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Journal of Catalysis 245 (2007) 466–469

JOURNAL OF CATALYSIS

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Research Note

On the involvement of radical oxygen species O^- in catalytic oxidation of benzene to phenol by nitrous oxide

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Received 13 July 2006; revised 23 October 2006; accepted 26 October 2006

Abstract

Catalytic oxidation of benzene to phenol by nitrous oxide over Fe-MFI zeolites was studied in relation to the active oxygen species taking part in the oxidation. A linear dependence of the reaction rate on the concentration of independently identified active sites generating O^- radicals (α sites) was obtained within a broad range of values. The dependence is interpreted as convincing evidence of the O^- involvement in the catalytic (not only stoichiometric) oxidation of benzene to phenol. This conclusion is of particular importance in connection with a long discussion in the literature on a possible role of O^- radicals in selective oxidation catalysis over V and Mo oxides. Reliable evidence of the catalytic role of O^- obtained with zeolites may renew general interest in the once-suggested but not recognized role of radical oxygen in oxidation over widely used metal oxide catalysts.

Keywords: Selective oxidation; N_2O; Fe-MFI; α-Oxygen; Oxygen radicals; Benzene to phenol oxidation

1. Introduction

It is generally understood that identification of catalytically active sites may provide breakthrough progress in understanding the mechanism of catalysis. But this approach involves significant experimental difficulties. Therefore, despite much effort, the number of catalytic reactions, which were quantitatively correlated with the identified active sites, is very small and limited to several reactions of the acidic type [1–3]. This problem is particularly difficult for selective oxidation catalysis, which is conducted mainly over vanadium- and molybdenum-based oxide systems [4–8]. The chemical composition of these systems is quite labile and may readily vary with changing reaction conditions, making the situation especially unfavorable for experimental studies.

In this connection, of great interest are Fe-containing MFI zeolites that perform the oxidation of benzene to phenol by nitrous oxide (BTOP reaction) with a very high selectivity,

$$C_6H_6 + N_2O \rightarrow C_6H_5OH + N_2. \quad (1)$$

This reaction has been the subject of many experimental and theoretical studies [9–15]; many recent results were published in a special issue of *Catalysis Today* [16]. Mössbauer spectroscopy has proven to be a particularly efficient technique for investigating the iron state in zeolites; it provides evidence that the active sites of Fe-MFI zeolites (alpha sites) are extralattice complexes of bivalent iron capable of redox transformation of $Fe^{2+} \leftrightarrow Fe^{3+}$ in the presence of N_2O [17–21]. On N_2O dissociation, these sites generate a radical form of surface oxygen O^-, designated as O_α^- (alpha-oxygen). Similar to O^- radicals on V and Mo oxides [22], O_α^- on Fe-MFI exhibits very high reactivity, which strongly distinguishes it from the rest oxygen of a zeolite catalyst, thus allowing reliable identification and quantification of α-oxygen and α sites. At room tempera-

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2006.10.023

Table 1
Catalytic properties of Fe-containing MFI zeolites of alumosilicate (AS), borosilicate (BS) and titanosilicate (TS) composition[a]

	Sample	C_{Fe} (wt%)	C_α (10^{17} sites/g)	g_{cat} (g)	N_α (10^{17} sites)	Conversion (mol%)		Reaction rate		
						C_6H_6	N_2O	R_g (mmol/(g h))	R_{Fe} (10^{-19} mmol/(Fe h))	R_α (10^{-19} mmol/(site h))
1	Fe-AS (0.006)	0.006	0.6	1.05	0.63	0.3	2.6	0.4	6.3	63
2	Fe-AS (0.03)	0.03	6.5	1.03	6.7	1.4	15	2.3	7.2	36
3	Fe-AS (0.05)	0.05	20	0.34	6.7	1.2	12	5.4	10.0	27
4	Fe-AS (0.06)	0.06	22	0.30	6.8	1.5	16	8.0	12.5	36
5	Fe-AS (0.18)	0.19	60	0.11	6.8	1.1	12	15	7.5	25
6	Fe-AS (0.53)	0.53	190	0.04	6.8	1.0	12	42	7.4	22
7	Fe-BS (1.0)	1.0	30.0	0.22	6.7	1.1	13	8.0	0.7	27
8	Fe-BS (2.5)	2.5	130	0.05	7.0	0.9	11	28	1.0	22
9	Fe-TS (0.95)	0.95	55.0	0.12	6.7	1.2	13	15	1.5	27
10	Fe-TS (1.8)	1.8	92.0	0.08	7.2	1.1	13	23	1.2	25

[a] Reaction conditions: feed mixture: 5.5 mol% N_2O, 50 mol% C_6H_6, helium balance; space rate 2 ccm/s; reaction temperature 375 °C. Reagents conversions and reaction rates correspond to the reaction time of 15 min.

ture, α-oxygen can readily perform stoichiometric oxidation of various hydrocarbons, including benzene, to yield hydroxylated products [23,24].

The electronic state of α-oxygen studied in [18,25,26] is of particular interest. Dubkov et al. [18] using Mössbauer spectroscopy showed that one O_α atom performs one-electron oxidation of the active iron according to

$$Fe_\alpha^{2+} + N_2O \rightarrow Fe_\alpha^{3+}\text{–}O_\alpha^- + N_2, \tag{2}$$

which identified α-oxygen as a monocharged radical species, O_α^-. The formal charge of α-oxygen was investigated and discussed in detail by Starokon et al. [25]. A thorough quantitative study of the "autoreduction" process of the iron taking place in the course of α-site formation allowed these authors to conclude that in terms of the charge one regular oxygen anion, O^{2-}, is equivalent to two atoms of α-oxygen, thus again revealing its radical nature, O_α^-. This conclusion has been supported by theoretical calculations of Malykhin et al. [26].

The radical nature of α-oxygen has sparked great interest related to a long discussion in the literature on a possible role of O^- radicals in selective oxidation over metal oxides, and may affect the present-day mechanistic concepts of the oxidation catalysis. This situation makes particularly high demand on the conclusion cogency that α sites, generating O_α^- radicals, are precisely the sites that perform not only the stoichiometric, but also catalytic, oxidation of benzene to phenol. Some arguments for this conclusion were given in previous work [9,11, 27,28]. The most convincing additional evidence for the catalytic role of O_α^- would be a reliable linear dependence of the reaction rate on the concentration of α sites, C_α. Verifying such dependence within a broad range of C_α values is the aim of the present work.

2. Experimental

Samples for performing the BTOP experiments were selected from the previously studied iron-containing MFI zeolites [27,29]. The idea behind this selection was to provide a representative collection of samples with a wide variation of α-site concentration. The samples were prepared via hydrothermal synthesis and have the alumosilicate (AS), borosilicate (BS), and titanosilicate (TS) composition of the zeolite matrices. The previously accepted nomenclature was used to denote the samples (Table 1); for example, Fe-AS (0.05) denotes the zeolite sample of alumosilicate composition containing 0.05 wt% Fe.

The concentrations of α sites, C_α, listed in Table 1 were given previously [27,29]. The values of C_α were measured based on the amount of dinitrogen evolved in reaction (2), as well as on the amount of α oxygen $^{16}O_\alpha^-$ deposited to the surface and detected by isotopic exchange with dioxygen $^{18}O_2$, in a vacuum setup at room temperature. For the samples studied, C_α differs by more than two orders of magnitude.

Catalytic experiments were conducted in an automated-flow setup with chromatographic analysis of the gas phase. An important purpose of the work was to provide the most reliable comparison of the reaction rates for different samples, despite great differences in their BTOP activity. To avoid extrapolation, all samples were tested at the same temperature (375 °C) and with the same composition of a feed mixture (5.5 mol% N_2O, 50 mol% C_6H_6, balance helium). Depending on the value of C_α, the catalyst weight was varied from 0.04 to 1.05 g (Table 1) to provide approximately equal number of α sites, N_α, engaged in the reaction. In most cases, $N_\alpha = (6\text{–}8) \cdot 10^{17}$ sites (Table 1).

The samples were loaded into the reactor made of a quartz tube with 7 mm i.d. The volume of the loaded material in all cases was 2 cm^3. If the volume of catalyst was less than that, it was mixed with crushed quartz to bring the total volume to 2 cm^3. The only exception is sample Fe-AS (0.006), which has a very low concentration of α sites. In this case, with the volume of loaded catalyst of 2 cm^3, the value of N_α is nearly 10 times lower than in other samples.

The reaction mixture was fed at a space rate of 2 cm^3/s. Under these conditions, conversion of the reagents was quite low, $X_{C_6H_6} = 0.9\text{–}1.5\%$ for benzene and $X_{N_2O} = 11\text{–}16\%$ for nitrous oxide (Table 1). This allowed us to calculate the reaction rate using a model of differential reactor. The reaction rate normalized to the catalyst weight, R_g, was obtained by the following equation:

$$R_g = V \cdot C_{PhOH} \cdot g_{cat}^{-1}, \tag{3}$$

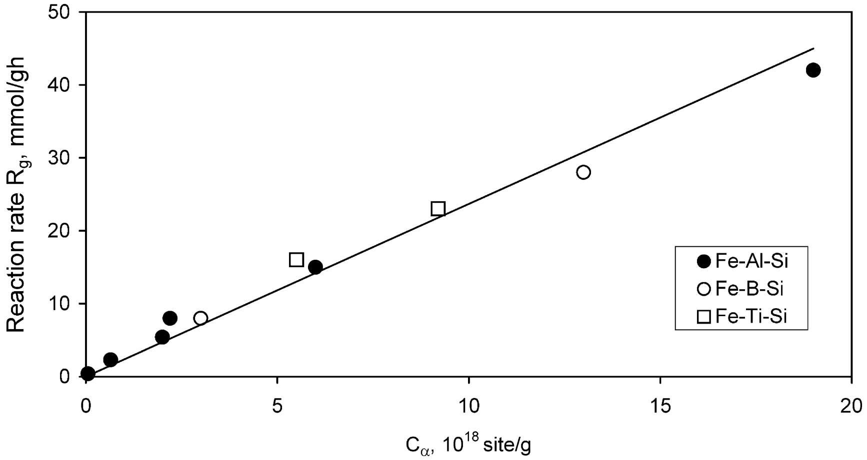

Fig. 1. The rate of benzene oxidation normalized to the catalyst weight vs α-sites concentration. (See Table 1 for reaction conditions.)

where V is the rate of a feed mixture, C_{PhOH} is the concentration of phenol at the reactor outlet, and g_{cat} is the catalyst weight. In all cases, the reaction selectivity to phenol based on benzene was >99%, and the selectivity based on N_2O was >70%. More experimental details on measuring catalytic activity are given elsewhere [29].

3. Results and discussion

Table 1 shows BTOP reaction rates normalized to various characteristics of the samples: the weight of catalyst (R_g), the number of iron atoms (R_{Fe}), and the number of α sites (R_α). It can be seen that in each zeolite system, the value of R_g varies over a wide range and increases with increasing iron content, C_{Fe}. This is clearly seen for the zeolites of Al–Si composition, which represent the majority of the samples. Thus, Fe-AS (0.006), containing iron as a very small admixture (60 ppm), shows only a slightly noticeable activity (0.4 mmol/(g h)). Increasing C_{Fe} leads to systematic growth of the reaction rate, which for the sample Fe-AS (0.53) increases by two orders of magnitude and attains 42 mmol/(g h). Similar regularity is observed for zeolites of borosilicate and titanosilicate composition, although in these cases it is less pronounced due to the comparatively small changes in the iron content.

Unlike the R_g values, the difference in the iron atomic rate, R_{Fe}, is much smaller and does not exceed twofold for each zeolite system. However, for matrices of different composition, the values of R_{Fe} differ significantly from each other. Zeolites of Al–Si composition show the greatest R_{Fe} values, falling within the range of $(6.3\text{–}12.5) \cdot 10^{-19}$ mmol/(Fe h), which is approximately an order of magnitude greater as compared to the atomic rate of iron in the B–Si and Ti–Si matrices. This difference is due to the fact that the reaction rate actually depends not on the total content of iron, but only on its active fraction represented by α sites. The fraction of active iron varies significantly, depending on the efficiency of α site formation in different matrices, as thoroughly studied by Pirutko et al. [27].

Indeed, being normalized to the number of α sites, the reaction rate R_α appears to be nearly the same for all samples, irrespective of the zeolite matrix composition, and falls within the range of $(22\text{–}36) \cdot 10^{-19}$ mmol/(site h). This corresponds to the turnover rate at a single α site, 0.4–0.6 s^{-1}. The exception to this is Fe-AS (0.006), with activity approximately twofold that other samples. This somewhat falling out value, which possibly goes beyond the limits of experimental error, may be explained by insufficient accuracy of measuring both the low concentration of α sites and the low reaction rate for this sample.

The constancy of R_α indicates that BTOP reaction is catalyzed precisely by α sites. This is shown most clearly in Fig. 1, which presents the results in a graphic form. We can see that the reaction rate R_g normalized to the catalyst weight increases linearly with increasing α site concentration within the entire range of C_α values. This dependence provides convincing evidence that not only stoichiometric oxidation of benzene to phenol at room temperature, but also its steady-state catalytic oxidation at high temperature proceed with participation of O_α^- oxygen species.

A relationship between the rate of BTOP reaction and the concentration of active iron in Fe-MFI was studied earlier by Yuranov et al. [28]. These authors also discovered a linear dependence similar to the one shown in Fig. 1.

Surface radicals, O^-, were discovered several decades ago on adsorption of O_2 or N_2O on preliminary reduced V and Mo oxides. The possibility of observing the radicals by the ESR technique and an idea of their probable involvement in catalytic oxidation stimulated intensive studies over the last century [30–33]. It was found that stoichiometric reactions of O^- radicals at room temperature leads to the formation of selective oxidation products on the catalyst surface [34–37]. However, the role of O^- in steady-state catalytic reactions appears to be a difficult experimental problem, and no conclusive results have been obtained. Therefore, the radical oxygen idea has not been recognized in selective oxidation. The current concept assumes that the reaction involves strongly bonded lattice oxygen of an oxide catalyst in the form of either terminal (M=O) or bridging species (M–O–M) [4–8,38]. This concept is supported by many experimental results, which, however, do not exclude preliminary transformation of the lattice oxygen into a much more reactive radical species. In particular, this may occur due to thermal activation of electron transfer from the oxygen to metal cation [22,34],

$$M^{n+}{=}O \rightarrow M^{(n-1)+}{-}O^{-}. \tag{4}$$

Insufficiency of the lattice oxygen concept is periodically noted in the literature, and has been discussed in more detail in a recent paper [39]. To rationalize experimental results, the researchers should admit a hypothesis of O^- involvement. Among recent examples, one may mention papers by Grasselli [40], Millet and co-workers [41,42], and some other authors. One may think that identification of the catalytic role of O^- radicals obtained in the present work with zeolite catalysts will renew general interest in the radical oxygen idea and stimulate new mechanistic studies of selective oxidation reactions over classic oxide catalysts.

Acknowledgments

The authors thank Dr. E. Starokon for useful discussions and comments. They also gratefully acknowledge financial support from the Russian Foundation for Basic Research (project 06-03-72551-CNRSL_a).

References

[1] D.H. Olson, W.O. Haag, R.M. Lago, J. Catal. 61 (1980) 390.
[2] S.J. DeCanio, J.R. Sohn, P.O. Fritz, J.H. Lunsford, J. Catal. 101 (1986) 132.
[3] F.H. Ribeiro, A.E. Schoch von Wittenau, C.H. Bartholomew, G.A. Somorjai, Catal. Rev. Sci. Eng. 39 (1997) 49.
[4] G.I. Golodets, Heterogeneous Catalytic Reactions Involving Molecular Oxygen, Stud. Surf. Sci. Catal., vol. 15, Elsevier, Amsterdam, 1983.
[5] R.K. Grasselli, in: G. Ertl, H. Knösinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 5, Wiley–VCH, New York, 1997, p. 2307.
[6] G. Centi, F. Cavani, F. Trifiro, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic/Plenum Publishers, New York, 2001.
[7] G.K. Boreskov, Heterogeneous Catalysis, Nova Science Publishers Inc., New York, 2003.
[8] O.V. Krylov, Heterogeneous Catalysis, Akademkniga, Moscow, 2004 [in Russian].
[9] G.I. Panov, A.S. Kharitonov, V.I. Sobolev, Appl. Catal. A Gen. 98 (1993) 1.
[10] A. Reizman, M. Häfele, G. Emig, Trends Chem. Eng. 3 (1996) 63.
[11] G. Panov, A. Uriarte, M. Rodkin, V. Sobolev, Catal. Today 4 (1998) 365.
[12] G. Centi, S. Perathoner, F. Vazzana, CHEMTECH (1999) 48.
[13] G. Panov, CATTECH 4 (2000) 18.
[14] A. Leontiev, O. Fomicheva, M. Proskurina, N. Zefirov, Usp. Khim. 70 (2001) 107.
[15] V.N. Parmon, G.I. Panov, A.K. Uriarte, A.S. Noskov, Catal. Today 100 (2005) 115.
[16] E. Hensen, B. Weckhuysen, F. Kapteijn (Eds.), Catal. Today 110 (2005), p. 228.
[17] N.S. Ovanesyan, A.A. Shteinman, K.A. Dubkov, V.I. Sobolev, G.I. Panov, Kinet. Katal. 39 (1998) 792.
[18] K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon, G.I. Panov, J. Catal. 207 (2002) 341.
[19] E.J.M. Hensen, Q. Zhu, M.M.R.M. Hendrix, A.R. Overweg, P.J. Kooyman, M.V. Sychev, R.A. van Santen, J. Catal. 221 (2004) 560.
[20] J.B. Taboada, A.R. Overweg, P.J. Kooyman, I.W.C.E. Arends, G. Mul, J. Catal. 231 (2005) 56.
[21] K. Lazar, A. Szegedi, G. Pal-Borbely, A.N. Kotasthane, P. Fejes, Catal. Today 110 (2005) 239.
[22] M. Che, A.J. Tench, Adv. Catal. 32 (1983) 1.
[23] K.A. Dubkov, V.I. Sobolev, E.P. Talsi, M.A. Rodkin, N.H. Watkins, A.A. Steinman, G.I. Panov, J. Mol. Catal. A Chem. 123 (1997) 155.
[24] M.A. Rodkin, V.I. Sobolev, K.A. Dubkov, N.H. Watkins, G.I. Panov, Stud. Surf. Sci. Catal. 130 (2000) 875.
[25] E.V. Starokon, K.A. Dubkov, L.V. Pirutko, G.I. Panov, Top. Catal. 23 (2003) 137.
[26] S.E. Malykhin, I.L. Zilberberg, G.M. Zhidomirov, Chem. Phys. Lett. 414 (2005) 434.
[27] L.V. Pirutko, V.S. Chernyavsky, A.K. Uriarte, G.I. Panov, Appl. Catal. A Gen. 227 (2002) 143.
[28] I. Yuranov, Z. Bulushev, A. Renken, L. Kiwi-Minsker, J. Catal. 227 (2004) 138.
[29] L.V. Pirutko, A.K. Uriarte, V.S. Chernyavsky, A.S. Kharitonov, G.I. Panov, Microporous Mesoporous Mater. 48 (2001) 345.
[30] V.B. Kazansky, Kinet. Catal. 14 (1973) 95.
[31] J.H. Lunsford, Catal. Rev. 8 (1973) 135.
[32] M. Che, A.J. Tench, Adv. Catal. 31 (1982) 77;
M. Che, A.J. Tench, Adv. Catal. 32 (1983) 1.
[33] Z. Sojka, Catal. Rev. Sci. Eng. 37 (1995) 461.
[34] M.B. Ward, M.J. Lin, J.H. Lunsford, J. Catal. 50 (1977) 306.
[35] R. Liu, M. Iwamoto, J.H. Lunsford, J. Chem. Soc. Chem. Commun. (1982) 78.
[36] A. Goto, K. Aika, Bull. Chem. Soc. Jpn. 7 (1998) 95.
[37] M. Iwamoto, I. Hirata, K. Matsukami, S. Kagawa, J. Phys. Chem. 87 (1983) 903.
[38] J. Haber, E. Latic, Catal. Today 33 (1997) 119.
[39] G.I. Panov, K.A. Dubkov, E.V. Starokon, Catal. Today 117 (2006) 148.
[40] R.K. Grasselli, Catal. Today 99 (2005) 23.
[41] I.C. Marcu, J.M.M. Millet, J.M. Herrmann, Catal. Lett. 78 (2002) 273.
[42] J.M.M. Millet, I.C. Marcu, J.M. Herrmann, J. Mol. Catal. A Chem. 226 (2005) 111.