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A Study of the Reactivity of Surface-Adsorbed Oxygen Species with C_2H_6 on V_2O_5/SiO_2

Eiji Iwamatsu, Ken-ichi Aika,* and Takaharu Onishi
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta,
Midori-ku, Yokohama 227

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The properties and reactivities of surface oxygen species including O^- on V_2O_5/SiO_2 were studied in connection with the oxidative dehydrogenation of C_2H_6 by N_2O. O^- was formed through N_2O on reduced V_2O_5 supported on SiO_2 which had been prepared from tetraethyl silicate, whereas it was not formed on V_2O_5 supported on SiO_2 obtained from other sources. One mole of O^- on V_2O_5/SiO_2 was found to react with one mole of C_2H_6 at 298K. No oxygen species other than O^- reacted with C_2H_6 at 298K. The surface reaction mechanism was discussed, and ethoxide was considered to be one of the surface intermediates. All the other surface oxygens but O^- reacted with C_2H_6 above 573K. Since a catalytic oxidative dehydrogenation reaction of C_2H_6 was active above 573K, the surface oxygens other than O^- were considered to be responsible for this reaction. The possibility of O^- as the reaction intermediate was also discussed.

Paramagnetic oxygen species, such as O^-, O_2^-, and O_3^- have been studied on oxide catalysts by means of EPR techniques.[1] O^- on the MgO surface has been found to react with alkanes under mild conditions, and the mechanism of the surface reaction has been studied.[2] On the other hand, as O^- is formed through N_2O, several attempts at getting useful products by means of the reaction of N_2O with alkane have been carried out. Methanol and formaldehyde have been obtained selectively over MoO_3/SiO_2 and other oxide systems by a reaction of CH_4 with N_2O in the presence of H_2O.[3,4] Phenol has also been obtained by a reaction of benzene with N_2O under similar conditions.[5] In these works, O^- is treated as an active intermediate.[3–5] However, since the conditions of O^- formation are very different from the conditions of the catalytic reactions, no relationship between the catalytic reactions and the surface reactions involving O^- have yet been studied well. The present authors intended to study both the catalytic reaction of C_2H_6 oxidation and the surface reaction of O^- with C_2H_6 on the same catalyst. C_2H_6 was used for the reactant because of the ease of handling and product analysis. V_2O_5/SiO_2 was chosen because it was an active catalyst of C_2H_6 oxidation and because it was a rare system in yielding O^- from O_2.[6] The reaction of O^- with hydrocarbons on this catalyst has not been studied extensively, although the reactivity of O_2^- has been studied well.[6] Thus, we will start by investigating the conditions of O^- formation and will thus study the surface reactivity of both O^- and other surface oxygen species on V_2O_5/SiO_2; finally, these results will be compared with the catalytic performance of the oxidative dehydrogenation reaction of C_2H_6 by the use of N_2O.

Experimental

Materials. Three kinds of SiO_2 were used as supports. SiO_2(A): A reference catalyst supplied by the Catalysis Society of Japan (JRC-SIO-1). SiO_2(B): Obtained by the hydration of tetraethyl silicate in a water–ethanol mixture at boiling point, followed by evaporation at 353K and calcination at 773 K for 5 h.[6] SiO_2(C): Commercial powdered silica (Cab-O-Sil). V_2O_5/SiO_2 was prepared by the impregnation of SiO_2 with 0.3 mol L^{-1} ammonia solution containing ammonium metavanadate (Wako Pure Chemical). The V_2O_5 content was 2.6% by weight. The supported catalysts were calcined at 773 K for 10 h. Unsupported V_2O_5 obtained from Wako Pure Chemical was also used.

Apparatus and Procedure. The surface reactions and catalytic reactions were carried out in a conventional closed-circulation system. Two g of the catalyst were used. The condensable gases are purified by vacuum distillation in the apparatus. The helium was purified through a copper-Kieselgur column. The reactants and products were analyzed by means of a gas chromatograph (FID, TCD) with Porapak Q and MS 5 A columns. The EPR spectra were recorded with a JEOL JES-FE-1X spectrometer (X-band) at 77 K. The concentrations and g-factors of O^- were determined by a method similar to one described elsewhere.[2] The catalysts were evacuated at 773 K for 3 h and then oxidized with O_2 at the same temperature overnight before use (standard pretreatment). CO was used as a reduction agent, and the degree of reduction, as measured by CO_2 production, was represented by the percentage change of the V^{5+} ion to the V metal.

Results

Formations of Surface-Adsorbed Oxygen Species. N_2O decomposition took place at 298 K over V_2O_5/SiO_2(B), which had been reduced by CO at 693 K overnight. About 6×10^{-2} mmol of N_2 was produced in 15 min, but O_2 was not produced on this catalyst, unlike as in the Co–MgO system.[7] Following the N_2O decomposition, a concentration of the O^- thus produced was determined by the EPR measurement, while the amount of adsorbed oxygen was determined from the amount of N_2 produced. These values are plotted as a function of the reduction temperature in Fig. 1, where the degree of reduction is also shown. It may be seen that the amounts of O^- are much less than those of the total oxygen adsorbed. The material balance of N_2O suggested that a comparable number of N_2O atoms were also adsorbed as well as oxygen atoms. It

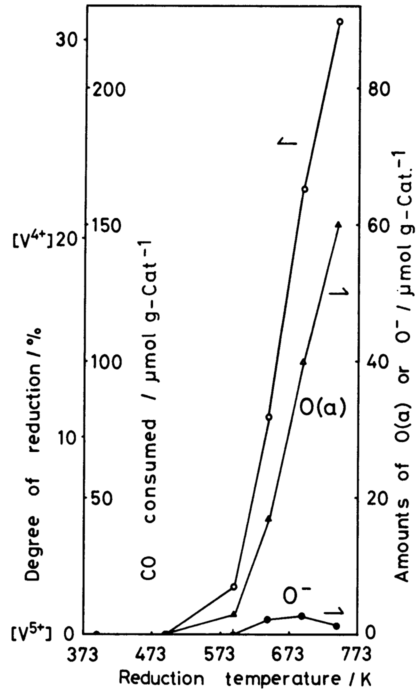

Fig. 1. Variation of the reduction degree of the catalyst and the amount of adsorbed oxygen and O^- after N_2O treatment as a function of the reduction temperature on 2.6wt%V_2O_5/SiO_2(B). 100% reduction corresponds to the whole reduction of V^{5+} ion to V metal.

may also be seen that the concentration of O(a) is roughly proportional to the degree of reduction. It should be noted that O^- was not observed on other V_2O_5 systems, such as V_2O_5/SiO_2(A), V_2O_5/SiO_2(C), or unsupported V_2O_5, after the same pretreatment. O^- was not formed through O_2(1.5 Torr (1 Torr=133.3 Pa)), even on the well-reduced V_2O_5/SiO_2(B), where just O_2^- was produced. The amount of O_2^- produced from O_2 was about ten times more than that of the O^- produced from N_2O.

Stability of O^-. Figure 2 shows an EPR spectrum of V_2O_5/SiO_2(B) (a) after a standard pretreatment (reduction by CO at 693 K) and (b) after the introduction of N_2O at 298 K. The two peaks in Fig. 2(a) were assigned to parts of the octet spectra of the V^{4+} ions. The spectra in Fig. 2(b) was identified with O^- (g=2.032), for they show a hyperfine structure (A=13.2G) attributable to the V nucleus. After the gas phase had been evacuated, O_2 was introduced. The resultant EPR spectra are shown in Fig. 2(c); they should be identified with O_2^- ($g_{/\!/}=2.021$, $A_{/\!/}=9.8$G; $g_\perp=2.003$, $A_\perp=6.0$G).[6] Contrary to the cases of MgO[1] and Co-MgO,[7] where O^- reacted with O_2 giving O_3^-, no new signals showing O_3^- were observed. Instead, O_2^- was observed. The amount of O_2^- was about ten times that of O^-. As is observed at a low magnetic field in Fig. 2(c), a weak peak which is identified as a part of the O^- spectrum remains. This suggests that at least a part of the O^- does not react with O_2. Probably, O_2 is adsorbed on the other sites, independent of the sites for O^- formation.

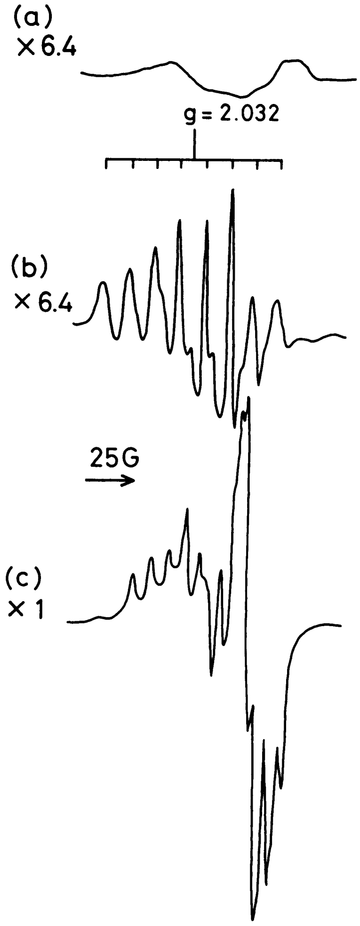

Fig. 2. EPR spectra of 2.6wt% V_2O_5/SiO(B); (a) sample reduced by CO at 693K for 15 h: (b) Sample contacted with N_2O at 298K after (a): (c) Sample contacted with O_2 at 298K after (b).

The thermal stability of O^- was studied in an evacuated sample tube. The amounts of O^- were not changed, even after 260 h at 77 K. They decreased to two-thirds of the initial value after 100 h at 195 K. Finally, most of the O^- disappeared after 1 h at 373 K. The O^- on V_2O_5/SiO_2 was found to be thermally unstable above 373 K. Thus, it seems questionable that such O^- exists in a practical oxidation reaction at an elevated temperature.

A Surface Reaction between the O^- Anion Radical and C_2H_6. After the concentration of O^- had been determined, an excess amount of C_2H_6 was introduced to the catalyst at 298 K for 20 min. The O^- spectra (Fig. 2(b)) completely disappeared upon a reaction with C_2H_6 at 298 K. However, the V^{4+} signal (Fig. 2(a)) remained.

The reaction stoichiometry between O^- and C_2H_6 was also studied. The amount of O^- was controlled by changing the reduction conditions. The maximum concentration of O^- on V_2O_5/SiO_2(B) was several times larger than those on MgO[2] and Co-MgO.[9] As is shown

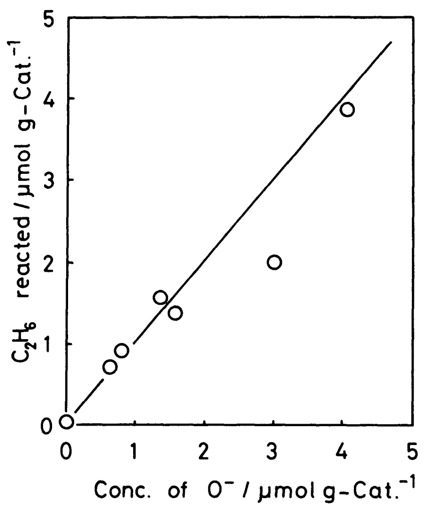

Fig. 3. Variation of the amount of C_2H_6 reacted with O^- at 298K as a function of the concentration of O^- evaluated from its EPR spectrum. 2g of 2.6wt% V_2O_5/SiO_2(B) was used as a sample.

in Fig. 3, one mole of O^- was proved to react with one mole of C_2H_6 as has been observed in the case of MgO.[2] It was also proved that C_2H_6 hardly reacted at all with other oxygen species on this catalyst at 298 K (see the zero point in Fig. 3). Contrary to this, it has been reported that adsorbed oxygen other than O^- also reacts with C_2H_6 at 298 K on Co–MgO.[9] No gas-phase products were observed by the surface reaction at 298 K.

TPD Behavior Following the Surface Reaction between O^- and C_2H_6 at 298 K. In order to assign the adsorbed species formed by the surface reaction between O^- and C_2H_6 on V_2O_5/SiO_2(B), temperature-programmed-desorption (TPD) experiments were carried out. After the gas phase had been evacuated, 100 Torr of He was introduced into the reactor. The temperature was then raised step-by-step while desorption products were trapped at 77 K in the closed circulation system. Figure 4 shows the accumulated amounts of desorption products as a function of the temperature. The main product, C_2H_4, desorbed above 473 K. The products recovered up to 773 K corresponded to 18% of the total carbon reacted. In order to discuss the adsorbed species, the TPD patterns of the model compounds were compared with the above results. The TPD pattern of adsorbed ethanol is shown in Fig. 5. However, the starting temperature of C_2H_4 desorption was higher in Fig. 5 that in Fig. 4. In this case, 94% of the adsorbed carbon source was recovered up to 773 K. On the other hand, the TPD products of adsorbed acetaldehyde, which were C_1 to C_4 alkanes and C_2H_4, were quite different from those in Fig. 4 and 5. In this instance, 41% of the adsorbed carbon source was recovered.

The Reaction between C_2H_6 and Adsorbed Oxygen Species other than O^- above 573 K. Following the N_2O decomposition on V_2O_5/SiO_2(B) at 298 K, the O^- produced was consumed by the reaction with C_2H_6 and the gas phase was evacuated. Then, C_2H_6–He gas was introduced again, and the temperature was raised. C_2H_6 reacted above 573 K yielding C_2H_4 as is shown in Fig. 6. The adsorbed oxygen was proved to be much less reactive than O^-.

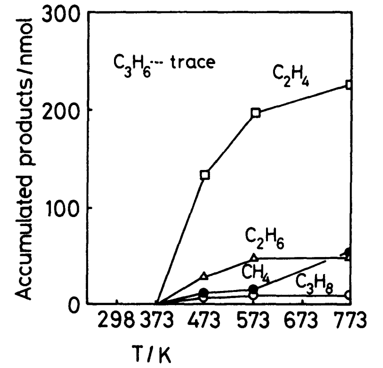

Fig. 4. TPD of surface species following the surface reaction of C_2H_6 and O^- at 298K on 2.6wt%V_2O_5/SiO_2(B) (2g).

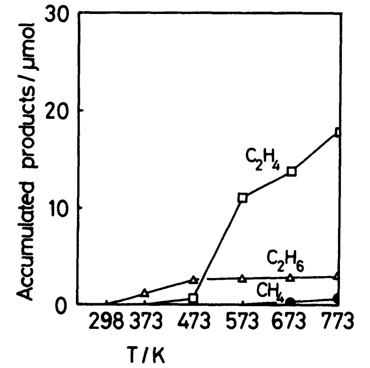

Fig. 5. TPD of C_2H_5OH adsorbed at 298K on 2.6wt%V_2O_5/SiO_2(B) (2g).

Oxidative Dehydrogenation Reaction of C_2H_6 with N_2O above 573 K (Catalytic Reaction). In order to examine the role of O^- and the other oxygen species during the catalytic reaction over V_2O_5/SiO_2, a reaction between C_2H_6 and N_2O was carried out. Two kinds of catalysts, V_2O_5/SiO_2(A) and V_2O_5/SiO_2(B) (2 g each), were used. The catalysts were evacuated at 773 K for 3 h (Pretreatment a) or reduced by CO at 693 K overnight after the evacuation (Pretreatment b). Figure 7 shows a typical example of the time course of the reaction over V_2O_5/SiO_2(B) at 773 K after Pretreatment a. Both C_2H_4 and CO_2 were formed, while C_2H_4 was predominant in the early stage of the reaction. Figure 8 shows the conversions and the C_2H_4 selectivities of the reactions in 15 min over the two catalysts with the two kinds of pretreatments as a function of the reaction temperatures. When these figures are compared, the following facts are observed: 1) The reaction behavior over V_2O_5/SiO_2(B) (Fig. 8(c), (d)) and V_2O_5/SiO_2(A) (Fig. 8(a), (b)) resemble one another, although only the first sample can yield O^-. 2) The activity of N_2O

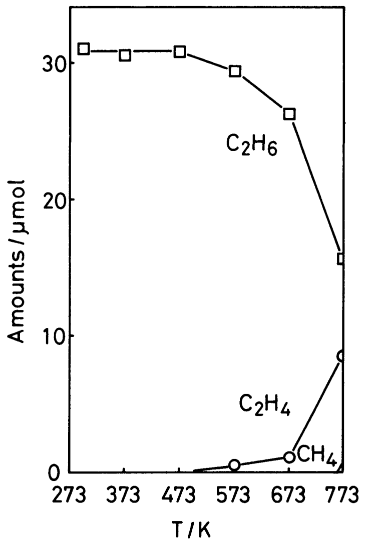

Fig. 6. Reaction of C_2H_6 with adsorbed oxygen other than O^- on 2.6wt%V_2O_5/SiO_2(B). Changes of the amount of the reactant and the products as a function of a reaction temperature.

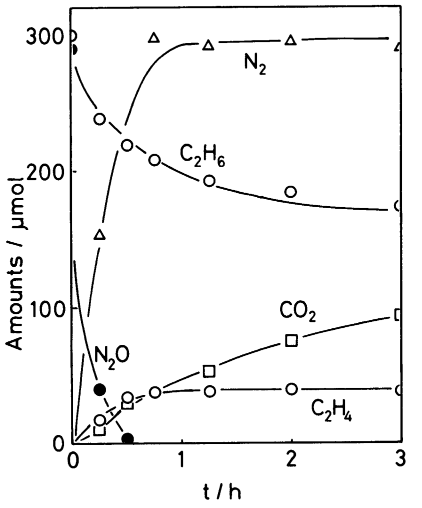

Fig. 7. Time course of the reaction between N_2O and C_2H_6 at 773K on V_2O_5/SiO_2(B) (2g) which is not reduced before the reaction.

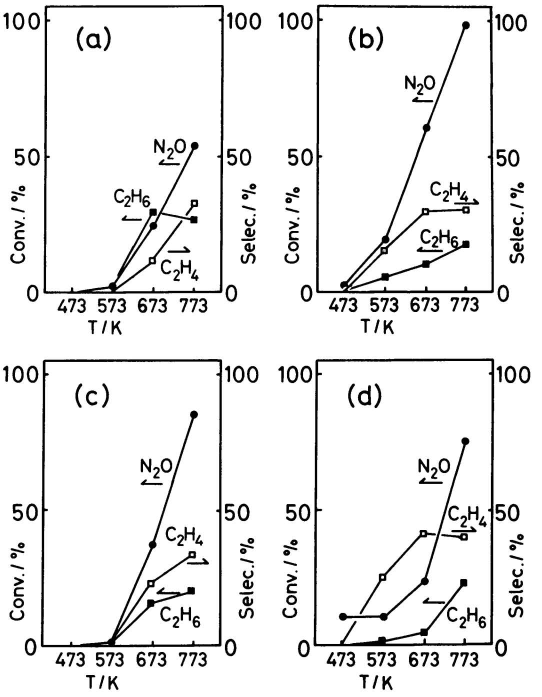

Fig. 8. Conversions and selectivities of the reaction between C_2H_6 and N_2O over 2g of various vanadium catalysts; (a) non reduced 2.6wt%V_2O_5/SiO_2(A): (b) reduced 2.6wt%V_2O_5/SiO_2(A): (c) non reduced 2.6wt%V_2O_5/SiO_2(B): (d) reduced 2.6wt%V_2O_5/SiO_2 (B).

decomposition at a lower reaction temperature was high over the samples treated with the Pretreatment b (Fig. 8(b), (d)), perhaps because N_2O was partly consumed to reoxidize the reduced V_2O_5. 3) On oxidized surfaces (Pretreatment a), the N_2O decomposition and the oxidation of C_2H_6 start at the same temperature (573 K in Fig. 8(a), (c)). This also roughly coincides with the temperature at which the adsorbed oxygen other than O^- reacts with C_2H_6 (Fig. 6). 4) The selectivity for C_2H_4 is rather high at higher temperatures (673 to 773 K).

Discussion

Conditions of O^- Formation. As is shown in Fig. 1, the O^- concentration is the highest under the reduction at 693 K, where the reduction of V^{5+} to V^{4+} is completed (22% of reduction). This suggests that V^{4+} ions are necessary for the formation of O^- ($V^{4+}+N_2O \rightarrow V^{5+}-O^-+N_2$). Furthermore, the formation conditions also depend upon the kind of support. Probably the circumstance of the vanadium ion, which might be controlled by the surface state of the SiO_2 support, is important. In order to investigate any differences among the vanadium ions of the samples, the EPR spectra of V^{4+} ions of the 4 samples used in this work were compared. The shapes of the EPR spectra of V^{4+} were classified into three kinds. However, the shapes of the spectra are not related to the conditions of O^- formation. V_2O_5/SiO_2(B) and V_2O_5/SiO_2(C) have spectra of the same shape, although only the former is active in O^- formation. The nature of the site for O^- formation could not be clarified in detail.

O^- could not be formed through O_2 under the same conditions as in the literature.[6] It has been reported that O^- is formed only when the pressure of O_2 is low (several Torr).[6] It seems that the conditions in our system are too restricted.

Surface Reactions of O^- and C_2H_6 at 298 K. One-to-one stoichiometry between O^- and C_2H_6 was found more clearly on V_2O_5/SiO_2 than on other systems. Thus, O^- is considered to abstract one hydrogen atom from C_2H_6, as has been suggested in the case of MgO.[2]

$$C_2H_6 + O^- \longrightarrow C_2H_5\cdot + OH^- \qquad (1)$$

The subsequent reactions of the ethyl radical to form surface ethoxide and hydroxide are assumed to be as in Eqs. 2 and 3, because ethylene desorption still occurs at 573 K (Fig. 4), at which point ethoxide decomposition is observed (Fig. 5):

$$C_2H_5\cdot + O^{2-} + \boxed{} \longrightarrow C_2H_5O^- + \boxed{e^-} \tag{2}$$

$$C_2H_5O^- \longrightarrow C_2H_4 + OH^- \tag{3}$$

However, as is shown in Fig. 4, a majority of ethylene desorbs at lower temperature (473 K). This may suggest the existence of an other intermediate, for example, a carbonium ion, which releases ethylene at a lower temperature, as has been discussed in the case of MgO.[2)]

$$C_2H_5\cdot + \boxed{} \longrightarrow C_2H_5^+ + \boxed{e^-} \tag{4}$$

$$C_2H_5^+ + O^{2-} \longrightarrow C_2H_4 + OH^- \tag{5}$$

Since the amount of recovered carbon atoms was low (18%), other processes, such as the polymerization of ethylene or further oxidation, might also occur.

Active Oxygen Species in the Oxidative Dehydrogenation of C_2H_6 by N_2O above 573 K. As has been described earlier, the adsorbed oxygen other than O^- is reactive above 573 K, where the catalytic reaction occurs. On the other hand, O^- reacts with C_2H_6 even at room temperature, and it is not thermally stable. After all, O^- is not considered to be present during the catalytic reaction conditions. The active species during the oxidative dehydrogenation above 573 K was considered to be the adsorbed oxygen other than O^-. This is also supported by the fact that the reactivity of V_2O_5/SiO_2 is not related to the ability to produce O^-.

If there are new circumstances under which only O^- is formed at a high temperature with a dynamic balance of O^- evolution and disappearance, the possibility that O^- is involved in the reaction should be discussed.[10)] It should also be pointed out that an oxygen species which is not detected by EPR is also very active against C_2H_6, even at room temperature.[9)] Regarding this system too, the authors suggest the importance of an adsorbed oxygen other than O^- as the active species of the reaction at the higher temperature.

Conclusions

The nature of O^- and the surface reaction mechanism between O^- and C_2H_6 were studied in order to elucidate the catalytic oxidative dehydrogenation of C_2H_6 with N_2O over V_2O_5/SiO_2. V_2O_5 must be supported on SiO_2 made from tetraethyl silicate in order to get O^-, and the amount of O^- formed is related to the concentration of V^{4+}. One mole of O^- is proved to react with one mole of C_2H_6 on V_2O_5/SiO_2 at 298 K. The adsorbed oxygen species other than O^- is less reactive than O^- toward C_2H_6. This species, EPR-undetectable oxygen, was found to be reactive with C_2H_6 above 573 K, and it is considered to be responsible for the catalytic reaction of C_2H_6 with N_2O above 573 K.

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