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Oxygen Species on the Surface of La_2O_3/CaO and Its Role in the Oxidative Coupling of Methane

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The paramagnetic superoxide ions detectable by EPR can be generated on La_2O_3/CaO by oxygen adsorption at room temperature or at 1053 K. In both cases, the O_2^- ions are all located on the catalyst surface. They are unstable at >473 K in the absence of gas-phase O_2. The reaction of methane with the catalyst surface leading to the decrease of the intensity of the O_2^- signal implies that the O_2^- is the active oxygen species or the precursor of the active oxygen species for the activation of methane. The adsorption of CO_2 and its effect on the O_2^- species are also investigated by EPR, as well as by FTIR and TPD. © 1994 Academic Press, Inc.

INTRODUCTION

The conception of the heterogeneous–homogeneous nature of methane oxidative coupling reaction is now beyond any doubt. Different viewpoints concerning the reaction mechanism are centered mainly on the participation of different oxygen species in this process, and recent studies focus on the characterization of active oxygen species. Following the creative works of Keller and Bhasin (1), many catalyst systems for methane oxidative coupling have been developed (2), and O_2^- (3), $O_2^{=}$ (4), O^- (5), and nucleophilic ions $O^{=}$ (6) have been regarded as the probable active oxygen species involved in the activation of methane. In the case of alkali-doped magnesium oxide catalysts, which have been extensively investigated by Lunsford and his colleagues, the $[M^+O^-]$ ion pairs were suggested to be active sites by which the intermediate radicals $CH_3^{\cdot}$ were generated through hydrogen atom abstraction from methane. Nevertheless, in the case of pure alkaline earth or rare earth oxides or their composition compounds, a promising kind of catalysts which have not only high methane conversion and C_2 hydrocarbon selectivity but also good thermal stability, significant amounts of O_2^- ions, instead of O^- ions, have been found by EPR (7, 8) and XPS (9). It is obvious that the active oxygen species and activation mechanism of methane on these catalysts are different from those on alkali-doped alkaline oxides.

One of the major undesirable by-products of methane oxidative coupling is carbon dioxide which is present in significant concentrations under reaction conditions. A study of its interaction with the active sites on the catalyst surface and its effect on the adsorption of oxygen is therefore of interest. The present work is an attempt to characterize directly the active oxygen species on the surface of a practical La_2O_3/CaO catalyst, which is of good activity (C_{CH_4} = 21.2%) and C_2 selectivity (S_{O_2} = 62.1%), by electron paramagnetic resonance (EPR). FTIR and TPD are employed to study the adsorption of carbon dioxide, and on this basis the effect of carbon dioxide adsorption on the formation of O_2^- ions and the interaction of methane with the catalyst surface at higher temperature are investigated.

EXPERIMENTAL

La_2O_3/CaO catalyst (10 wt%) was prepared by impregnating the powder of $CaCO_3$ in a water solution of $La(NO_3)_3 \cdot 6H_2O$. The paste was dried at 393K overnight and subsequently calcined at 1053 K for 6 h. The XRD result indicates that the phase composition of the resultant material is a mixture of La_2O_3 and CaO.

The sample was pretreated by oxidation in 66.7 kPa O_2 at 1053 K for 0.5 h followed by evacuation at the same temperature for 1 h, prior to the each EPR or FTIR experiment.

The EPR experiment was conducted in a quartz sample tube that is connected with a vacuum system and can be disconnected after the catalyst is pretreated with gases or evacuated and sealed. The EPR spectra were recorded at 77 K with a Varian E-115 EPR spectrometer operating in the X-band.

For the FTIR experiment, the catalyst was pressed into a self-supporting disk and placed in a quartz IR cell with KBr windows. IR spectra were recorded on a Nicolet

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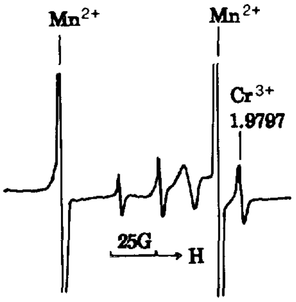

FIG. 1. EPR spectrum of La_2O_3/CaO outgassed at 1053 K for 1 h and subsequently quenched to 77 K under vacuum.

10DX-FT-IR spectrometer in the single beam mode and plotted in transmittance.

The CO_2-TPD experiment was performed in a quartz reactor (O.D. 6 mm) from 298 to1073 K at a linear heating rate of 31 K/min in a flow of helium. Before collection of the TPD data, the catalyst (0.25 g) packed in the quartz reactor was calcined *in situ* at 1053 K for 0.5 h in a flow of helium. The chmisorption of CO_2 at 298 K was carried out by saturating the catalyst by CO_2 and then removing the physically adsorbed carbon dioxide at 298 K by the flow of helium for 1.5 h. The products desorbed in the TPD were detected by a Finnigan-Mat ion trap detector (ITD).

The gases were of the following purities and not further purified before use: O_2(99.99%), CO_2(99.9%), and CH_4(99.9%).

RESULTS

The experiments fell into three categories: (1) the determination of the nature of the oxygen surface species on La_2O_3/CaO; (2) the investigation of CO_2 adsorption on the surface of La_2O_3/CaO catalyst and its interaction with surface oxygen species; and (3) the reaction of methane with the surface oxygen species at higher temperature.

1. Characterization of Surface Oxygen Species

1.1. "Clean" surface. Figure 1 shows the EPR spectrum of the sample outgassed at 1053 K. The two strong bands come from Mn^{2+} ions contained in the sample as impurities. The peak at $g = 1.9797$ results from Cr^{3+} impurities, and we take it as a intrinsic standard for measuring g-values. The other peaks may come from the paramagnetic impurities in the sample. Because they stayed constant before or after the adsorption of oxygen, we differentiated them as a background from the EPR spectra.

1.2. The adsorption of oxygen on the catalyst surface. Exposure of the 1053-K outgassed sample to 13.3 kPa of oxygen at room temperature for 10 min caused the appearance of EPR bands at $g_{xx} = 2.002$, $g_{yy} = 2.008$, and $g_{zz} = 2.043$ (Fig. 2). We designate these bands to be O_2^- superoxide ions formed by adsorption of oxygen on the surface. The g-values are in close agreement with those of O_2^- obtained by Osada *et al.* (10) on a Y_2O_3–CaO catalyst. When the sample was quenched to 77 K or slowly cooled to room temperature after it was oxidized under 66.7 kPa O_2 at 1053 K for 0.5 h, the O_2^- EPR spectrum of Fig. 2 was also obtained. However, the intensity of the O_2^- signal was much stronger than that obtained by O_2 adsorption at room temperature. It should be noted that the intensity of the O_2^- signal obtained by quenching is nearly identical to that obtained by slow cooling. These results seem to imply that the O_2^- ions could be formed at higher temperature in the presence of gas-phase oxygen and were not transformed during quenching or cooling, or the change was too fast to be trapped even by rapid quenching. Figure 3 shows the thermal stability of the O_2^- ions under vacuum. They were thermally stable at room temperature for a long time. But it was found that the O_2^- EPR signal decreased slightly at 373 K and almost completely disappeared at 473 K within 5 min. Yu (11) observed by O_2-TPD on a La_2O_3/CaO catalyst that the desorption of O_2 occurred at 552 K. Therefore, the disappearance of the O_2^- EPR signal in this case at 473 K may be due to the desorption of O_2 from the surface while evacuating. The EPR signal of the O_2^- ions could not be observed at 77 K in the presence of gas-phase O_2, indicating that the O_2^- ions were located on the catalyst surface. The disappearance of the O_2^- signal results from the dipole-exchange interaction between paramagnetic molecular oxygen and the surface O_2^- ions, which leads to the broadening of the EPR signal to beyond detection.

Because the superhyperfine structure, which could be

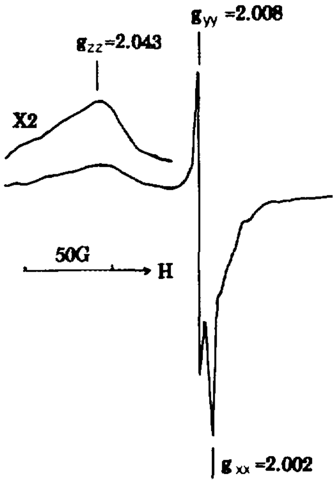

FIG. 2. EPR spectrum of O_2^- ions obtained by O_2 adsorption on La_2O_3/CaO at room temperature.

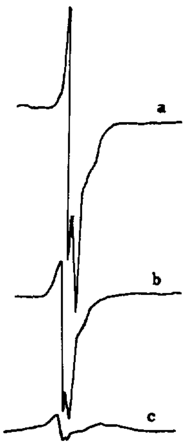

FIG. 3. EPR spectra of O_2^- ions on La_2O_3/CaO heated under vacuum at each of the following temperatures for 5 min: (a) 298 K, (b) 373 K, and (c) 473 K.

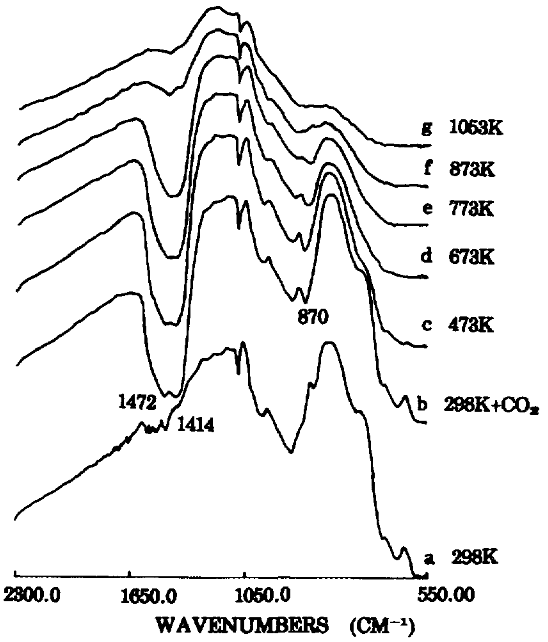

FIG. 4. IR spectra of CO_2 adsorption on La_2O_3/CaO: (a) clean surface at 298 K, (b) exposed to 700 Pa CO_2 for 10 min and then evacuated at 298 K; subsequently heated to (c) 473 K, (d) 673 K, (e) 773 K, (f) 873 K, and (g) 1053 K.

produced from ^{139}La (natural abundance = 99.1%, I = 7/2) was not observed, and the peak of the g_{zz} component is a broad band, it is still not confirmed that the O_2^- ions are absorbed on La^{3+} or Ca^{2+}. In the case of pure La_2O_3 or CaO, which is also a good catalyst for OCM, the O_2^- ions can be formed by the same ways as above, otherwise, their EPR signal intensity is lower compared with those on the composition catalyst La_2O_3/CaO. The promotion of CaO by La_2O_3 may result in the increase of oxygen vacancies and lead to the increase of O_2^- concentration on the composition catalyst eventually, corresponding to the promotion of CH_4 conversion and C_2 selectivity on this catalyst.

2. Surface Carbonate Species and Its Interaction with Superoxide Ions

2.1. The adsorption of CO_2 on the surface of the La_2O_3/CaO catalyst. Exposure of freshly outgassed La_2O_3/CaO to 0.67 kPa of CO_2 at room temperature caused the immediate appearance of infrared bands at 870 cm^{-1} and a doublet with absorbance maxima at 1472 and 1414 cm^{-1} (Fig. 4b). We ascribe these bands to deformation and antisymmetric stretching modes, respectively, of a unidentate carbonate species formed by interaction of CO_2 molecules with basic oxide ions on the surface, in close agreement with those on La_2O_3 (12) and CaO (13). Evacuation at each of several temperatures up to 873 K (Fig. 4) caused a narrowing of the 1472–1414 cm^{-1} doublet, as well as a gradual decrease in intensity of all three $CO_3^{=}$ bands as CO_2 desorbed and evacuation at >973 K was required to remove all evidences of the carbonate species. This behavior of the CO_2–La_2O_3/CaO system is very similar to that of carbonate species on hydroxylated La_2O_3 (12), indicating that hydroxyl groups existed on the surface of La_2O_3/CaO, although no infrared evidence was observed at about 3590 cm^{-1}.

The bands that occur in the 800–1050 cm^{-1} region of the background spectrum (a) in Fig. 4 are caused by crystal lattice vibrations (13). They gradually disappeared with increasing temperature, but they could be recovered completely when the temperature went down to room temperature.

Figure 5 gives the profile of the desorption of CO_2 from the surface of La_2O_3, CaO, and La_2O_3/CaO with the temperature programmed, respectively. The results reveal that the surface basic sites of only intermediate strength

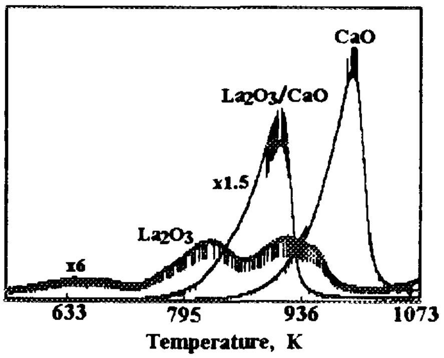

FIG. 5. Thermal desorption spectra of CO_2 for the clean surface of La_2O_3, CaO, and La_2O_3/CaO, respectively.

are observed on the composition catalyst La_2O_3/CaO. The removal of the stronger and weaker basic sites, which exist on the pure La_2O_3 and CaO catalysts, may relate to the increase of O_2^- EPR signal intensity on this catalyst. The carbonate formed on La_2O_3/CaO thermally dissociated at about 916.7 K, in agreement with the IR results described above. Because CO_2 desorptions occurred in nearly the same region on pure La_2O_3 and CaO as on La_2O_3/CaO, it is difficult to decide whether CO_2 adsorbs on the La_2O_3 or CaO component in the case of the CO_2–La_2O_3/CaO system.

2.2. O_2/CO_2 coadsorption. At room temperature, when the freshly outgassed La_2O_3/CaO was exposed to 26.6 kPa of O_2/CO_2 (1 : 1) mixture gas for 10 min, a weaker O_2^- EPR band was detected at 77 K. If the sample was fully carbonated first, the postadsorption of O_2 at room temperature gave no EPR evidence of the formation of O_2^- ions. However, it is very interesting that the postadsorption of CO_2 on the sample containing the O_2^- ions could result in an increase of the O_2^- signal intensity by a factor of 3. This effect was also observed by Louis *et al.* (8) on the surface of La_2O_3. When the sample was quenched under an O_2/CO_2 (360 : 100) mixture from 1053 to 77 K, no O_2^- EPR signal was found. It seems likely that surface O_2^- ions could only be formed on the surface oxygen vacancies, while CO_2 could absorb not only on the surface lattice oxide ions, but also on anion vacancies on the surface. The existence of CO_2 is an obstacle to the adsorption of O_2 on the surface, especially at higher temperature.

3. *The Interaction of Methane with the La_2O_3/CaO Surface at Higher Temperature in the Presence of Gas-Phase Oxygen*

As reported in literature (14), surface superoxides O_2^- did not react with methane at <473 K. Under vacuum, O_2^- ions were unstable at >473 K. Therefore it is difficult to investigate the interaction of methane with the surface O_2^- ions in the absence of gas-phase O_2 at higher temperature. When gas-phase O_2 is present, it is not confirmed yet by *in situ* experiment whether or not the O_2^- ions can exist on the surface at the reaction temperatures (973–1053 K). Perhaps, O_2^- is a precursor of active oxygen species for OCM, when the temperature goes high, it rapidly transforms to O_2^- or O^-. However, the possibility of the existence O_2^- on the surface at higher temperature in the presence of gas-phase O_2 could not be excluded. To ensure that the generating superoxide ions or those as precursor intermediates of active oxygen species will react with methane, we investigated the relationship between reactivity with methane and intensity of the O_2^- signal by the following experiment.

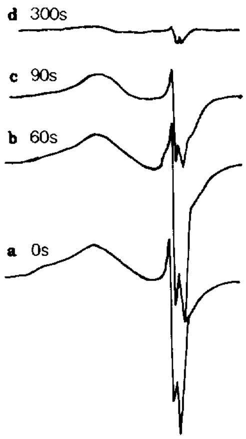

FIG. 6. EPR spectra of O_2^- ions on La_2O_3/CaO treated in the following manner: after evacuating at 1053 K for 1 h and introducing 1.33×10^4 Pa O_2 at the same temperature for 0.5 h, 1.33×10^4 Pa of CH_4/O_2 mixture gas in the ratio 1 : 1 was allowed to diffuse into the sample tube for (a) 0 s, (b) 60 s, (c) 90 s, and (d) 300 s, respectively, followed by rapidly quenching to 77 K.

After the sample tube packed with 0.5 g of 10 wt% La_2O_3/CaO catalyst was evacuated at 1053 K for 1 h, molecular oxygen (13.3 kPa) was passed at the same temperature for 30 min, and the reactor was then sealed by using a stopcock. The volume of the tube containing the catalyst is ca. 6.5 ml. The rest of the space (ca. 205 ml) was filled with a reactant gas mixture of methane and oxygen at the total pressure of 13.3 kPa approximating the pressure of oxygen in the other side. As the stopcock was opened, the reactant diffused to the catalyst and reacted with it. Because the diffusing time of the reactant is a probable factor controlling the reaction, we first examined the relationship between the diffusing time and the intensity of the O_2^- signal with a constant O_2/CH_4 ratio of 1 : 1. After the reactant mixture diffused for 0, 60, 90, and 300 s, respectively, the sample tube was quenched in liquid nitrogen, evacuated, and then the EPR spectrum was run (Fig. 6). It is obvious that the diffusing process is the rate-controlled step and 90-s diffusing of the reactant led to a noticeable decrease of the O_2^- signal in intensity. For the partial pressure of methane in the mixture varied at 0, 2.66, 6.65, and 13.3 kPa with the diffusing time of 90 s, the corresponding intensities of the O_2^- signals obtained by quenching are depicted in Fig. 7. The intensity of the O_2^- signal decreased with increasing partial pressure of methane. In the case of pure methane, the O_2^- signal intensity has been appreciably diminished. In order to rule out the effect of carbon dioxide, which produced by complete oxidation of methane in gas phase or on the surface at 1053 K, the mixture of O_2/CO_2 (1 : 1) was subjected to diffuse to the catalyst in the same way as above. In this case, the intensity of the O_2^- signal was much stronger than that obtained in the case of reactant mixture at an O_2/CH_4 ratio of 1 : 1. These results suggest that

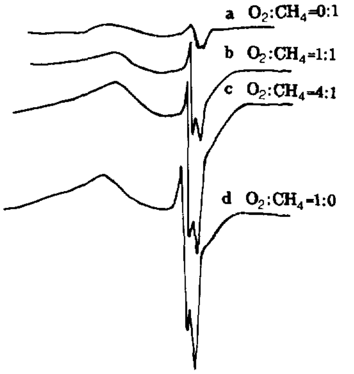

FIG. 7. EPR spectra of O_2^- ions on La_2O_3/CaO treated in the following manner: after evacuating at 1053 K for 1 h and introducing 1.33×10^4 Pa O_2 at the same temperature for 0.5 h, 1.33×10^4 Pa of CH_4/O_2 mixture gas in the ratios (a) $O_2:CH_4 = 0:1$, (b) $O_2:CH_4 = 1:1$, (c) $O_2:CH_4 = 4:1$; and (d) $O_2:CH_4 = 1:0$, respectively, was allowed to diffuse into the sample tube for 90 s followed by rapidly quenching to 77 K.

methane molecules reacted with O_2^- or other oxygen species, such as $O_2^=$ or O^-, formed from O_2^- at higher temperature accounting for the elimination of O_2^- EPR signals.

DISCUSSION

1. Mechanism of O_2^- Formation

The superhyperfine structure of the O_2^- EPR signal, observed by Wang and Lunsford (7) on La_2O_3 and by Yang *et al.* (15) on La_2O_3/MgO indicates that La^{3+} is the adsorption site for O_2^-. In addition, our results have shown that the O_2^- species on La_2O_3/CaO are located on the surface. Their stabilization sites probably arise from the creation of oxygen vacancies, owing to oxygen mobility during the temperature treatment. The width of the g_{zz} component of the O_2^- EPR signal and the relative breadth of the 1414–1472 cm^{-1} pair reflect the heterogeneity of the surface.

The O_2 adsorption is accompanied by an electron transfer towards O_2. Because lanthanum and calcium are not multivalent, they are not the origins of the electrons. Dubois and Cameron (16) have suggested a correlation between the electron capture by adsorbed O_2 and the electrical conductivity of the solid and, in particular, the semiconductivity. According to the literature, La_2O_3 exhibits electrical conductivities with some contribution from ionic conductivity and major contribution from *p*-type electronic conductivity at temperature in the 673–1273 K range under oxygen (17, 18). The formation of O_2^- ions on the surface of La_2O_3/CaO at higher temperature can probably be elucidated by its *p*-type semiconductivity. The valence band of the semiconductor may be the resource of the electrons. However, this cannot be invoked to explain the O_2^- formation at room temperature. Although the existence of F centers were not observed by EPR due to some unknown reasons, we believe that they could be formed on the freshly outgassed catalyst. Indeed, we detected the EPR signal of F centers at $g = 2.005$ on pure CaO and at $g_\perp = 2.013$, $g_\parallel = 1.951$ on Li/ZnO catalyst (19). The F centers can be formed when the oxygen vacancies capture electrons, which could be provided by the valence band of the *p*-type semiconductor at high temperature. When the oxygen was absorbed at room temperature, the electrons of F centers transferred to O_2 and O_2^- ions resulted.

2. Adsorption of CO_2 and Its Effect on the O_2^- Species

Because the hydroxyl groups are firmly bound to the surface of the La_2O_3/CaO and their complete removal by heating is too difficult, they might be present in a quite significant concentration on the surface outgassed for only 1 h. Therefore, only unidentate carbonates were formed whtn CO_2 was absorbed. No infrared evidence of bidentate carbonates was found. These results were in accordance with the adsorption of CO_2 on the hydroxylated La_2O_3 (12). The superoxide species, which are regarded to be stabilized on the surface oxygen vacancies, were isolated by the unidentate carbonates formed by interaction of CO_2 molecules with basic oxide ions $O^=$, leading to the elimination of the dipole-exchange broadening between the oxygen species closed each other, and consequently the increase of the intensity of the O_2^- EPR signal. The lack of the formation of O_2^- ions on the fully carbonated surface at room temperature is probably due to the steric hindrance and damage of the F centers by the adsorption of CO_2. When the freshly outgassed catalyst was exposed to the mixture of O_2 and CO_2, O_2 has a privilege in competing for diffusing to and being absorbed on the surface because of its smaller molecular weight and stronger electronic negativity, and therefore the weaker O_2^- signal was observed.

3. The Performance of O_2^- Ions in the Oxidative Coupling of Methane

In general, at <473 K, a superoxide ion does not as effectively extract a hydrogen atom from methane as do othe monovalent oxygen ions, i.e., O^-, O_3^-. Their activity is known to decrease in the order of $O^- > O_3^- > O_2^-$ (14, 20, 21). Lin *et al.* have suggested that the O_2^- on La_2O_3 can activate a methane molecule (3), but did not rule out the possibility that a transient O^- species which is formed via O_2^- may play a role in generating a methyl radical. It has also been suggested by Otsuka *et al.* (22), Dubois *et al.* (23), and Louis *et al.* (8) that peroxides, which could be produced via O_2^- in the presence of surface carbonates as

$$CO_3^= + O_2^- \rightleftharpoons CO_4^= + O^- \text{ and } 2O^- \rightleftharpoons O_2^= \qquad [1]$$

would be the active oxygen species. However, the presence of O^- or $O_2^=$ is not yet confirmed by experiment. The reaction of methane with the catalyst surface leading to the decrease of the O_2^- signal indicates that the active oxygen species for the methane activation is associated with O_2^- ions. O_2^- is probably a precursor of the active oxygen species and there is an equilibrium between them. On the other hand, the formation of O_2^- ions can be considered as a parameter for evaluating the ability of the catalyst surface to activate oxygen. Further work on the O_2^- ions formed on catalysts for oxidative coupling of methane should be interesting.

CONCLUSION

The superoxide O_2^- on La_2O_3/CaO can be formed either by cooling the sample from 1053 K to room temperature under O_2 or by adsorption of O_2 on the catalyst at room temperature. The O_2^- species are probably located in the surface oxygen vacancies in the coordination sphere of cations, created during thermal treatment.

The adsorption of CO_2 on La_2O_3/CaO at room temperature leads to the formation of unidentate carbonates. They can inhibit the formation of O_2^- as O_2 absorbs, while the postadsorption of CO_2 increases the intensity of O_2^- formed by preadsorption of O_2.

The reaction of methane with the catalyst surface at the elevated temperature results in the decrease of the O_2^- EPR signal intensity. Superoxide O_2^- or other oxygen species, such as $O_2^=$ or O^-, formed from O_2^- is a probable active oxygen species for the activation of methane. If the latter is true, it seems likely that there is an equilibrium between O_2^- and the active oxygen species for OCM, such as $O_2^=$ or O^-.

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