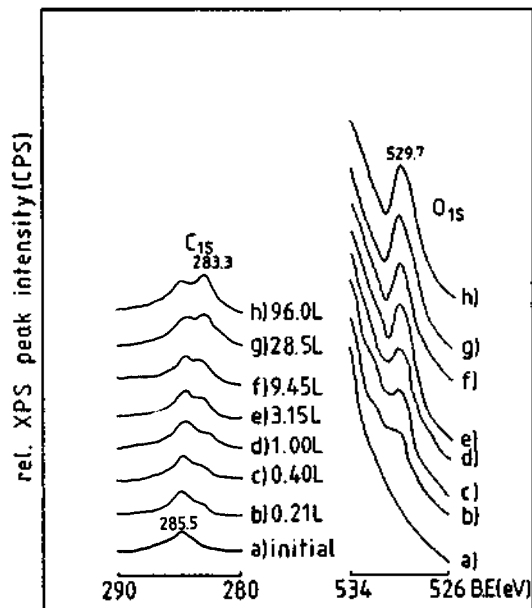
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Figure 7. The xps spectra of C 1s and O 1s at 413K with varying CO exposure.

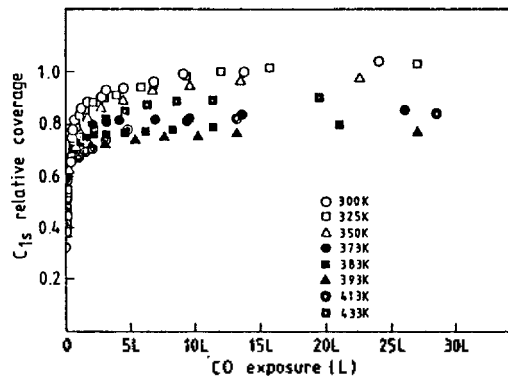**Figure 8.** The xps spectra of C 1s and O 1s at 433K with varying CO exposure.

Figure 9. Adsorption isotherms of CO on polycrystalline nickel surface at various temperatures between 300K and 433K.

thermal dissociation if the temperature is raised. In fact, this thermal dissociation has been observed by many authors,[8,19,29,30] though their reported lower temperature bound for this dissociation varies widely between 390K and 450K. It has been known, also, that this lower temperature bound can be brought down by the incorporation of defects or steps on the surface.[10,11,13,14]

4. The spectra at 413K and 433K The spectra of C 1s and O 1s at 413K and 433K are shown in Figures 7 and 8. The spectra at these temperatures are quite different from those obtained at lower temperatures. The C 1s peaks and the intense O 1s peak at 529.7eV indicate that the CO molecules adsorbed are mostly dissociated even at the initial stage exposure. Meanwhile, the partial pressure of CO_2 was found to be relatively low. It is concluded, accordingly, that CO molecules are dissociated mostly by the simple cleavage of C-O bond at this temperature range.[13,14]

The C 1s peak shoulder at 284.5eV in these figures is due to the graphitic carbon which is probably converted from the carbidic carbon due to the increased temperature.[18,19,25,35] In support of this interpretation, the shoulder becomes more distinct at higher temperature, namely 433K. The shift of the O 1s peak from 530.2eV to 529.7eV is an indication of the initiation of NiO formation.

The valence band spectral region is also investigated at 433K. It is found that the peaks due to the CO valence electrons which is observed at 300K are mostly displaced by a clear O 2p shoulder at 4.9eV. This indicated, again, that the CO molecules are mostly adsorbed dissociatively to leave relatively free atomic oxygen species.

B. The Activation Energy of CO Dissociation

The total C 1s peak areas are measured, and then calibrated to the Ni $2p_{3/2}$ area at the initial exposure stage. This area, being proportional to the CO adsorption on a constant Ni surface area, is plotted against the exposure to obtain adsorption isotherms of the Ni-CO system. The results are shown in Figure 9. The area on the ordinate of this figure are taken relatively. Quite similar CO adsorption isotherms are obtained from the measurement of the total O 1s peak area. All the isotherms follow the Langmuir type isotherms. According to this figure, the isotherms become saturated with less amount of adsorption with the increase in temperature. The isotherms are, also, saturated more easily at less CO exposure with the increase in temperature. It is not certain how much fraction of the surface is covered with the adsorbate at

displace the peaks due to the molecularly adsorbed species, though the latter peaks remain persistently up to the very high exposure. Carbon dioxide was detected in the gas phase, though its partial pressure was not high enough to account for the increase in this peak intensity of the dissociated carbon species. The results are interpreted as due to the concurrently occurring thermal cleavage of C-O bond on the adsorbent surface in addition to the disproportionation reaction. Rabo et al.[24] reported a similar observation of concurrently occurring two modes of dissociation, though the temperature range they have observed the result is a little bit higher, being 437K through 573K. It is quite convincible that CO molecules adsorbed on nickel surface are liable to the

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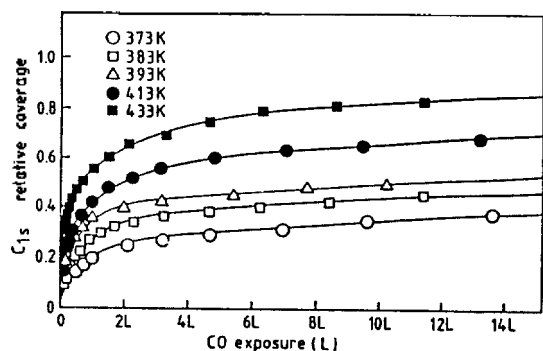
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Figure 10. Adsorption isotherms of dissociative adsorption of CO molecules on polycrystalline nickel surface at various temperatures between 373K and 433K.
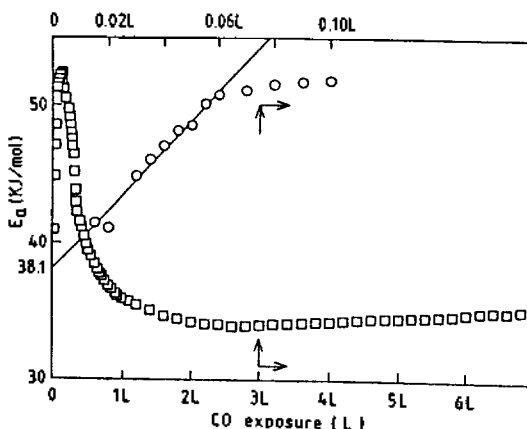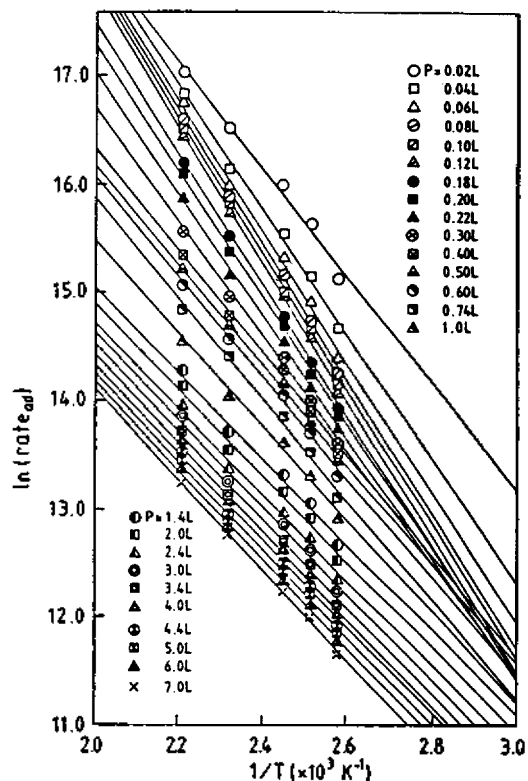

Figure 11. Arrhenius plots for the dissociative CO adsorption at various exposures.

the saturated state. It is 0.69 according to Tracy[8] with Ni(100) surface, and 0.53-0.57 according to Ertl *et al.*[9,20] in case of Ni(111) surface. Instead of estimating the absolute fraction and hence the absolute amount of adsorption on a unit surface area, the saturating amount at 300K is taken arbitrarily as unity for convenience in this work.

The C 1s spectra are deconvoluted to obtain the carbidic carbon peak (283.3eV) area, and the results are plotted against the CO exposure after the calibration to the initial Ni $2p_{3/2}$ area as above. Resultant isotherms are shown in Figure 10. The relative rate of dissociative adsorption of CO molecules are calculated from the slope of these isotherms taking the saturation coverage at 300K as a standard unit coverage. The Arrhenius plots are, then, made to obtain the activation energy of the dissociative CO adsorption. The results are shown in Figure 11. It should be noted that the proportionality constant between the absolute and the relative rates of

Figure 12. Activation energy of the dissociative CO adsorption.

adsorption cancels out in the Arrhenius plot. The resulting activation energy, as shown in Figure 12, increases with the exposure, reaching the maximum at ca 0.1L.

The activation energy extrapolated to the zero coverage is certainly the one for the simple dissociative adsorption. It is found to be 38.1 kJ/mol. This value is very close to those obtained by others. Benziger *et al.*[18] reported 15 kJ/mol, Keim *et al.*[31] 55.9 kJ/mol, and Ponec *et al.*[5] 46 kJ/mol for this activation energy. It is quite probable that the dissociation products on the surface hinder the further adsorption thereby increasing activation energy with the increase in exposure. After passing through the maximum, the activation energy resumes again a steady value. This suggests the dissociation might proceed through a different way at high coverages. It is not quite sure with this experiment alone whether the latter steady value should be the one for the disproportionation reaction.

Conclusion

1. The chemisorption of CO on polycrystalline nickel surface follows two different patterns, one undissociative and the other dissociative with the temperature borderline of ca 373K. CO molecules are adsorbed molecularly on polycrystalline nickel surface at the initial stage of adsorption in the low temperature range (T<373K). The adsorbed molecules are fairly stable, and can dissociate disproportionately to a very small extent upon the increase of the adsorbate gas pressure. It is uncertain, however, whether the dissociation is taking place between the two adsorbed molecules or by the bombardment of a gas molecule on the adsorbed one.

2. The adsorbed molecules dissociate by the thermal dissociation of C-O bond cleavage in addition to the disproportionation reaction when the temperature is increased above 383K. It is found that the former dissociation predominates gradually over the latter as the temperature is increased. The thermal dissociation through the molecularly adsorbed precursor state has been reported by many authors.[36-38] However the temperature range in which the dissociation takes place vary to some extent with the authors.

3. Two activation energy values are obtained in this work. The activation energy extrapolated to the zero coverage is the activation energy of chemisorption in which thermal C-O bond cleavage takes place. It is 38.1 kJ/mol. The other one, reached steady value at high coverage over 3L, is not clear if it stands for the disproportionation reaction.

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