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Active oxygen in selective oxidation catalysis

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Abstract

The paper reviews literature data related to oxygen species available on the surface of metal oxides and their possible role in selective oxidation. With some reservations, one may conclude that the main concept accepted presently in oxidation catalysis assumes that selective oxidation is provided by strongly bonded lattice oxygen, while the full oxidation is provided by weakly bonded reactive oxygen.

Recent studies on the oxidation mechanism over FeZSM-5 zeolites with N_2O give ground to reconsider this concept in order to integrate the earlier suggested radical oxygen idea, which supposes an important role of O^- radicals in selective oxidation. This highly reactive oxygen species can be considered as a powerful tool for activation of organic molecules.

Keywords: Oxygen activation; Selective oxidation; Nitrous oxide; Oxygen radicals

1. Introduction

There are a great number of selective oxidation reactions in heterogeneous catalysis. Surprisingly, nearly all these reactions with high or significant selectivity proceed over a small number of high-valent metal oxides. Among them V_2O_5 and MoO_3 oxides are most efficient and frequently used, being classic selective oxidation catalysts [1–6]. Further, referring to metal oxide catalysts we shall primarily mean V_2O_5 and MoO_3-based catalytic systems.

In this work, we try to consider the oxidation catalysis in terms of reactivity of various surface oxygen species and their possible involvement in selective oxidation. Such attempts have been made earlier. An impetus to the present work was given by recent mechanistic studies on the oxidation with N_2O over iron-containing FeZSM-5 zeolites. Selective oxidation in these systems was shown to involve the so-called α-oxygen, which proved to be anion radical O^-. This result gives ground to reconsider the present-day situation in selective oxidation and renew the radical oxygen idea, which has been once suggested but not generally accepted because of insufficient experimental support.

By reason of a limited size recommended for the manuscripts included in the present issue, this paper presents a short version of our review.

2. Oxygen species on V_2O_5 and MoO_3

It is assumed that oxygen, upon adsorption on the catalyst surface, can accept electrons one by one until its transformation into the fully reduced form:

$$\begin{tikzcd}
O_2 \arrow[r] & (O_2)_S \arrow[r] \arrow[rrr, bend left, "(O)_S"] & (O_2^-)_S \arrow[r] & (O_2^{2-})_S \arrow[r] & (O^-)_S \arrow[r] & (O^{2-})_S \arrow[r] & (O^{2-})_{Latt}
\end{tikzcd} \tag{1}$$

Oxygen species may differ not only in charge, but also in coordination, bond energy, etc. What species are really available under catalytic conditions and especially which one of them is the active oxidant, i.e., the species which can interact directly with the molecule to be oxidized—these questions are of great experimental difficulties and subject of many studies and discussions.

To date, four oxygen species are identified on the surface of oxide catalysts: the terminal M=O and bridging M–O–M species called also lattice oxygen; two anion radicals, molecular O_2^- and atomic O^-. Further, we shall consider their properties and discuss probable role in catalysis.

2.1. Lattice oxygen (M=O and M–O–M)

Terminal oxygen M=O was first identified by Japanese researchers in 1964 [7] due to the absorption band at 900–

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1000 cm^{-1} in IR spectra, as opposed to bridging M–O–M oxygen with the absorption band at 800–900 cm^{-1}. After studying a significant number of metal oxides, Trifiro et al. [8] discovered that terminal oxygen is observed on selective oxidation catalysts (V_2O_5, MoO_3 and molybdates), but is not observed on full oxidation catalysts (MnO_2, Co_3O_4, NiO, CuO and Fe_2O_3), which allows concluding that the doubly bonded lattice oxygen is responsible for selective oxidation. However, later some researchers made a different conclusion suggesting that the bridging oxygen participates in the oxidation rather than the terminal one [9].

By the present time, a great amount of experimental data was collected, providing convincing arguments for the involvement of lattice oxygen (terminal or bridging) in selective oxidation. Among the most important ones one may mention the following:

(a) Selective oxidation catalysts may often serve themselves as a source of oxygen and perform the oxidation for some time in the absence of O_2 in the gas phase [10,11].
(b) If in the course of catalytic reaction one substitutes oxygen $^{18}O_2$ for $^{16}O_2$, a delayed isotopic response of the oxidation products will be observed [10].
(c) The heat of dissociative O_2 adsorption, which is commonly used as a characteristic of the surface oxygen bond energy, strongly differs for selective and non-selective oxide catalysts. In the first case (V_2O_5, MoO_3 and Sb_2O_5) the heat is 45–55 kcal/mol, while in the second case (Mn, Co, Ni and Cu oxides) only 16–20 kcal/mol [12,13].

These important experimental observations make a basis for the present-day concept, the essence of which can be presented in the following somewhat simplified way:

1. Selective oxidation is provided by strongly bonded lattice oxygen having nucleophilic nature.
2. Complete oxidation is provided by weakly bonded reactive oxygen having electrophilic nature.

This concept is a valuable guideline proven by a broad practice in the oxidation catalysis. Nevertheless, actually we should admit that one can hardly find in the literature reliable experimental evidences that would show direct interaction of terminal or bridging oxygen with the molecules to be oxidized. Due to its rather low reactivity, mechanistic studies of the lattice oxygen are usually conducted at high temperature when interconversion of various oxygen species may occur. Under this condition one may find no clear distinction between different oxygen species available on the catalyst surface. Therefore, one cannot exclude that the lattice oxygen may react via its preliminary conversion into some more reactive form, e.g., like radical species discussed below. A difficult problem of identification of catalytically active oxygen species is nicely illustrated with a thorough review paper by Otsuka and Wang [14] related to selective oxidation of methane and its coupling reaction.

2.2. Radical species O^- and O_2^-

These oxygen species are generally prepared by N_2O or O_2 adsorption at room temperature on metal oxides preliminary reduced by a high temperature treatment in CO or H_2. Silica supported V_2O_5 and MoO_3 are most frequently used for this purpose [15,16].

Dioxygen adsorption yields a mixture of the radicals:

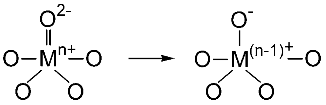
$$O_2 + Mo^V \rightarrow Mo^{VI}O_2^- \quad (2)$$

$$O_2 + 2Mo^V \rightarrow 2Mo^{VI}O^- \quad (3)$$

while N_2O adsorption yields O^- radical:

$$N_2O + Mo^V \rightarrow Mo^{VI}O^- + N_2 \quad (4)$$

It is assumed that at sufficiently high temperatures O^- may be also formed spontaneously by reaction (5) due to electron transfer from the oxygen to metal cation [17]:



(5)

O_2^- and O^- species are paramagnetic and can be readily observed by the ESR. This fact, coupled with an idea of their possible involvement in the oxidation catalysis, stimulated intensive studies in this field, especially in the 1970–1980s of the last century. Results of these studies were summarized in a number of reviews [15,16,18–20]. Since the molecular radical seems less important for catalysis, further we shall consider mainly atomic radical O^-.

Thermal stability of O^- is quite low. At heating, it readily disappears due to reoxidation of the surface. However, on supported V and Mo oxides it is stable up to 100 °C and even 300 °C [18]. O^- shows a very high reactivity [21–24], which sometimes can be observed even at the liquid nitrogen temperature.

2.3. Role of O^- in the oxidation

When considering a possible role in the oxidation, one should distinguish two reaction types of the radical: a stoichiometric (i.e., single turnover) oxidation at low temperature and catalytic oxidation at high temperature.

Stoichiometric studies carried out primarily on supported V and Mo oxides showed that the reaction with O^- at room temperature leads to the formation of selective oxidation products, which can be identified by either in situ IR spectroscopy or after desorption from the surface at heating [25–28]. Thus, methane yields methanol [25,28] and benzene yields phenol [29] as main products. The authors' conclusion that O^- radical performs selective oxidation seems to be quite convincing and causes no discussions in relation to stoichiometric reactions.

Table 1
Methane oxidation by N_2O over 1.7% MoO_3/SiO_2 [28]

Temperature	CH_4 conversion (%)	Selectivity (%)			
		CH_3OH	HCHO	CO	CO_2
550	1.6	20.5	79.5	–	–
560	1.9	19.9	80.1	–	–
570	2.9	13.8	64.3	19.1	2.8
580	4.0	10.0	58.8	27.7	3.4
594	6.0	7.8	49.5	38.1	4.6

Reaction conditions—catalyst weight 1 g; GHSV 4400 l/kg h; feed composition: 10% CH_4, 37% N_2O, 34% H_2O, He balance.

The role of O^- in catalytic reactions is not so clear. Catalytic oxidations of methane [25,27,28], ethane [17,26] and benzene [29] were studied over silica supported MoO_3 and V_2O_5 using N_2O oxidant. All these reactions proceed in the temperature range 550–600 °C, providing significant selectivity to the partial oxidation products, especially in the presence of water. As an example, Table 1 presents data on methane obtained by Lunsford and co-workers [28]. At low conversions, the total selectivity to methanol and formaldehyde attains 100%. High selectivity of methane oxidation was also observed by Somorjai and co-workers over MoO_3/SiO_2 [30] and V_2O_5/SiO_2 [31].

The reaction mechanism was suggested, which includes two most important steps [28]:

$$Mo^{V} + N_2O \rightarrow Mo^{VI}O^- + N_2 \quad (6.1)$$

$$Mo^{VI}O^- + CH_4 \rightarrow Mo^{VI}OH^- + {}^{\bullet}CH_3 \quad (6.2)$$

The first step is formation of O^- radical by decomposition of N_2O and the second step is activation of methane via the hydrogen abstraction provided by O^- radical.

In the case of ethane, catalytic oxidation by N_2O leads to formaldehyde and ethylene with the total selectivity up to 85% [17,26,32,33] and the oxidation of benzene [29] leads to phenol with 71.5% selectivity. Similar products, although with a lower selectivity, were observed over the same type catalysts for the oxidation of CH_4 and C_2H_6 with O_2 [34,35].

So, in all these cases catalytic reactions provided the same selective oxidation products that were observed in stoichiometric reactions with O^-. Therefore, the authors [17,25–35] concluded that their formation in catalytic reactions also proceeds due to O^- radicals.

However, this conclusion was not generally accepted. The above reasoning was considered to be not fully convincing, in particular, because availability of O^- species under catalytic conditions seems unlikely. These conditions are quite far from conditions at which O^- is usually prepared and studied. Therefore, when postulating the reaction mechanism, researchers usually prefer to operate with the really available terminal or bridging lattice oxygen rather than with a quite exotic radical O^-. However, it is worth noting that sometimes the works appear, whose authors resort to the O^- hypothesis for providing a rational explanation of their experimental results. This relates mainly to the hydrogen abstraction step at oxidative activation of alkenes [36–38] and oxidative dimidiation of methane [14,39]. But these infrequent works do not change the situation significantly. Therefore, one may conclude that the radical oxygen idea is not being generally recognized in selective oxidation catalysis.

Recently, convincing arguments were obtained for the involvement of O^- in selective oxidation over FeZSM-5 zeolites. These results will be considered further.

3. Oxidation over FeZSM-5 with N_2O

Zeolites are particular class of crystal silica-based materials, having an intracrystalline micropore system of molecular size. Being of poor efficiency with dioxygen, zeolites may exhibit remarkable catalytic performance if monooxygen donors are used as an oxidant. Two most known examples are titanosilicates TS-1, which are excellent catalysts for the liquid phase oxidation with hydrogen peroxide [40–42] and iron-modified zeolites FeZSM-5 for the gas phase oxidation with N_2O [43,44]. Over the latter zeolites, direct oxidation of benzene to phenol:

$$C_6H_6 + N_2O = C_6H_5OH + N_2 \quad (7)$$

proceeds with nearly 100% selectivity. A new process of phenol preparation (AlphOx process) was developed on this basis. The process has been successfully tested with a pilot plant [45] and commercial plant is expected.

In addition to practical importance, the FeZSM-5–N_2O system appeared to be a very convenient model for studying the oxidation mechanism.

3.1. α-Sites and α-oxygen

Initially iron usually exists in zeolites in a trivalent state, Fe^{3+}. To transfer it into the active form, the zeolite should be activated by high-temperature calcination (600–1000 °C) in steam, vacuum or inert atmosphere. As Mössbauer spectra show [46], the activation causes dramatic changes of the state of iron, leading finally to its reduction into a special very stable bivalent state, which forms the so-called α-sites, $Fe^{3+} \rightarrow Fe_{\alpha}{}^{2+}$ [46,47].

The iron composing α-sites is not oxidized anymore by O_2, but it is readily oxidized by N_2O into the trivalent statewith deposition of the so-called α-oxygen. At temperature below 300 °C the reaction is stoichiometric and proceeds by Eq. (8):

$$N_2O + (\ \ )_{\alpha} = (O)_{\alpha} + N_2 \quad (8)$$

When all α-sites are occupied, the reaction stops. Desorption of α-oxygen into the gas phase proceeds at above 300 °C.

Concentration of α-oxygen, $C_{O_{\alpha}}$ (and hence the α-sites concentration C_{α}), can be determined by several ways [48]. For this purpose, one can measure the amount of N_2 evolved (or N_2O decomposed) by reaction (8). The isotopic exchange with dioxygen at 25–50 °C is another very convenient method:

$$({}^{16}O)_{\alpha} + {}^{18}O_2 = ({}^{18}O)_{\alpha} + {}^{16}O^{18}O \quad (9)$$

After attaining equilibrium, the isotopic balance of reaction (9) allows calculating the amount of α-oxygen. Low-temperature oxidation of CO to CO_2 by α-oxygen [49] can be also used for the purpose. All these methods usually give close results, providing a quantitative basis for studying the role of O_α in both stoichiometric and catalytic reactions.

Properties of α-oxygen were studied in many experimental [50–60] and quantum–chemical [53,61–65] works. Some characteristics are described in reviews [43,48].

3.2. Stoichiometric reactions of α-oxygen

The most important question one has to answer with the stoichiometric reactions is whether α-oxygen is really able to oxidize benzene to phenol. The most conclusive answer to this question has been given by direct stoichiometric synthesis of phenol according to the following scheme [66]:

$$N_2O + (\ )_\alpha \xrightarrow{250^\circ C} (O)_\alpha + N_2 \tag{10}$$

$$C_6H_6 + (O)_\alpha \xrightarrow{R.T.} (C_6H_6 \cdot O)_\alpha \tag{11}$$

$$(C_6H_5 \cdot O)_\alpha \xrightarrow[\text{extraction}]{R.T.} C_6H_5OH + (\ )_\alpha \tag{12}$$

This scheme includes O_α deposition by N_2O decomposition at 250 °C (Eq. (10)), its reaction with benzene at room temperature (Eq. (11)) and product extraction from the surface (Eq. (12)) followed by its chromatographic and GC–MS analysis. Only phenol was detected in the extract, which amount is around 90% of the amount of α-oxygen deposited. Similar stoichiometric experiments were carried out with methane, resulting in 90–100% yield of methanol. Isotopic experiments with $^{18}O_\alpha$ showed that it was exactly α-oxygen that forms the phenol and the methanol [67].

Later, quite a broad screening of substrates was performed on the stoichiometric oxidation by α-oxygen at room temperature, including alkanes, cycloalkanes, alkenes and aromatics [68,69] as well as CO and H_2 [49]. Analysis of the extracted products showed that in all cases with hydrocarbon substrates, selective formation of hydroxylated products was observed. The oxidation mechanism of hydrogen, methane and benzene was studied in more detail to measure kinetic isotope effects ($KIE = k_H/k_D$) and to identify the surface complexes formed.

In the case of hydrogen, KIE was measured by comparing reaction rates of H_2 and D_2 with α-oxygen [70]. In the case of methane and benzene, an intramolecular method of KIE measurement was used, when the molecules under study include both H and D isotopes, i.e., CH_2D_2 and $C_6H_3D_3$ [71]. After extraction from the surface, methanol and phenol were analyzed by the NMR and GC–MS techniques to determine their isotopic composition and calculate the KIE. The value of KIE for H_2 was found to be in the range from 3.5 to 41 depending on temperature (+25/−100 °C), and for CH_4 from 1.9 to 5.5 (+100/−50 °C). These high KIE values indicate that the rate limiting stages of both reactions include cleavage of H–H or C–H bonds.

The oxidation of benzene by α-oxygen gave quite a different result, with KIE = 1. It means that the rate limiting stage of this reaction proceeds without cleavage of C–H bond.

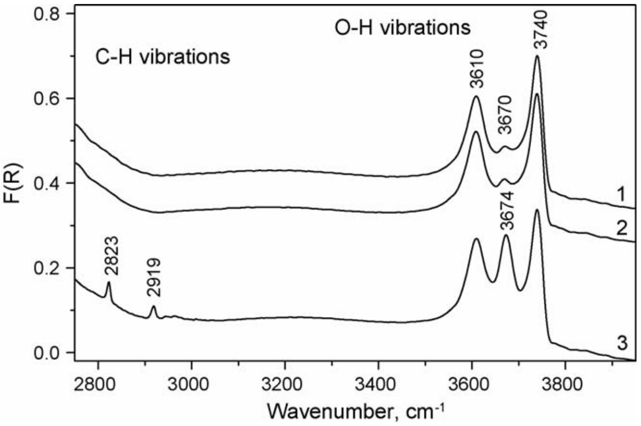


Fig. 1. IR spectra of FeZSM-5 zeolite [72]: (1) initial sample, (2) sample 1 after CH_4 adsorption and evacuation at 25 °C and (3) sample 1 after O_α deposition (1.8×10^{19} O_α/g) followed by CH_4 adsorption and evacuation at 25 °C.

The results of KIE measurements agree well with the composition of surface complexes identified by IR diffusion reflection spectroscopy upon interaction of H_2, CH_4 and C_6H_6 with O_α [70,72]. Fig. 1 presents the spectra obtained with methane. The spectrum of initial FeZSM-5 sample (spectrum 1) comprises three typical absorption bands attributed to the vibrations of OH-groups: the terminal Si–OH (3740 cm^{-1}), the bridging Al–OH–Si (3610 cm^{-1}) and OH groups bonded to the extralattice Al species (3670 cm^{-1}). Methane adsorption on this sample at room temperature is weak and reversible. Therefore, spectrum 2 taken after evacuation of methane is identical to the initial spectrum 1.

However, if CH_4 is adsorbed after preliminary deposition of α-oxygen, significant changes take place at the surface (spectrum 3). An intensive absorption band appears at 3675 cm^{-1}, indicating the formation of new OH groups. Concurrently, new absorption bands appear in the region of C–H vibrations due to formation of methoxy groups. These changes are most clearly seen in the differential spectrum (not shown), revealing the hydrogen abstraction mechanism of methane interaction with O_α:

$$CH_4 + 2O_\alpha \rightarrow CH_3O_\alpha + HO_\alpha \tag{13}$$

The same dissociative type mechanism was identified for dihydrogen [70]. This mechanism is well consistent with high KIE values observed with H_2 and CH_4 molecules.

Unlike that, benzene reaction with α-oxygen proceeds via non-dissociative mechanism and provides no formation of surface OH groups [72]. This result correlates with the absence of KIE for the oxidation of benzene. The IR spectra allow one to assume a possible formation of benzene oxide-like complexes similar to those formed at hydroxylation of aromatic compounds with enzyme monooxygenases [73].

3.3. Electronic state (the charge) of α-oxygen

As we have noted above, deposition of α-oxygen from N_2O leads to the oxidation of active iron composing α-sites from bivalent to trivalent state, $Fe_\alpha^{2+} \rightarrow Fe_\alpha^{3+}$. Consequently, α-oxygen is a charged species and can be represented by either

O^- radical or regular anion O^{2-}:

$$Fe_\alpha{}^{2+} + N_2O \rightarrow Fe_\alpha{}^{3+}O^- + N_2 \tag{14}$$

$$2Fe_\alpha{}^{2+} + N_2O \rightarrow (Fe_\alpha{}^{3+})_2O^{2-} + N_2 \tag{15}$$

As one can see from Eqs. (14) and (15), the formal charge of O_α can be determined from the stoichiometry of iron oxidation. This determination has been done by Dubkov et al. [46] using a careful comparison of two experimental values: the number of iron atoms subjected to the oxidation, $N_{Fe_\alpha{}^{2+} \rightarrow Fe_\alpha{}^{3+}}$ (Mössbauer data) and the number of α-oxygen atoms causing this oxidation, N_{O_α} (adsorption data).

Thorough measurements carried out with two ^{57}FeZSM-5 samples having different Fe content and different type of activation are presented in Table 2 [46]. With the first sample (0.14 wt% Fe) activated in vacuum, the number of deposited α-oxygen atoms is 6.5×10^{18} O_α/g. The number of iron atoms oxidized into the trivalent state is 7.0×10^{18} Fe/g. The ratio of these values, $N_{Fe_\alpha{}^{2+} \rightarrow Fe_\alpha{}^{3+}} : N_{O_\alpha}$, is 1.1. A similar comparison for the second sample (0.31 wt% Fe) after vacuum activation gives the ratio 1.2, and after steam activation 0.9. Thus, within experimental error, the average ratio equals 1, which corresponds to the stoichiometry of reaction (14). It means that α-oxygen has a mononegative charge and represents the anion radical O^-.

This conclusion was confirmed by some other independent experiments [47].

Comparison of α-oxygen characteristics with those of O^- radicals available on V, Mo and W oxides shows that their chemical properties are quite similar [48]. The both radicals exhibit a very high reactivity. The hydrogen abstraction mechanism is typical of both species in the oxidation of methane. So, inspite of being formed in different catalytic systems, radical species $O_\alpha{}^-$ and O^- exhibit identical oxidation chemistry.

3.4. *Involvement of* $O_\alpha{}^-$ *in catalytic reactions*

The above results showed that in stoichiometric reactions $O_\alpha{}^-$ is a selective oxidant, similar to O^- radicals observed on V and Mo oxides. Now we have to answer the following most important question: does α-oxygen participate in catalytic reactions? This particular question once became a stumbling block for the radical oxygen idea because of experimental difficulties with O^- on metal oxide catalysts, which did not allow one to get a conclusive answer for the reasons discussed earlier.

Unlike that, there are some significant advantages with α-oxygen on FeZSM-5. In particular, there is a known concentration of the α-sites generating $O_\alpha{}^-$. Being obtained under severe activation conditions, α-sites have a very stable structure and retain their identity at both catalytic reactions and various high-temperature treatments. This allows conducting direct experiments to verify a catalytic role of α-oxygen. One might expect a linear dependence of the reaction rate on the α-sites concentration, which would be the most convincing evidence for the $O_\alpha{}^-$ involvement.

Two catalytic reactions, i.e., N_2O decomposition and oxidation of benzene to phenol, were studied in detail over FeZSM-5 zeolites including measurements of the reaction rates and concentration of α-sites. Catalytic decomposition of nitrous oxide

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$

was studied by Sobolev et al. [74] over FeZSM-5 zeolites of silicate (Fe–Si) and alumosilicate (Fe–Al–Si) composition. The samples had widely variable concentration of both iron (from 0.003 to 4.8 wt%) and α-sites (from 1.6×10^{16} to 8.3×10^{18} site/g). Results are presented in Fig. 2. One can see that, irrespective of the zeolite matrix composition and amount of iron introduced, the reaction rate referred to the catalyst weight (W_g) increases linearly with increasing C_α values. Since W_g and C_α vary in a broad range; Fig. 2 is depicted in logarithmic coordinates.

There are several works revealing effect of α-site concentration on the catalytic oxidation of benzene to phenol by N_2O. Kharitonov et al. [75] and Pirutko et al. [76] showed that phenol productivity, starting from zero, increases with the increasing concentration of α-sites. But linear dependences were observed only at small concentrations of α-sites. At high C_α values, phenol productivity was striving to plateau because of high reagent conversions.

A linear dependence of the reaction rate in the entire range of α-site concentration was recently obtained by Chernyavsky et al. [77]. In this work, activity of various FeZSM-5 samples was measured at the same temperature under conditions providing low reagent conversions even at high C_α values, which varied from 6×10^{17} to 1.9×10^{19} site/g. For that, depending on C_α, different amount of samples was loaded into reactor so as to provide for all measurements approximately equal number of α-sites.

From results presented in Fig. 3 one can see that the reaction rate really increases linearly in the whole range of C_α values.

Table 2
Stoichiometry of iron oxidation by α-oxygen [46]

Parameters	^{57}FeZSM-5 (0.14 wt% Fe), vacuum activation at 900 °C	^{57}FeZSM-5 (0.31 wt% Fe)	
		Vacuum activation at 900 °C	Steam activation at 650 °C
Number of O_α atoms deposited, N_{O_α} (O_α/g)	6.5×10^{18}	1.3×10^{19}	1.3×10^{19}
Number of Fe atoms oxidized, $N_{Fe_\alpha{}^{2+} \rightarrow Fe_\alpha{}^{3+}}$ (Fe/g)	7.0×10^{18}	1.5×10^{19}	1.2×10^{19}
The stoichiometry, $N_{Fe_\alpha{}^{2+} \rightarrow Fe_\alpha{}^{3+}} : N_{O_\alpha}$	1.1	1.2	0.9

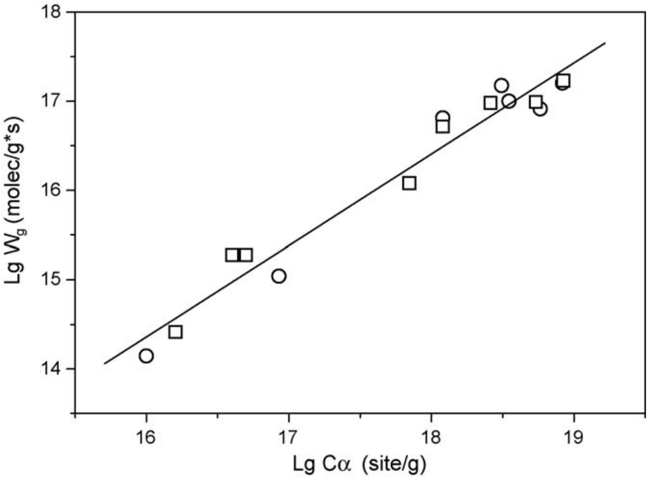


Fig. 2. Rate of catalytic decomposition of N_2O vs. concentration of α-sites for FeZSM-5 zeolites of Fe–Si (○) and Fe–Al–Si (□) composition [74].

Note that not only zeolites of Al–Si composition, but also those of B–Si and Ti–Si compositions fall on the dependence.

A similar linear dependence was obtained earlier by Yuranov et al. [50].

The presented results show convincingly that both catalytic reactions (N_2O decomposition and hydroxylation of benzene) proceed with participation of α-oxygen. One may think that this conclusion holds also for hydroxylation of other aromatic compounds over FeZSM-5 zeolites [78–82] as well as for oxidehydrogenation of low alkanes [83–85], although no measurements of α-site concentration were made in these cases. Interesting results on N_2O oxidation of methane over $FePO_4$-type catalysts to methanol and formaldehyde [14,86] may possibly relate also to this type catalysis.

4. Radical O^- in catalytic oxidation with O_2

Identification of α-oxygen as an active and selective oxidant in reactions with N_2O over zeolites stimulates more careful analysis of the literature data for revealing a possible role of O^- radicals in the oxidation with O_2 over oxide catalysts. Such reactions are quite numerous, but only a few of them are suitable for this analysis without additional mechanistic study.

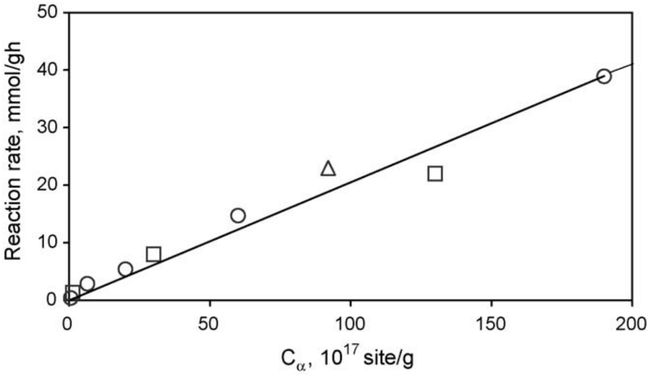


Fig. 3. Rate of catalytic oxidation of benzene to phenol by N_2O at 375 °C vs. α-site concentration for FeZSM-5 zeolites of Fe–Al–Si (○), Fe–B–Si (□) and Fe–Ti–Si (△) composition [77].

In addition to selective oxidation of methane and ethane with O_2 over V_2O_5 and MoO_3 oxides mentioned earlier [34,35], of particular interest are recent studies on oxidehydrogenation of propane carried out jointly by two research groups of Bell and Iglesia [87–95]. These works present a thorough investigation of the reaction mechanism over supported V_2O_5, MoO_3, WO_3 and Nb_2O_5 oxides. Al_2O_3, ZrO_2 and MgO were used as supports, on which active oxides were deposited in various amounts, 0.7–15 wt%.

The samples were characterized by X-ray diffraction, X-ray absorption, Raman and UV–vis spectroscopies. At these surface densities, the active oxides were shown to consist predominantly of two-dimensional oligomeric domains, which expose most MO_x species at surfaces. Due to the effective access of reactants to MO_x species, the authors can normalize the reaction rates by the number of deposited metal atoms. It allows one to present the catalytic activity in terms of turnover rates, thus providing an adequate basis for the rigorous comparison of various catalytic systems. In all cases, propane conversion was less than 2% and propene selectivity was higher than 80%.

In a concluding paper [95], analyzing the entire amount of results, the authors discovered a fundamental relationship (Fig. 4) between the turnover reaction rate of propane and the absorption edge energy (E_{ee}) of the oxides measured with diffuse reflectance UV–vis spectra. The physical meaning of E_{ee} may be interpreted as the energy needed for electron transfer from the oxygen of oxide to the metal cation. From Fig. 4 one can see that there is an exponential growth of the

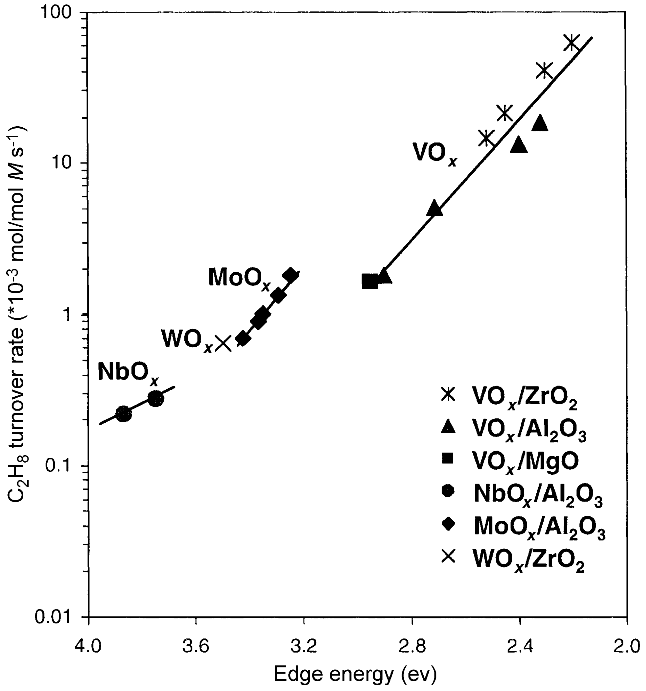


Fig. 4. Dependence of the turnover rate of propane oxidehydrogenation on the UV–vis absorption edge energy for MO_x catalysts [95]. Reproduced by permission of Elsevier.

reaction rate (within two to three orders of magnitude) with the edge energy decrease, almost irrespective of the chemical identity of the supported oxide. This result gives a safe ground to the authors [95] to conclude that the hydrogen abstraction step of propane activation involves the process of electron transfer from the lattice oxygen to metal centers. Molecular simulations for the case of V_2O_5 [91] suggest that the transfer results in one electron reduction of V^{5+} center to V^{4+}. But in another terms, it is exactly the process of O^- radical formation presented earlier by Eq. (5). Therefore, the relationship in Fig. 4 may be considered as a convincing evidence of O^- radical involvement in the selective oxidation of propane by O_2 over metal oxides.

A qualitative effect of the absorption edge energy on catalytic activity of metal oxides was also noted earlier by Krylov [96].

5. Conclusions

Summarizing the above analysis of the literature data, we can conclude that the present-day concept of oxidation catalysis needs some reconsideration in order to integrate the radical oxygen idea assuming an important role of O^- species in selective oxidation. In many cases this species can be considered as a powerful tool for the activation of organic molecules, thus initiating a selective oxidation route.

This idea may be not only of theoretical but also of practical importance, in particular, for preparing active and selective catalysts. The present-day concept assumes that one should exclude the presence of high-active oxygen species at the catalyst surface. Unlike that, the radical oxygen idea assumes that, having the active species available, one should exclude their multiple attack on the molecule to be oxidized. This can be done in a different way, e.g., due to a micropore system of zeolites or due to a special structure and composition of oxide catalysts. One may think that the practical value of such well-known approaches in the oxidation catalysis like the site isolation, site cooperation and remote control may relate to the fact that they assist to achieve this particular purpose.

Clearly, more mechanistic studies are needed in this field, especially related to identification of various oxygen species on the catalyst surface and their possible role in the oxidation.

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