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NOTES

Dynamic ESR Study of Oxygen Chemisorption on TiO_2-Based Catalysts

The process of methane oxidative coupling (MOC) is promising for the development of methane-based industries. Many papers exist on the preparation of catalysts and the mechanism of the reaction (*1*, *2*). In the MOC reaction, methane is supposed to be activated through abstraction of an H atom from CH_4 by an active oxygen species (*2*). Lunsford and his co-workers (*3*) detected (Li^+O^-) centers in an Li/MgO catalyst by ESR and proposed that O^- species were responsible for the activation of methane over Li/MgO. For TiO_2-based catalysts, when TiO_2 alone was used as a catalyst, whether as anatase or rutile, little or no coupling activity was observed (*4–6*). However, the addition of Li drastically improved the selectivity to C2 hydrocarbons, with optimum effectiveness at 10 wt% (*6*) or 16.2 wt% (*7*) Li. At selected conditions, the selectivity to C2 hydrocarbons and the conversion of methane reached 75.3 and 13.5%, respectively, for a 10-wt% Li/TiO_2 catalyst (*6*). Therefore, it is interesting to study the role of Li and other promoters in the MOC reaction. In this paper we report the results of a dynamic ESR study for O_2 chemisorption on model TiO_2-based catalysts to elucidate the active species which exist on the surface of catalysts.

The TiO_2 used in this study was 40–60 mesh AR grade (purity > 99.99%) from the Chemical Company of Tianjin and had a BET specific surface area of 51.1 m^2/g. Before use, TiO_2 was calcined at 1123 K for 3.5 hr and the rutile phase determined using XRD. $Li_2SO_4 \cdot H_2O$ and $La(NO_3)_3 \cdot nH_2O$ AR grade from the Chemical Company of Shanghai were used as the Li^+ and La^{3+} ion sources, respectively. The samples were prepared by adding an Li or La salt solution in certain proportions to TiO_2, stirring for 2 hr, leaving to stand for 24 hr, and then evaporating the solvent at 473 K and calcining the slurry at 1123 K for 4 hr.

The ESR spectra were recorded on a Bruker ER 200D-SRC ESR spectrometer. The g values were determined relative to the DPPH standard with $g = 2.0037$. The samples were placed in a test tube and evacuated at 773 K for 4 hr, then cooled to room temperature without exposure to air. The spectra were recorded from 295 to 105 K before O_2 admission. After the temperature of the samples was returned to room temperature, O_2 was admitted to the tube to 10 Torr (1 Torr = 133.3 Nm^{-2}) pressure for an ESR measurement from 295 to 105 K. All spectra, except where otherwise indicated, were recorded with the gain set at 4×10^4. The O_2 used was of ultrahigh purity (>99.99%) and dehydroxylated before being admitted to the test tube. The catalytic activity was tested in a quartz microflow reactor at 1073 K. The catalyst charge was 0.5 g. The reactant was a mixture of CH_4 (>99.99%), O_2 (>99.5%), and N_2 (>99.5%). The products were detected by a GC equipped with a TCD. The conversion of methane and the selectivity to C_2H_4 and C_2H_6 were calculated using the carbon-balance method.

After TiO_2 was pre-outgassed at 773 K, there were two distinct peaks with $g = 2.003$ (peak 1) and $g = 1.961$ (peak 2) as shown in Fig. 1a. Peak 1 was sharp and symmetrical in shape at 295 K and remained unchanged

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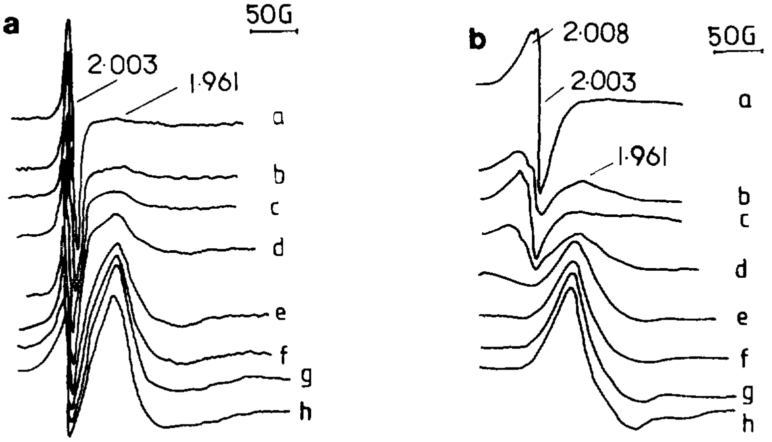

FIG. 1. ESR spectra of O_2 chemisorption on rutile TiO_2 (a) before O_2 admission and (b) with 10 Torr O_2: a, 295 K; b, 273 K; c, 250 K; d, 200 K; e, 150 K; f, 130 K; g, 110 K; and h, 105 K.

to 200 K. Peak 2 was wide and asymmetrical at 105 K, but was not detected at 295 K, and its height increased as the temperature was decreased. On adsorption of O_2, a third peak (peak 3) with $g = 2.008$ appeared beside peak 1 and peak 2, as shown in Fig. 1b. Peak 3 overlapped with peak 1, but it could be identified in the spectra. Peak 1 and peak 3 decayed as the temperature was decreased and vanished at 150 K. The decay rate of peak 1 is obviously higher than that of peak 3. The behaviour of peak 2 was the same as in the absence of O_2.

A La promoter greatly increased the height of peak 2 at all temperatures before O_2 admission (Fig. 2a). O_2 adsorption resulted in the decay of peak 1 and peak 2 compared with those before O_2 admission (Fig. 2b), but the height of peak 2 was of the same order of magnitude as for TiO_2, which implied that the effect of La was not considerable.

The effect of a Li promoter on the ESR spectra of TiO_2 before and after O_2 admission is shown in Fig. 3. Before O_2 adsorption, peak 1 in Li/TiO_2 was considerably reduced compared with that in TiO_2. Peak 2 could not be observed, but some new peaks were detected below 130 K with $g1 = 2.001$, $g2 = 1.985$, $g3 = 1.937$, $g4 = 1.905$, $g5 = 1.834$, and $g6 = 1.762$. After O_2 admission, these peaks appeared at 200 K and expanded when compared to those without O_2. Peak 1 decayed as the temperature was decreased and vanished approximately at 200 K.

The catalytic reactivities of model TiO_2-based catalysts for the MOC reaction are listed in Table 1. The products were mainly C_2H_4, C_2H_6, CO_2, and H_2O. CO and hydrocarbons larger than C_3H_8 were not detectable under our test conditions. As can be seen from Table 1, on TiO_2 the conversion of CH_4 and the selectivity to C2 hydrocarbons was poor; La-doped TiO_2 showed some modification; however, Li-doped TiO_2 showed a drastic improvement in the selectivity to C2 hydrocarbons from 13.8 to 75.3%. The selectivity to ethylene for Li/TiO_2 increased from 7.5% (TiO_2) or 12.7% (La/TiO_2) to 58.4%. More tests over the active catalyst Li/TiO_2 and other catalysts were carried out and have been previously reported (*6*).

A perfect rutile crystal of TiO_2 is tetragonal. Six O atoms are at the interstitials of a distorted octahedron and Ti atoms are at the corners of the rutile primitive cell (*8*), but on evacuation at high temperature TiO_2 loses part of O atom from the surface producing Ti^{4+} which then dissociates (*9*, *10*):

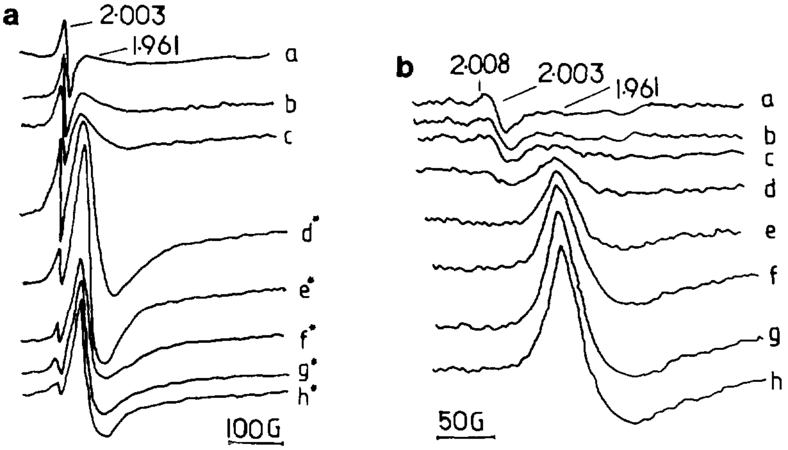

FIG. 2. ESR spectra of O_2 chemisorption on La/TiO_2. (a) before O_2 admission; (b) with 10 Torr O_2: a, 295 K; b, 273 K; c, 250 K; d, 200 K; e, 150 K; f, 130 K; g, 110 K; and h, 105 K. Curves d* and e* were recorded with gain at 1.25 × 10^3, f*, g*, and h* were at 4 × 10^3, and all other tests were at 4 × 10^4.

$$Ti^{4+} \rightarrow Ti^{3+} + \text{Hole}. \quad (1)$$

Ti^{3+} gives an ESR signal at $g = 1.959$, noted as Ti^{3+} (I); the hole captures a free electron to form a localized electron center, known as the F-center (*10*), which gives an ESR signal at $g = 2.002$. Therefore after being evacuated at high temperature, TiO_2 formed two ESR active centers, the F-center and Ti^{3+}. Both centers could be seen in Fig. 1a as peak 1 and peak 2. The Ti^{3+} signal was not observed at room temperature because of spin–lattice relaxation and electron rapid movement from one Ti^{3+} ion to another (*10*). However, as the temperature was decreased, it was observed that the Ti^{3+} signal would gradually increase.

On O_2 admission, the F-center signal decayed, which was in agreement with its assignment as the surface center, and implied that O_2 reacted with the F-center to form a kind of oxygen species. At the same time the O_2 did not react with Ti^{3+} (I) because the Ti^{3+} (I) signal (peak 2) behaved the same

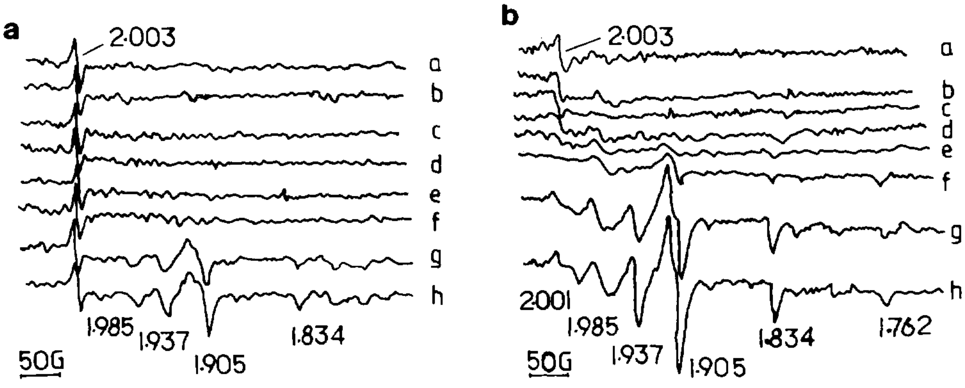

FIG. 3. ESR spectra of O_2 chemisorption on Li/TiO_2 (a) before O_2 admission and (b) with 10 Torr O_2: a, 295 K; b, 273 K; c, 250 K; d, 200 K; e, 150 K; f, 130 K; g, 110 K; and h, 105 K.

TABLE 1

Reactivity of TiO_2-Based Catalysts for MOC (%)

Catalyst	Conv. (CH_4)	*S* (C2)	*Y* (C2)	*S* (C_2H_4)	*Y* (C_2H_4)
TiO_2	6.3	13.8	0.88	7.5	0.45
La/TiO_2	14.9	20.1	2.8	12.7	1.8
Li/TiO_2	13.5	75.3	10.2	58.4	7.9

Note. *S*, selectivity; *Y*, yield; C2, ethane + ethylene. Li 10 wt%, La 4 wt%, catalyst charge 0.5 g, temperature 1073 K; $CH_4 : O_2 : N_2 = 3 : 1 : 1$. GHSV = 1700 hr^{-1}.

as in the absence of oxygen. Possible adsorptive oxygen species are O_2^-, O_2^{2-}, O_3^-, and O^-. Peak 1 and peak 3 in Fig. 1b were overlapped. Simulation of the curve from the signal of the F-center and O_2^- showed a good correlation with experimental data. Therefore peak 3 was assigned to O_2^-. The assignment of peak 3 is coincidental with the results of other authors (*10–14*). Naccache *et al.* (*11*) indicated that O^- ions could not be detected even by quenching the sample from 773 to 77 K. Under our experimental conditions, O^- ions were also not detected in the spectra.

When the temperature was decreased, both the F-center and the O_2^- ion signals decayed and vanished at 150 K. The decay rate of the F-center signal was higher than that of the O_2^- ion signal. This fact indicated that electrons in F-centers would transfer to O_2^- ions at low temperature and that an inactive ESR species was formed. The process for O_2 adsorption on TiO_2 can be represented by the following reactions:

$$O_2 + F(e) \rightarrow O_2^- \qquad (2)$$

$$O_2^- + 3F(e) \rightarrow \xrightarrow{?} 2O^{2-}. \qquad (3)$$

F(e) stands for an electron localized in the F-center. Lattice oxygen O^{2-} is an inactive ESR species. The formation of O^{2-} leads to the decay of the F-center and the O_2^- signal. As the consumed number of F-centers was more than that of the O_2^-, the signal of the F-center decayed faster than that of the O_2^-. The intermediates between the O_2^- and the lattice oxygen O^{2-} ions are not clear from our experimental data. Some authors (*14–17*) suggested the following process on TiO_2,

$$O_2 \xrightarrow{e} O_2^- \xrightarrow{e} O_2^{2-} \Leftrightarrow$$

$$2O^- \xrightarrow{2e} 2O^{2-}, \qquad (4)$$

where O^{2-} was the lattice oxygen as in formula (3). According to this scheme, the formation of O^- would precede that of O^{2-}. However, there is the ambiguous fact that O^- was not detected on TiO_2 at any temperature, or even in the presence of atomic oxygen (*16*). A possible explanation is O^- may be a transient state on the TiO_2 under these experimental conditions. It can transform to O^{2-} so quickly that no O^- can be detected on TiO_2.

La-doped TiO_2 showed a large signal of Ti^{3+} (I). This is due to the dissolution of La^{3+} ions into interstitial sites of TiO_2, which increase the stability of Ti^{3+} (I). After admission of O_2, the F-center signal decayed and the O_2^- signal was so weak that it could not be clearly recognized in the spectra. This implies that the processes (2)–(3) take place, but O_2^- is more unstable on La/TiO_2 than on TiO_2 alone. O^- was not detected on La/TiO_2. The Ti^{3+} (I) signal was reduced compared with that before O_2 admission, but the effect was not considerable. The reason for this is that O_2 can react with surface Ti^{3+} (I) but not with bulk Ti^{3+} (I). Therefore the effect of La^{3+} on the characteristics of TiO_2 is limited. It corresponds with the fact that La-doped TiO_2 showed only a small improvement of reactivity compared with TiO_2 alone, as in Table 1. This is also a coincidence in that La^{3+} behaved mainly as a structure promoter not as an active component in TiO_2-based catalysts (*6*).

In the spectra of Li-doped TiO_2, the F-center signal was much smaller than that of TiO_2 alone. This is due to the substitution of Li^+ ions for Ti^{4+} ions in the lattice causing the decrease of free electrons in the n-type semiconductor of TiO_2. Attention should be paid to the new peaks in the spectra. They appear to be some new forms of Ti^{3+}, noted as Ti^{3+} (II), with different coordination numbers than Ti^{3+} (I). On admission of O_2, the signals of Ti^{3+} (II) increased, which implied that some Ti^{4+} reduced to Ti^{3+} (II). The following reduction process is suggested:

$$O_2^- + Ti^{4+} \rightarrow O_2^- \cdot Ti^{4+} \rightarrow [O_2 \cdot Ti^{3+}] \quad (5)$$

On admission of O_2, low-coordinated Ti^{4+} reacts with O_2^- to form a coordination compound $[O_2 \cdot Ti^{3+}]$ where Ti^{4+} and Ti^{3+} are low coordinated and there are spaces for O_2 or O_2^- to enable coordination with them. Therefore the signals of Ti^{3+} (II) increased on admission of O_2.

Process (5) was found only on Li/TiO_2. The reason for this is that the promoter Li^+ (low valence) can induce the formation of "low-coordinated" Ti^{4+} (high valence) through the substitution of Li^+ for lattice Ti^{4+}. The radii of Li^+ and Ti^{4+} ions are almost the same (68 pm, 1 pm = 10^{-12} m) (*18*), therefore Li^+ ions probably substitute for Ti^{4+} ions in the lattice. As the radius of the La^{3+} ion (101.6 pm) is much larger than that of the Ti^{4+} ion, La^{3+} ions could not substitute for Ti^{4+} ions. Therefore, it is understandable that the characteristics of La/TiO_2 are very different from that of Li/TiO_2.

Adsorption of O_2 is a process of electron-acceptance. The adsorbent is an electron donor. The less free electrons in the sample, the more difficult is the adsorption of O_2. Therefore, Li/TiO_2 has more difficulty in adsorbing the O_2 than other samples. There are also less O_2^- ions detected on the surface of Li/TiO_2 than that of TiO_2 alone because of less O_2 adsorption. The capacity of O_2 adsorption on samples in this research is related to the electronic characteristics of the samples, and according to the results of DTA, TGA, and XRD studies, all samples do not change their structures up to 1123 K (*19*), so there should be less O_2 or O_2^- on the surface of Li/TiO_2 under the reaction conditions. This implies that the amount of adsorbing O_2 or O_2^- may not play an important role in the coupling activity of CH_4 because the least active catalyst, TiO_2, has the most O_2^- ions, and the most active catalyst, Li/TiO_2, has the least O_2^- ions stable on the surface. In fact, increasing the amount of O_2 may increase the selectivity to complete oxidation, as many authors have noted.

O^- ions were not detected on Li/TiO_2. As there are no O^- ions stable on TiO_2, La/TiO_2, and Li/TiO_2 catalysts at low or high temperature, O^- ions are not the stable active oxygen species in the coupling activity of CH_4. If O^- ions came from O_2^- ions and took an active role in the MOC reaction, TiO_2 itself would be the best catalyst. This is contrary to the present experimental results.

As O_2^- and O^- do not play key roles in the coupling activity, it may be reasonable to suggest that the lattice oxygen O^{2-} related to the lower degrees of coordination of Ti^{4+} is the active species under our research conditions. More investigation is needed to show the role of the lattice oxygen O^{2-} in the MOC reaction.

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