Kinetics and Catalysis, Vol. 41, No. 6, 2000, pp. 771–775. Translated from Kinetika i Kataliz, Vol. 41, No. 6, 2000, pp. 850–854.
Original Russian Text Copyright © 2000 by Ivanov, Rodkin, Dubkov, Kharitonov, Panov.

Mechanism of Coke Influence on the Catalytic Activity of FeZSM-5 in the Reaction of Benzene Oxidation into Phenol

D. P. Ivanov*, M. A. Rodkin, K. A. Dubkov*, A. S. Kharitonov*, and G. I. Panov***

** Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

*** Solutia Inc., Gonzales, Florida, USA*

Received April 7, 1999

Abstract—The influence of coke formation in the reaction of benzene oxidation by nitrous oxide into phenol on the catalytic activity and concentration of iron-containing active sites (α-sites), which are stabilized in the microporous structure of FeZSM-5 zeolite, is studied. The deactivation by coke is explained by the poisoning of α-sites, whose concentration decreases linearly with an increase in the coke content, rather than by the blocking of zeolite pores. The activity per one α-site remains unchanged. This fact indicates the absence of diffusion limitations associated with coke formation. The toxicity of coke for the α-sites is determined. The coke amount equivalent to 100–120 benzene molecules is shown to result in the deactivation of one active site.

INTRODUCTION

The reaction of benzene oxidation with nitrous oxide is of a significant interest for both academic scientists and chemical companies [1–5] as a one-step process of phenol production:

$$C_6H_6 + N_2O \longrightarrow C_6H_5OH + N_2. \qquad \text{(I)}$$

Iron-containing pentasil-type zeolites as the catalysts enable the process with a selectivity of about 100%. Solutia Company and the Institute of Catalysis, (Siberian Division, Russian Academy of Sciences) developed a new technology of phenol synthesis on the basis of such catalysts, and this process is considered as a potential alternative to the three-stage cumene process [6, 7]. The investigation of the mechanism of this reaction has shown that the catalytic properties of zeolites are related to the presence of so-called α-sites, which represent iron complexes stabilized in the micropores of the zeolite matrix [8, 9]. The decomposition of N_2O on the α-sites leads to the formation of active surface oxygen species (α-oxygen), which further take part in reaction (I) [10].

Benzene oxidation into phenol has been shown by many authors [11–15] to be accompanied by coke formation, which leads to a gradual decrease in the catalytic activity of the zeolite. The elucidation of the mechanism of coke formation and its deactivating influence is important for the enhancement of the catalyst stability. It is known that, depending on the catalyst composition and type of the reaction, the mechanisms of deactivation by coke are very different. That is why the elucidation of the real mechanism is not easy [16, 17]. In our case, the solution to this problem is simplified by the fact that α-sites, which are responsible for benzene oxidation into phenol, can be reliably identified and quantitatively determined.

In this work, we use a method based on the measurement of the concentration of α-sites in coked samples to relate catalyst deactivation with direct coke influence on the concentration of α-sites.

EXPERIMENTAL

NaZSM-5 zeolite manufactured by Angarsknefteorgsintez was used as a catalyst. The zeolite was converted into the *H*-form by ion exchange with an NH_4Cl solution with further calcination of the sample. The chemical composition of the *H*-form of the zeolite ZSM-5 and its textural characteristics (external surface area S_{ext} and microporous volume V_μ) are given below:

Chemical composition			Textural characteristics	
Si/Al	[Fe], wt %	[Na], wt %	S_{ext}, m^2/g	V_μ, cm^3/g
21	0.08	0.02	37	0.135

The reaction of benzene oxidation into phenol was studied using a fixed-bed, automatically controlled unit at 400°C. The catalyst fraction 0.5–1 mm was placed into the quartz reactor with an inner diameter of 7 mm. Benzene (chemical purity grade) was fed into the evaporator using a liquid pump. Nitrous oxide (medically pure) was supplied from the metallic cylinder. Samples of the gas mixture after the reactor were taken automatically every 12 min and were analyzed by an online chromatograph. The chromatograph was equipped with flame-ionization and thermal-conductivity detectors that interfaced a computer. The detailed technique of the catalytic activity measurements is described elsewhere [18].

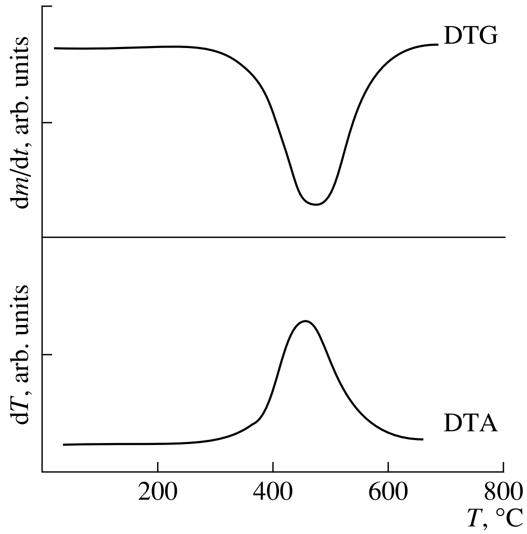

Fig. 1. Thermal gravimetric analysis of the sample containing 1.8 wt % of coke.

To study the mechanism of catalyst deactivation, a series of samples was prepared and the concentration of α-sites was measured for each sample. The coke concentration was varied by changing the time-on-stream in the reaction (1). After the specified time, the reaction mixture was substituted for the helium flow and the temperature was increased to 450°C. The catalyst was kept at this temperature for 30 min to remove phenol and other reaction products that can easily desorb. Carbon deposits, which cannot be removed under these conditions, were considered to be coke. After purging with an inert gas, the reactor was cooled and the coked catalyst was discharged into a hermetically sealed container.

The amount of coke in the sample was determined by thermogravimetry with a Q-1500D derivatograph. The weighed sample was placed into a platinum crucible and heated in air with a heating rate of 10°C/min and changes in the temperature and weight were recorded. The sensitivity of this method to the weight changes is 5×10^{-4} g. The analysis of each sample was repeated twice to make the results more reliable.

The concentration of α-sites C_α in the samples was measured in a vacuum static unit with the mass spectrometric analysis of the gas phase [19, 20]. α-Oxygen was prepared by stoichiometric N_2O decomposition on the surface α-sites at 250°C according to the reaction

$$N_2O + (\ )_\alpha \longrightarrow (O)_\alpha + N_2. \qquad \text{(II)}$$

The concentration of α-oxygen produced was determined using isotope $(O)_\alpha$ exchange with molecular oxygen in the gas phase at room temperature:

$$({}^{16}O)_\alpha + {}^{18}O^{18}O = ({}^{18}O)_\alpha + {}^{16}O^{18}O. \qquad \text{(III)}$$

The value of C_α was calculated from the weight balance for isotope ^{18}O after attaining isotopic equilibrium in the system. Oxygen in the zeolite framework was inactive in the reaction of isotope exchange and did not affect the concentration of α-sites. The C_α value for the initial (fresh) zeolite was 2.6×10^{18} g^{-1}. This means that if we assume a binuclear structure of the α-site [8], then approximately 60% of iron atoms would be catalytically active and would compose α-sites.

RESULTS

1. The Influence of the Coke on the Catalytic Activity

Figure 1 presents typical DTG and DTA curves for coked FeZSM-5 samples. It follows from Fig. 1 that heating of the sample up to 400°C does not result in any changes. The weight decrease starts at 400°C in parallel with the appearance of the exothermic effect. This fact indicates that coke starts to burn.

The data on the coke amount and temperatures of the maximal exothermic effects T_{max} for the samples differing in the time of exposure to the reaction mixture are given in the table. Note that no matter how long the samples were exposed to the reaction conditions, the temperature of coke burning is the same for all the cases and is equal to 530°C even for the catalysts with the time of exposure differing by almost two orders of magnitude. The value of T_{max} enables us to conclude the nature of the coke, in particular on its aromaticity. The temperature of burning of nonaromatic coke for ZSM-5 zeolites falls within the interval 400–450°C, while aromatic coke burns out at a considerably higher tempera-

Coke influence on the concentration of α-sites and catalytic activity of the zeolite in the reaction of benzene oxidation into phenol

Sample	Coke content, wt %	T_{max}, °C	$C_\alpha \times 10^{-18}$, g^{-1}	Productivity to phenol, mmol g^{-1} h^{-1}
1 (initial)	0.0	–	2.6	6.3
2	0.8	528	2.0	5.1
3	1.4	528	1.6	4.1
4	1.8	531	1.3	3.6
5	2.5	532	1.0	2.5
6	3.5	528	0.4	1.8

ture [21]. It is quite natural to suggest that, in our case, coke formed by benzene conversion is aromatic and has a higher burning temperature. It is seen from the data on the productivity presented in the table that the coke accumulation leads to a considerable decrease in catalytic activity. A coke content of 3.5 wt % results in more than 70% catalyst deactivation.

2. *Influence of Coke on the Concentration of α-Sites*

According to the data of Moesbauer spectroscopy [22, 23] and quantum-chemical calculations [24, 25], α-sites are binuclear iron complexes stabilized in the micropores of the zeolite matrix. Such complexes are easily oxidized by nitrous oxide. The reaction is accompanied by α-oxygen formation and $Fe^{2+} \longrightarrow Fe^{3+}$ transition.

α-Oxygen possesses an enhanced reactivity. It takes part in isotope exchange even at room temperature and oxidizes various hydrocarbons (including methane) to form hydroxyl-containing compounds [1, 9]. α-Oxygen participates in benzene oxidation into phenol [10].

The concentration of α-sites (C_α) in the investigated samples is presented in the table. The dependence of C_α on the coke concentration in the samples, which is given in Fig. 2, was plotted using these data. This dependence is rather simple: the growth of the coke content leads to a linear decrease in the concentration of α-sites according to the equation

$$C_\alpha = C_\alpha^0 - bC_{\text{coke}}. \qquad (1)$$

Here, C_α^0 is the concentration of α-sites in the initial sample, C_{coke} is the current coke concentration, and b is a correlation coefficient. At a coke content of 3.5%, the concentration of α-sites decreases ~6 times. A further growth of the coke content up to 4–4.5% results in a decrease in C_α to zero.

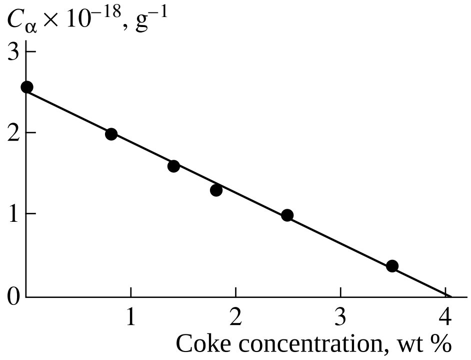

Fig. 2. Influence of the coke amount on the concentration of α-sites in FeZSM-5 zeolite.

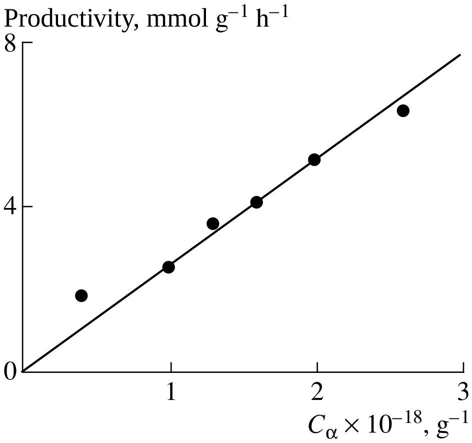

Fig. 3. Dependence of the productivity to phenol for coked ZSM-5 zeolites on the concentration of α-sites.

DISCUSSION

A decrease in C_α caused by coke accumulation is expected to lead to a decrease in the catalytic activity of the zeolite. Figure 3 shows the dependence of the productivity of the catalysts based on phenol (G_{PhOH}) on the concentration of α-sites, which was obtained from the data presented in the table. The value of G_{PhOH} changes in proportion to the concentration of α-sites:

$$G_{\text{PhOH}} = G_{\text{PhOH}}^{\text{sp}} C_\alpha, \qquad (2)$$

where $G_{\text{PhOH}}^{\text{sp}}$ is the productivity based on phenol per one active site. The value $G_{\text{PhOH}}^{\text{sp}} = 2.5 \times 10^{-18}$ mmol/site, which is obtained for the given reaction conditions, corresponds to a turnover frequency of 0.42 s^{-1}. The productivity based on phenol for the case of complete deactivation of α-sites is equal to zero, and the reaction stops. In Fig. 3, the position of the first point outside of the linear dependence and close to the origin of coordinates is probably associated with an insufficient accuracy in the measurements of the low concentrations of C_α and G_{PhOH} in the case of the most deactivated sample.

The linear dependence of the productivity on the concentration of α-sites enables us to draw some important conclusions on the mechanism of deactivation and the role of diffusion. The deactivating influence of coke is very often associated with diffusional constraints as a result of the molecular motion restrictions in the microporous structure of the coked zeolites [26, 27]. The fact that the activity of one α-site in the oxidation of benzene into phenol is constant, whereas the total activity decreases several times, indicates that the deactivating influence of coke in our case is associated with the poisoning of active sites and impossibility of their participation in the catalytic reaction, but not with diffusion limitations.

The most intensive deactivation of the catalysts often occurs at the starting period of time and then the

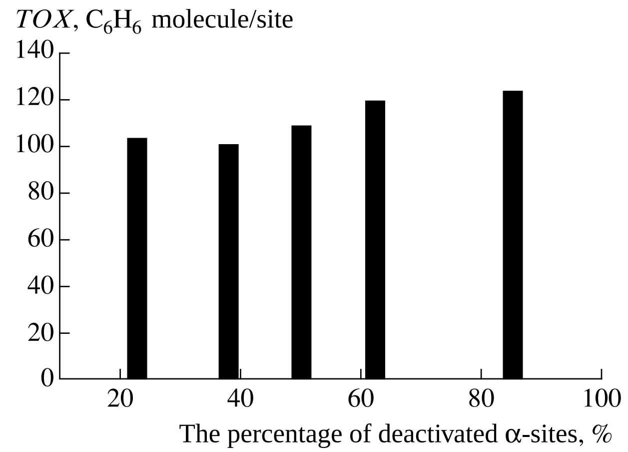

Fig. 4. Dependence of the coke toxicity (*TOX*) on the zeolite deactivation degree.

deactivation rate decreases with coke accumulation. This may be a result of a stronger toxicity of the first portion of coke, which poisons the most active catalytic sites [28]. The data presented in the table enable us to quantitatively characterize the toxicity of coke and to trace its dependence on the degree of the catalyst deactivation. Let us define toxicity as the amount of coke, which is necessary for the deactivation of one active site of the catalyst:

$$TOX = \frac{C_{\text{coke}}}{(C_\alpha^0 - C_\alpha)}. \qquad (3)$$

To assign a clearer physical meaning to the toxicity parameter, let us assume that a benzene molecule is a structural unit of coke. Compared to benzene, coke contains less hydrogen and may contain some amount of oxygen. Nevertheless, this does not affect the results and may introduce only a small quantitative correction.

Figure 4 illustrates the dependence of coke toxicity on the degree of catalyst deactivation. The value of *TOX* slightly increases in the course of coke accumulation and can be considered constant to a first approximation. As it is seen from Fig. 4, the conversion of 100 to 120 benzene molecules to coke leads to the deactivation of one α-site regardless of the total degree of catalyst deactivation. This indicates that the mechanism of coke formation, as well as the mechanism of its deactivating influence, remains the same during the whole process.

Coke deposition is generally known to proceed both at the outer and inner (microporous) surfaces of a zeolite. The deactivating influence of coke deposited on the outer surface can be associated with the deactivation of active sites, which are localized on the outer surface and, after the concentration of coke attains some critical value, with the blocking of the pore entrances, which complicates the diffusion of molecules into the volume of the zeolite [28]. Taking into account that active α-sites are localized in the micropores of the zeolite and that diffusion to these sites is not limited, then the deactivating effect should be induced by the coke, which is accumulated on the inner surface of the zeolite. The linear diminution of C_α with increasing coke content testifies that there is no blocking of the microporous structure. Otherwise, attaining of some critical concentration of coke would result in the deactivation of a significant part of the α-sites, which are located in the blocked space. It is unlikely, in this case, for the dependence presented in Fig. 2 to be linear.

ACKNOWLEDGMENTS

The authors are grateful to A.A. Ivanov for his participation in the discussion of the results and to G.S. Litvak for the thermal gravimetric analyses. The authors also would like to thank Solutia for financial support and for the permission to publish this article.

REFERENCES

1. Kharitonov, A.S., Sobolev, V.I., and Panov, G.I., *Usp. Khim.*, 1992, vol. 61, no. 11, p. 2062.
2. Burch, R. and Howitt, C., *Appl. Catal., A*, 1993, vol. 103, no. 1, p. 135.
3. Yoo, J.S., Sahail, A.R., Grimmer, S.S., and Choi-Feng, C., *Catal. Lett.*, 1994, vol. 29, p. 299.
4. Häfele, M., Reitzmann, A., Klemm, E., and Emig, G., *Stud. Surf. Sci. Catal.*, 1998, vol. 110, p. 847.
5. FRG Patent no. 19634406 A1.
6. Mc Coy, M., *Chem. Market Reporter*, 1996, vol. 250, no. 27, p. 1.
7. Uriarte, A.K., Rodkin, M.A., Gross, M.J., *et al.*, *Stud. Surf. Sci. Catal.*, 1998, vol. 110, p. 857.
8. Ovanesyan, N.S., Sobolev, V.I., Dubkov, K.A., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 6, p. 1583.
9. Panov, G.I., Sobolev, V.I., Dubkov, K.A., and Kharitonov, A.S., *Stud. Surf. Sci. Catal.*, 1996, vol. 101, p. 493.
10. Kharitonov, A.S., Aleksandrova, T.N., Panov, G.I., *et al.*, *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 296.
11. Burch, R. and Howitt, C., *Appl. Catal., A*, 1993, vol. 106, no. 1, p. 167.
12. Ranov, G.I., Kharitonov, A.S., and Sobolev, V.I., *Appl. Catal., A*, 1993, vol. 98, no. 1, p. 1.
13. Motz, J.L., Heinichem, H., and Hölderich, W.F., *J. Mol. Catal. A: Chem.*, 1998, vol. 136, no. 1, p. 175.
14. Häfele, M., Reitzmann, A., Roppelt, D., and Emig, G., *Appl. Catal., A*, 1997, vol. 150, no. 1, p. 153.
15. Vereshagin, S.N., Kirik, N.P., Shishkina, N.N., and Anshits, A.G., *Catal. Lett.*, 1998, vol. 56, p. 145.
16. Buyanov, R.A., *Zakoksovanie katalizatorov* (Catalyst Coking), Moscow: Nauka, 1983, p. 207.
17. *Catalyst Deactivation*, Delmon, B. and Froment, G.F., Eds., *Stud. Surf. Sci. Catal.*, 1994, vol. 88.
18. Sheveleva, G.A., Kharitonov, A.S., Panov, G.I., *et al.*, *Neftekhimiya*, 1993, vol. 33, no. 6, p. 531.

19. Dubkov, K.A., Sobolev, V.I., and Panov, G.I., *Kinet. Katal.*, 1998, vol. 39, no. 1, p. 79.
20. Panov, G.I., Sobolev, V.I., and Kharitonov, A.S., *J. Mol. Catal.*, 1990, vol. 61, no. 1, p. 85.
21. Slinkin, A.A., Bragina, G.O., Nissenbaum, V.N., and Kucherov, A.V., *Kinet. Katal.*, 1995, vol. 36, no. 3, p. 44.
22. Ovanesyan, N.S., Sobolev, V.I., Dubkov, K.A., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 6, p. 1583.
23. Ovanesyan, N.S., Shteinman, A.A., Dubkov, K.A., *et al.*, *Kinet. Katal.*, 1998, vol. 39, no. 6, p. 863.
24. Filatov, M., Pelmenschikov, A., and Zhidomirov, G., *J. Mol. Catal.*, 1993, vol. 80, no. 2, p. 243.
25. Zhidomirov, G.M., Yakovlev, A.L., Milov, M.A., Kachurovskaya, N.A., and Yudanov, I.V., *Catal. Today*, 1999, vol. 51, p. 397.
26. Bhatia, S., Beltramini, J., and Do, D.D., *Catal. Rev. - Sci. Eng.*, 1990, vol. 31, no. 4, p. 431.
27. Guisnet, M. and Magnoux, P., *Catal. Today*, 1997, vol. 36, p. 477.
28. Perot, G. and Guisnet, M., *J. Mol. Catal.*, 1990, vol. 61, no. 1, p. 173.