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https://doi.org/10.15017/17483

出版情報：九州大学大学院総合理工学報告. 1 (1), pp.3-9, 1979-10-09. 九州大学大学院総合理工学研究科
バージョン：
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Methylethylketone Oxidation over V_2O_5 Catalysts

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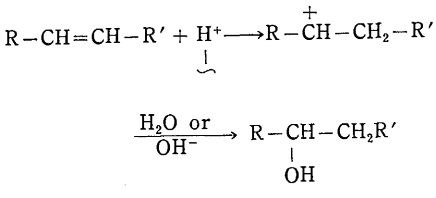
(received July 27, 1979)

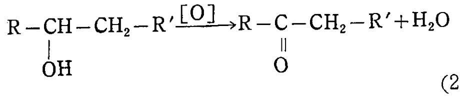
The reaction mechanism of methylethylketone (MEK) oxidation to acetaldehyde (AcH) and acetic acid (AcOH) which is characterized by the oxidative splitting of carbon skeleton has been investigated over V_2O_5 catalysts. Kinetics of MEK oxidation at 150°C over V_2O_5-MoO_3 suggested the participation of molecular oxygen in the reaction. The formation of O_2^- species on the catalyst surface under the reaction conditions was in fact confirmed with temperature programmed desorption and EPR techniques, by using a partially reduced V_2O_5 catalyst supported on silica gel. It was shown that the O_2^- species thus formed reacted with MEK to produce AcH and AcOH selectively, while the lattice oxygen of V_2O_5 converted MEK into CO_2. On the basis of these results it was concluded that the O_2^- was the oxygen species reacting with MEK in the oxidative scission reaction.

1. INTRODUCTION

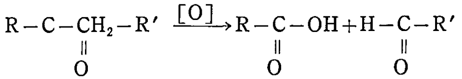
Selective AcOH formation has been known in the oxidation of n-butenes over metal oxide catalysts containing vanadium such as V_2O_5-MoO_3[1]. We have demonstrated that this type of oxidation is universal to other lower n-olefins and have proposed the following reaction paths[2]~[4].



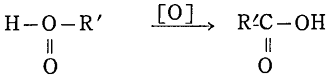
$$R-CH=CH-R' + \underset{\underset{\sim}{|}}{H^+} \longrightarrow R-\overset{+}{C}H-CH_2-R' \xrightarrow[OH^-]{H_2O\ or} R-\underset{\underset{OH}{|}}{CH}-CH_2R' \quad (1)$$



$$R-\underset{\underset{OH}{|}}{CH}-CH_2-R' \xrightarrow{[O]} R-\underset{\underset{O}{\|}}{C}-CH_2-R'+H_2O \quad (2)$$



$$R-\underset{\underset{O}{\|}}{C}-CH_2-R' \xrightarrow{[O]} R-\underset{\underset{O}{\|}}{C}-OH+H-\underset{\underset{O}{\|}}{C}-R' \quad (3)$$



$$H-\underset{\underset{O}{\|}}{O}-R' \xrightarrow{[O]} R'\underset{\underset{O}{\|}}{C}-OH \quad (4)$$

The steps through the formation of carbonyls, Eqs. 1 and 2, have been shown to be identical with those of the oxyhydration of olefins which were reported over other catalysts by one of the authors previously[5]~[8]. In the present case of oxidation, however, the carbonyl formation is followed by further oxidative scission to carboxylic acids (Eq. 3), so that the overall reaction has been designated as "oxyhydrative scission". Clearly the features most characteristc of the oxyhydrative scission and therefore the keys to approaching it seem to be related to this very step of oxidative scission.

A striking fact is that almost all the catalysts claimed to be effective for the oxyhydrative scission of olefins in patents contain V_2O_5. We have examined

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***) Department of Materials Science and Technology the catalytic activity of various single metal oxides for methylethylketone (MEK) oxidation⁹⁾. It shows that only V_2O_5 is endowed with high activity and high selectivity for the reaction, while high valent metal oxides such as MoO_3, WO_3, WO_3, and UO_3 are excellent in selectivity.

As is well known, V_2O_5 is a catalyst component which is extensively used in many practical oxidation processes such as maleic or phthalic anhydride synthesis, and a great many studies have been devoted to its catalytic properties. Vanadium pentoxide has a layer structure in which one may distinguish three types of oxide ions attached to one, two, and three vanadium ions¹⁰⁾. Tarama et al.¹¹⁾ were the first to point out the importance of the doubly bonded oxide ion (attached to one vanadium atom) in the catalysis. Besides these oxide ions, V_2O_5 has been shown to accommodate several kinds of adsorbed oxygen. The formation of O^- and O_2^- on partially reduced V_2O_5/SiO_2 was demonstrated by Shvets et al.¹²⁾ and Tarama et al.¹³⁾ Tarama et al. showed that the O_2^- ion on V_2O_5/SiO_2 directly interact with the double bond of propylene¹⁴⁾. Kazansky et al. also reported the formation of O_3^- by exposing the O^- ion on V_2O_5/SiO_2 to molecular oxygen¹⁵⁾. They claimed that the O_3^- is an intermediate of homomolecular oxygen isotope exchange at room temperature. Surveying these studies, one cannot exclude the possibility that certain adsorbed oxygen species take part in the oxyhydrative scission reaction. It is especially so when one consider that the scission reaction proceeds at such low temperatures as 170–250°C.

In this teport we have focused attention on the scission step (Eq. 3) of the oxyhydrative scission reaction, aiming at elucidating its mechanism. In particular, we have directed our efforts to determine whether the O_2^- ion is actually an active oxygen species taking part in the reactions.

2. EXPERIMENTAL

V_2O_5 catalyst was prepared by the thermal decomposition of ammonium metavanadate at 550°C for 5 h. V_2O_5–MoO_3 (V/Mo=9/1) was prepared from an aqueous solution containing ammonium metavanadate and ammonium paramolybdate by evaporation to dryness on a water bath followed by calcination at 550°C for 5 h. To obtain V_2O_5 (5 wt %)/SiO_2, silica gel was impregnated with aqueous ammonium metavanadate solution and calcined at 550°C for 5 h.

The kinctic study of MEK oxidation was carried out by using a conventional flow reactor²⁾. The feed contained varying concentrations of MEK and oxygen, 32.9 vol % water vapor and a balance gas (N_2). The products were analyzed by gas chromatography²⁾. The temperature programmed desorption experiments were performed in the same apparatus as was described elesewhere¹⁶⁾.

The superoxide ion, O_2^-, was prepared on V_2O_5/SiO_2 as follows. The V_2O_5/SiO_2 catalyst obtained above was reduced with 2.56 Torr of hydrogen at 500°C for 3 min and evacuated for 15 min at the same temperature. Then at room temperature, the catalyst was exposed to 150 Torr of oxygen for 5 min and evacuated for 5–10 min. The epr spectra of paramagnetic oxygen as well as of V^{4+} ions were recorded on a Hitachi 771 (X band) spectrometer at room temperature. The gaseous compounds produced between MEK and the O_2 species or surface oxygen of V_2O_5 was analysed with a mass spectrometer (Hitachi RMU).

3. RESULTS AND DISCUSSION

3. 1. Reaction Kinetics

In order to collect information on the reaction mechanism, especially concerning the oxygen species, the influence of partial pressures of MEK and O_2 (P_{MEK} and P_{O_2}) on the rate of ketone oxidation was studied over V_2O_5-MoO_3 at 150°C. As a result, the rate could be expressed by the following power rate equation.

$$V = -\frac{dP_{MEK}}{dt} = kP_{MEK}{}^{0.4}\,P_{O_2}{}^{1.0} \qquad (5)$$

over the partial pressure ranges of $P_{MEK} = 0.003-0.07$ atm and $P_{O_2} = 0.009-0.32$ atm. The apparent rate constant k was equal to 1.56 ($1/\mathrm{atm}^{0.4}\mathrm{s}$) at 150°C. It is noted that the dependence on P_{O_2} is extraordinarily high compared with many other cases of catalytic oxidation reactions. This suggests that molecular type oxygen takes part in the rate deermining step, and in fact such a reaction model was found to be consistent with the kinetic data as described below.

A Langmuir-Hinshelwood type surface reaction between MEK and molecular type oxygen should have a rate expressed in the following form provided that oxygen adsorption is weak.

$$V = kK_{O_2}P_{O_2}\frac{K_{MEK}P_{MEK}}{1+K_{MEK}P_{MEK}} \qquad (6)$$

Here K_{MEK} and K_{O_2} are adsorption constants for MEK and O_2. Eq. 6 can be transformed as follows.

$$\frac{1}{V} = \frac{1}{kK_{O_2}P_{O_2}K_{MEK}}\cdot\frac{1}{P_{MEK}} + \frac{1}{kK_{O_2}P_{O_2}} \qquad (7)$$

or

$$\frac{1}{V} = \frac{1+K_{MEK}P_{MEK}}{kK_{O_2}P_{O_2}K_{MEK}P_{MEK}} + \frac{1}{P_{O_2}} \qquad (8)$$

These equations show that, for constant P_{O_2} or constant P_{MEK}, $1/V$ should change linearly with $1/P_{MEK}$ or with $1/P_{O_2}$, respectively. This was in fact confirmed in **Fig. 1**. The slopes and intercepts of the straight lines gave $K_{MEK} = 202\ \mathrm{atm}^{-1}$ and $kK_{O_2} = 0.002\ \mathrm{atm}^{-2}\cdot\mathrm{s}^{-1}$.

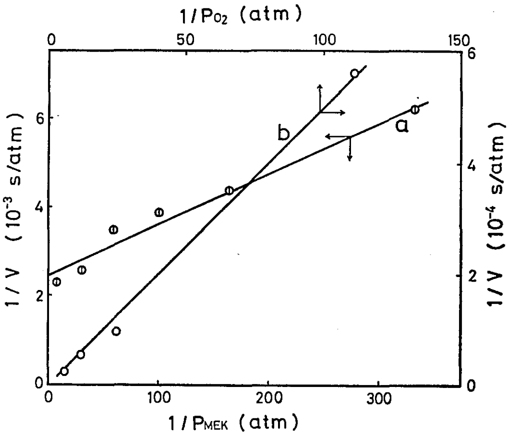


Fig. 1. The Langmuir plots for the rate of MEK oxidation.
Catalyst; V_2O_5-MoO_3 (V/Mo = 9/1) 0.27g, Temperature; 150°C, Feed gas comuosition (vol %); a) MEK 0.36-6.7, H_2O 32.9, O_2 32.9, N_2 balance. b) MEK 3.0, H_2O 32.9, O_2 0.9-32, N_2 balance.

3. 2. Oxygen Adsorption

The possibility of the formation of molecular type oxygen on V_2O_5 catalysts under the reaction conditions was examined by means of a temperature programmed desorption (TPD) technique and epr spectroscopy. The TPD technique, as one of the most useful technique, has been applied in many studies on gas adsorption. However, oxygen adsorbates on high valent transition metal oxides so far have been found only with epr, and few corresponding TPD spectra have been reported.

The TPD experiment consisted of oxygen adsorption under specified conditions, cooling to room temperature in vacuo, and programmed heating up to 500°C in a helium stream. The desorbed gas was monitored with a thermal conductivity detector. Three samples, V_2O_5, V_2O_5-MoO_3, and V_2O_5/SiO_2, were used for this experiment. After calcination in air at 500°C, no samples exhibited significant oxygen desorption following oxygen adsorption at any temperatures below 500°C. However, when partially reduced with 10 cm^3 of hydrogen pulse at 500°C and exposed to 150 Torr of oxygen at room temperature, V_2O_5/SiO_2 was found to give a broad peak of oxygen desorption as shown in **Fig. 2**, while the other two catalysts showed no such oxygen desorption. Moreover, epr measurements showed that the partial reduction of V_2O_5/SiO_2 followed by oxygen adsorption at room temperature produced a typical paramagnetic signal of O_2^- ions which agreed well with the signals reported by Kazansky et al.[12] and Tarama et al.[13]. It follows therefore that the O_2^- species is responsible for the TPD peak observed on V_2O_5/SiO_2. Only recently Suzuki et al.[17] reported a more detailed study of oxygen adsorption on partially reduced V_2O_5/SiO_2[17]. According to their results, O^- species can also be formed in addition to O_2^- on the prereduced catalyst, but its amount is far less than that of O_2^- when the catalyst prereduction is limited to minor extents.

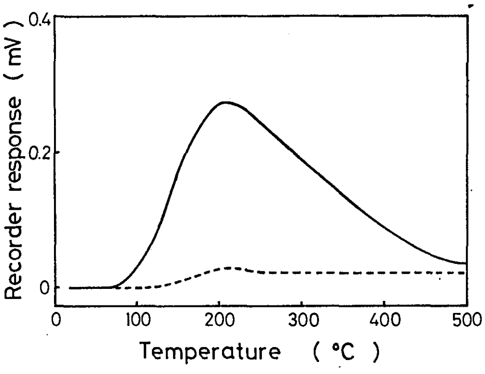


Fig. 2. TPD chromatograms of oxygen from V_2O_5/SiO_2.
Catalyst; V_2O_5(5 wt %)/SiO_2 0.5 g. Solid line is for the catalyst partially reduced with H_2 at 500°C and broken line is for one treated with oxygen at 500°C. The oxygen preadsorption was performed at room temperature.

According to our experiment, the optimum temperature for the MEK oxidation was around 150°C which is slightly lower than the temperature of the oxygen desorption maximum in **Fig. 2**. This assures that the O_2^- species can remain adsorbed or be formed on the catalyst surface under reaction conditions as a probable species reacting with MEK molecules.

Comments should probably be added on two respects. First is on the effect of prereduction. As stated above, oxygen can not be adsorbed significantly on the oxidized V_2O_5 surface and the O_2^- species forms only on partially reduced surface. It is now well known that the partial reduction produces loosely bound electrons which can be used for the reaction, $O_2 + e \rightarrow O_2^-$. The hyperfine structure of the epr signal of O_2^- shows that the adsorption site of O_2^- is the V^{4+} ions, the reduced surface sites. Second is on the absense of significant TPD peaks for V_2O_5 and V_2O_5-MoO_3. It has also been found that MoO_3, Bi_2O_3-MoO_3 and WO_3 do not show any significant oxygen desorption. All of these catalysts have lattice oxygen which has been shown to be mobile on the basis of isotopic tracer experiments. It is suspected that the O_2^- species would be formed on the partially reduced surface of these catalysts but on heating it tends to be rapidly incorporated into bulk as lattice oxygen rather than being desorbed. In the case of V_2O_5/SiO_2, V_2O_5 probably exists in a thin (or even mono-) layer covering the support and therefore the migration of the adsorbed species is no longer important.

3. 3. Direct Evidence of Reaction between O_2^- and MEK

On the basis of the foregoing results, the reaction between O_2^- and MEK was pursued in a epr *in situ* tube. After recording the epr spectrum of the O_2^- species formed on the prereduced V_2O_5/SiO_2, 33.2 Torr of MEK vapor was introduced in the sample tube at room temperature. The pressure decreased to less than 1 Torr within 10 min. Correspondingly, the signal intensity of O_2^- also decreased as shown in **Fig. 3**. After standing for 10 h at room temperature, the gas phase and the substances being desorbed by heating up to 170°C were collected separately and submitted to mass spectrometric analyses. The gas phase contained only MEK. However, the desorbed substances were found to consist of AcH, AcOH and a very small amount of carbon dioxide (**Table 1**). The ratio of AcH/AcOH was a little larger than that in the catalytic oxidation. This difference may be because a part of AcOH still remained on the solid surface.

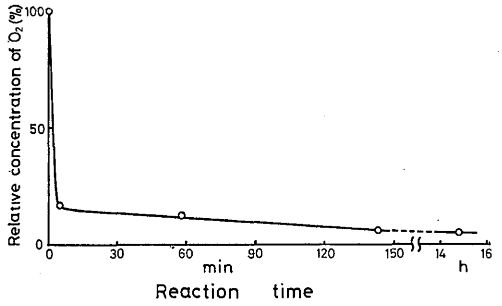


Fig. 3. Decay of the epr signal intensity of O_2^- after exposure to MEK at room temperature.
Catalyst; V_2O_5 (5 wt %) /SiO_2, MEK 33.2 Torr.

For comparison, the reactivity of lattice oxygen of V_2O_5/SiO_2 toward MEK was also examined in a similar manner. This time, the V_2O_5/SiO_2 catalyst was pretreated with 200 Torr of oxygen at 500°C, cooled down to room temperature and evacuated. On introduction of 34.7 Torr of MEK at room temperature, the pressure decreased much more slowly than in the previous case. After standing for 15 h, only MEK was found in the gas phase. On heating up to 160°C, a large amount of carbon dioxide was desorbed, but AcH and AcOH were less than the detection level (**Table 1**).

As mentioned above, the O_2^- ion can

Table 1. Reactivity of O^-_2 and lattice oxygen on V_2O_5/SiO_2 with methylethylketone

Oxygen Species	Reaction rate at room temp.	Mass analysis of the gas phase after reaction	
		At room temp.	After heating to T_D
O_2^-	rapid	MEK	CH_3CHO (67%)*, CH_3COOH (32%)* CO_2 (trace), MEK (T_D=170°C)
lattice oxygen	slow	MEK	CO_2 (T_D=160°C)

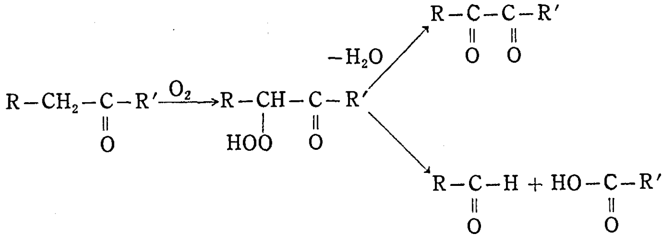
* The values show compositions of gas phase excluding MEK.

react with MEK and gives the expected scission products selectively, while the the lattice oxygen is less reactive giving only CO_2. These results provide convincing evidence that the O_2^- species is an indispensable surface oxygen species in the oxidative scission of MEK.

3. 4. Reaction Mechanism

So far, two types of reactions have been known between O_2^- and hydrocarbons on metal oxide catalysts. That is, O_2^- abstracts a hydrogen atom from hydrocarbons, or it adds an oxygen atom to hydrocarbons. The reaction of O_2^- with propylene on ZnO, TiO_2 or SnO_2 gives allyl type surface compounds and belongs to the former type[18][19]. The latter type is seen in the ethylene oxide formation on silver catalyst. Recently it was reported that the O_2^- ion on V_2O_5/SiO_2 converts propylene to propylene oxide although the product was converted further to acetone and propionaldehyde[14]. However, the present reaction between O_2^- and ketones leading to the oxidative scission of carbon skeletons belongs to none of these types. Rather, the present reaction has a similarity with the liquid phase autoxidation.

In the liquid phase autoxidation of ketones, it is known that a ketone can be oxidized to either α-diketone or a pair of aldehyde and carboxylic acid via a common α-ketohydroperoxide intermediate [20][21].

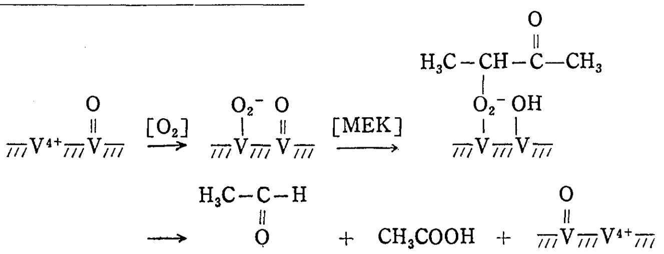


$$R-CH_2-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{O_2} R-\underset{\underset{HOO}{|}}{CH}-\underset{\underset{O}{\|}}{C}-R' \begin{array}{l} \xrightarrow{-H_2O} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R' \\ \longrightarrow R-\underset{\underset{O}{\|}}{C}-H + HO-\underset{\underset{O}{\|}}{C}-R' \end{array}$$

(9)

It is noticed that the scission products of MEK autoxidation are identical with those obtained in the present gas phase oxidation though α-diketone (biacetyl) was not formed in the present case. We have confirmed, however, that the biacetyl formation can become a dominant reaction in the gas phase oxidation of MEK over NiO. These considerations suggest that the intermediate compound involved in the gas phase oxidation is basically similar to that of the autoxidation.

We tentatively propose the following reaction mechanism for the MEK oxidation over V_2O_5 catalysts.



$$///V^{4+}///\overset{\overset{O}{\|}}{V}/// \xrightarrow{[O_2]} ///\overset{\overset{O_2^-}{|}}{V}///\overset{\overset{O}{\|}}{V}/// \xrightarrow{[MEK]} ///\overset{\overset{\overset{H_3C-\underset{|}{CH}-\overset{\overset{O}{\|}}{C}-CH_3}{O_2^-}}{|}}{V}///\overset{\overset{OH}{|}}{V}///$$

$$\longrightarrow H_3C-\underset{\underset{O}{\|}}{C}-H + CH_3COOH + ///\overset{\overset{O}{\|}}{V}///V^{4+}///$$

(10)

Oxygen adsorbs on the reduced sites (V^{4+}) as O^{2-} and reacts with MEK adsorbed on the surface lattice oxygen. The overall reaction consumes two oxygen atoms, which are assumed to be supplied from the O_2^- ion and the lattice oxygen. These assumptions are, however, speculative at present. A tracer study using ^{18}O may bring about useful information on the mechanism.

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