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Hydroxylation of aromatic compounds with nitrous oxide. New possibilities of oxidative catalysis on zeolites

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ABSTRACT. Studies on the use of zeolites in partial oxidation reactions are surveyed. Attention is concentrated on recent investigations of the gas-phase oxidative hydroxylation of aromatic compounds with nitrous oxide. Best results were achieved in the study of the simplest reaction of this type—the oxidation of benzene to phenol: in the presence of iron-containing ZSM-5 zeolites, the reaction proceeds with nearly 100% selectivity and a degree of conversion of benzene of 25–30%.

Further development of this method for the introduction of hydroxy-groups may lead to new possibilities for the creation of effective technologies in the field of organic synthesis.

The bibliography includes 87 references.

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I. Introduction

Oxidation processes constitute one of the commonest classes of chemical reactions. This applies both to natural proceses, where oxygen effects a continuous turnover of chemical reactions, and in the field of technical catalysis carried out by man. The endeavour by investigators to create economically more effective and ecologically clean technologies has stimulated the search for new catalysts exhibiting a high selectivity.

Zeolites were not regarded for a long time as promising catalysts for oxidation reactions despite their wide scale and successful use in many other fields of catalysis. Considerable changes occurred in this respect during the last decade. They are associated with the creation at the beginning of the 1980s of titanosilicate zeolites having a structure of the ZSM-type and the discovery of their unique properties in oxidation reactions involving H_2O_2. The titanosilicate zeolites proved to be effective catalysts of a wide range of reactions occurring in the liquid phase, such as the oxidation of alcohols, epoxidation of alkenes, hydroxylation of aromatic compounds, and the conversion of cyclohexanone into an oxime.[1–5] The range of these reactions is being expanded and communications concerning the selective oxidation of lower paraffins to secondary and tertiary alcohols in the presence of titanosilicates have appeared.[6–8] Some of these reactions can be achieved also in the presence of other zeolites of the pentasil type.[9–11]

Whereas in the reviews of recent years these advances in liquid-phase oxidation have been assessed as one of the most important achievements in the field of organic synthesis,[12–15] the results obtained in the gas-phase oxidative catalysis on zeolites appear much more modest. The transfer of reactions to the gas phase has many technological advantages. However, the consequent increase in temperature precludes the use in this instance of hydrogen peroxide because of its vigorous uncontrolled decomposition. On the other hand, the employment of molecular oxygen, which is a traditional oxidant for heterogeneous-catalytic gas-phase reactions, has not so far led to major successes.

The partial oxidation of hydrocarbons is achieved as a rule in the presence of transition metal oxides.[16,17] Their activity is due to the more or less facile electron transfer and their capacity for the reversibility of their oxidation state on interaction with oxygen and the substance oxidised. Zeolites themselves cannot serve as active oxidation catalysts, but the possibility of their use as carriers is nevertheless of great interest. The regular structure, high surface area, and high adsorption potential create preconditions for the attainment of a wide variety of states of the deposited component. Indeed, numerous studies have shown that, after its introduction into a zeolite, a metal can have different states:[18] it can exist in the form of isolated ions in the tetrahedral positions within the zeolite lattice, as isolated cations serving as the counterions, as small clusters and associated species within the porous system, and as part of the composition of the highly disperse oxide phase distributed on the outer surface of the zeolite. Such a wide variety of forms is hardly possible in other systems and it would appear that it should lead to extensive prospects for the acceleration of various oxidation reactions.

However, studies carried out mainly in the 1970s and examined extremely fully in a monograph[19] have not on the whole justified these expectations. In many instances, the authors were able to demonstrate fairly effective reaction parameters on zeolites (for example, the epoxidation of ethylene on Ag/CaX [20] and the oxidative ammonolysis of toluene on Cu/ZSM-5 [21]), but such parameters do not attain the level ensured by the best traditional systems.

One of the causes of this is that the transition metals introduced into a zeolite matrix (particularly in the form of isolated ions) lose their activity. The decrease in the atomic catalytic activity can reach several orders of magnitude compared with massive oxides.[19] O_2 isotope exchange data have shown[22–24] that this is associated primarily with the loss of ability to activate molecular oxygen. To some extent, this result is natural bearing in mind that O_2 is

activated via its dissociative adsorption on the catalyst surface[25,26] involving the transfer of four or at least two electrons, which can be hardly readily achieved on small clusters let alone isolated metal cations.

A change in the structure of the zeolite lattice and also in the coordination environment can affect significantly the oxidative catalytic properties of cations introduced into the zeolite.[27–31] The oxidation of hydrocarbons on zeolites is frequently complicated by a number of side reactions occurring on the acid surface centres and deactivating the catalyst as a consequence of the deposition of coke.

During the last decade, the interest in gas-phase oxidation on zeolites has been maintained at an extremely low level. Analysis of the literature shows that only isolated reports concerning this aspect of research have appeared at major international conferences on zeolites and also at congresses on catalysis (Table 1). It is remarkable that not a single study devoted to gas-phase oxidation on zeolites was presented at the Symposia on "Heterogeneous Catalysis and Fine Organic Synthesis"[12] and "New Advances in Selective Oxidation".[33,34]

Table 1. Studies on gas-phase oxidation in the presence of zeolites presented at International Congresses, Conferences, and Symposia.

Location (year) of Congresses, Conferences, and Symposia	Number of studies	Refs.
Congresses on catalysis		
Tokyo (1980)	0	[32]
Berlin (1984)	2	[26]
Calgary (1988)	2	[24]
Conferences on zeolites		
Lyons (1980)	1	[35]
Reno (1983)	2	[21]
Prague (1984)	0	[36]
Portoroz (1984)	0	[37]
Tokyo (1986)	2	[2]
Wurzburg (1988)	0	[13]
Amsterdam (1989)	2	[14]
Symposia on selective oxidation		
Louvian (1986)	0	[33]
Rimini (1989)	2	[4]
Louvain (1991)	0	[34]

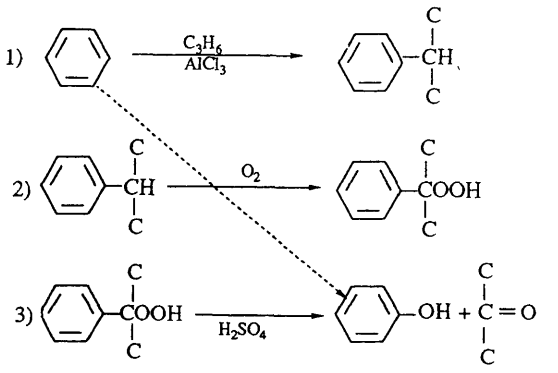
During the 1980s, a new trend arose in the field of oxidative heterogeneous catalysis. Namely it involved the use as the oxidant of not only free (molecular) oxygen but also of bound oxygen in the form of various oxygen-containing molecules.[38–45] To a large extent, this trend arose in the search for methods whereby the catalytic activation of methane and other lower paraffins could be achieved. The greatest interest among the non-traditional oxidants attaches to molecular nitrous oxide. The replacement of molecular oxygen by N_2O, including systems on zeolites,[39,40,45] frequently makes it possible to increase significantly the selectivity of the oxidation reactions.

The effective properties of nitrous oxide as a source of oxygen was manifested particularly strikingly in the study of the oxidative hydroxylation of an aromatic ring, which is a complex and difficult reaction. Studies on these lines were carried out mainly during the last 4–5 years. Although at the present stage it is difficult to reach a final assessment, nevertheless such investigations have yielded, in our view, extremely promising results and they become a basis for the creation of new ecologically clean technologies for organic synthesis and zeolites. The rest of the present review is in fact devoted to a consideration of these studies.

II. Hydroxylation of benzene in the presence of traditional catalysts

The introduction of a hydroxy-group into an aromatic ring is a difficult problem in the synthesis of organic intermediates: phenols naphthols, hydroxyamines, hydroxyacids, etc. Industrial hydroxylation procedures as a rule involve indirect multistage processes which frequently require the application of corrosive chemicals.[46,47] The simplest reaction of this type, the oxidation of benzene to phenol, is carried out via the so called cumene process comprising three stages (see the Scheme below): (1) alkylation of benzene with propene leading to the formation of isopropylbenzene (cumene); (2) oxidation of cumene to a hydroperoxide: (3) decomposition of cumenyl hydroperoxide to phenol and acetone. The first and third stages are carried out catalytically in the liquid phase using acid catalysts, which usually consist of $AlCl_3$ (stage 1) and H_2SO_4 (stage 3). Naturally this involves problems of the corrosion of the apparatus and negative environmental consequences. Furthermore, the cumene method suffers from a further disadvantage, namely the formation of each mole of phenol is accompanied by the formation of one mole of the accompanying product—acetone, which cannot always find an equivalent market for its sale because of the much smaller requirement for this product.[48] Therefore efforts have been made in numerous laboratories to seek new ways of synthesising phenol.

Scheme



The most radical procedure for the solution of this problem—the introduction of a hydroxy-group via the direct single-stage oxidation of benzene with oxygen, indicated by a dashed arrow in the Scheme, has attracted much attention by investigators. However, numerous attempts, undertaken on these lines in the course of several decades, did not lead to success. The interaction with oxygen is accompanied by the decomposition of the benzene ring and the formation of either maleic anhydride (in the presence of specially selected

catalysts) or extensive oxidation products. In the oxidation of alkylbenzenes, for example, toluene, the process involves primarily the substituent and leads to the formation of benzaldehyde or benzoic acid.[16]

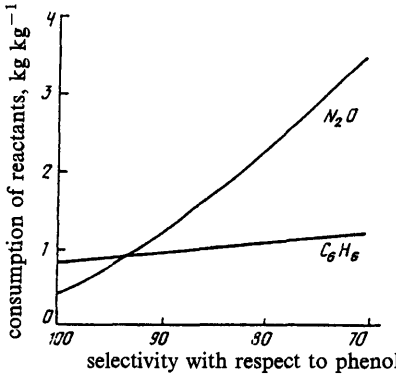


Figure 1. Consumption of benzene and nitrous oxide in the synthesis of phenol as a function of the selectivity of the oxidation of benzene to phenol.

A new reaction was discovered in 1982 — the oxidation of benzene with nitrous oxide:[49,50]

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

It made it possible to achieve a fundamentally new level of selectivity with respect to phenol. Best results were obtained in the presence of deposited vanadium, molybdenum, and tungsten oxides. At 550 °C and after the addition of 30% of H_2O to the reaction mixture, the selectivity with respect to phenol on deposited catalysts reached 71% for a benzene conversion of 10%. These results aroused lively responses,[51,52] in which the environmental safety of the new process was emphasised and extremely optimistic assessments of its practical prospects were made. Plans for pilot tests in a reactor with a fluidised catalyst bed were reported. However, the process was not realised in practice.

The parameters of the vanadium catalyst proved to be inadequate and it was not possible to find better catalysts, primarily as regards their selectivity. Selectivity is the most important parameter in partial oxidation processes. On the other hand, in processes involving N_2O, this parameter assumes a particularly great importance since, in contrast to molecular oxygen, nitrous oxide is a fairly expensive oxidant, whose cost is comparable to that of benzene. Whereas the conversion of one benzene molecule into phenol via reaction (1) requires one nitrous oxide molecule, the extensive oxidation to CO_2 and H_2O via the reaction

$$C_6H_6 + 15N_2O = 6CO_2 + 3H_2O + 15N_2, \quad (2)$$

requires 15 N_2O molecules. Fig. 1 shows that the decrease in selectivity leads not only to an increase in the consumption of benzene but, and this is particularly important, also to an increase in the consumption of nitrous oxide. For 70% selectivity, the consumption of N_2O exceeds almost by an order of magnitude the theoretical consumption corresponding to 100% selectivity. Taking this into account, one can hardly speak of the practical realisation of the process if selectivity at a level of 85–90% has not been achieved.

III. The search for new systems. Zeolites

The results of Iwamoto and co-workers[49,50] stimulated the search for new more effective catalytic systems. The reaction proved to have very stringent requirements. A large number of compounds of different chemical nature, some of which are listed in Table 2, were tested. Much attention was devoted to attempts at the improvement of vanadium catalysts, which made it possible to increase appreciably their stability.[53] However, the characteristics of vanadium catalysts could not be fundamentally improved in relation to the early investigation,[50] despite the use of different methods of preparation, the introduction of modifying additives, and the employment of various oxidants (O_2, N_2O, NO, SO_2). All the other compounds presented in Table 2 proved to be either inactive or the reaction proceeded in the direction of extensive oxidation in their presence, which is particularly characteristic of platinum group metals. Only a few catalysts yielded small amounts of phenol.

Table 2. Catalytic systems tested in the oxidation of benzene to phenol.

Systems based on V_2O_5	Systems with oxides	Systems with metals	Zeolites
		Catalysts	
V_2O_5	Al_2O_3, SiO_2	Ru/Al_2O_3,	A, X, Y
V_2O_5/SiO_2,	TiO_2, Fe_2O_3	Ag/Al_2O_3,	erionite
V_2O_5/TiO_2,	NiO, ZnO,	Ag/C,	clinoptilolite,
V-Mo-O/SiO_2,	Fe_2O_3·MoO_3,	Pd/SiO_2,	mordenite,
V-W-O/SiO_2,	NiO·Cr_2O_3,	Pd/C,	$AlPO_4$-5,
V-Cu-O/SiO_2,	Fe-Bi-Mo-P-O,	Pt/Al-Si-O	ZMS-5
V-Ti-O/SiO_2,	ZnO/SiO_2,		ZSM-11
V-Fe-O/SiO_2,	In_2O_3/SiO_2,		ZSM-5 zeolites
V-Na-O/SiO_2,	Bi_2O_3/SiO_2,		containing
V-Mg-O/SiO_2	CdO/SiO_2,		V, Cr,
	BaO/SiO_2,		Mn, Co, Ni,
	Fe_2O_3/SiO_2,		Ti, Zn, Se,
	ZnO/C		Pd, Pt
		Oxidants	
O_2, N_2O	N_2O, O_2	N_2O, O_2	N_2O_2, O_2
NO, SO_2			

The results obtained in the presence of zeolites were extremely unexpected. Table 3 presents the results of tests on certain zeolites under conditions close to those in experiments with vanadium catalysts. Evidently an appreciable amount of phenol was detected in the reaction products in a number of instances. Particularly promising results were obtained for zeolites of the type of pentasil ZSM-5 and $AlPO_4$-5. Three groups of investigators concluded independently in 1988 that ZSM-5 zeolites are extremely promising catalysts for the oxidation of benzene to phenol with nitrous oxide: Suzuki et al.[54] (Tokyo Technological Institute), Hubelman et al.[55]

(The Rhone-Poulenc Company), and Kharitonov et al.[56] (Institute of Catalysis, Novosibirsk). The zeolite catalysts made it possible to reduce the reaction temperature to 300–400 °C, to abandon the introduction of water vapour into the reaction mixture, and, what is most important, to ensure a high selectivity with respect to phenol. Although the maximum yield of phenol in these investigations was low (8–16%), it became clear that a system had been found which can serve as a basis for the creation of new effective catalysts. Further studies made it possible to improve greatly the parameters of the zeolite catalysts and to extend the range of reactions.[57–62]

Table 3. Catalytic properties of zeolites in the oxidation of benzene to phenol.

Type of zeolite	$SiO_2 : Al_2O_3$ molar ratio	Specific surface, $m^2 g^{-1}$	*X*, %	*S*, %
A	2.1	580	0.5	0
X	3.1	690	2.5	10
Y	4.8	890	6	5
Erionite	4.8	460	2.5	0
Clinoptilolite	10	80	16	0
Mordenite	14.9	620	12	0
ZSM-5	260	530	7.9	100
$AlPO_4$-5	–	300	4.5	100
Al_2O_3	–	200	11	0
SiO_2	–	190	0	–

Note. Composition of the reaction mixture (mol%); C_6H_6—5; N_2O—20; He—76; T = 500 °C; contact time 2 s; X = degree of conversion of benzene; S = selectivity with respect to phenol.

IV. The nature of the catalytic activity of zeolites

1. The role of iron

It appears unlikely that a reaction as involved and as stringent in its requirements as the oxidation of benzene to phenol could be achieved as a result of the influence of the aluminosilicate skeleton of the zeolite. According to Minachev and Kharlamov,[63] certain oxidation-reduction reactions can occur on alkali and alkaline earth metal cations forming part of the zeolite. However, in this instance all investigators emphasise the importance of the conversion of the ZSM-5 zeolite into the H-form. Indeed, as can be seen from Fig. 2, with increase in the sodium content with activity of the zeolite falls appreciably. Under these conditions, the selectivity of the reaction is unaffected and remains 100% in all cases.

It appears more natural to postulate that the activity may be associated with the presence in the zeolite of admixtures of transition metals to which no importance was attached in the first investigations. This may concern primarily iron, which is the commonest impurity introduced in the synthesis of zeolites. The influence of iron has been studied in detail.[64] For this purpose, a series of zeolite specimens with the ZSM-5 structure were synthesised. They had approximately the same $SiO_2 : Al_2O_3$ = 100 molar ratio but different iron contents, varying from 0.004 to 0.72 wt.% Fe_2O_3. The specimens of this iron-aluminosilicate series were designated by Fe(Al)-*N*, where *N* is a number indicating the content of iron expressed in wt.% Fe_2O_3.

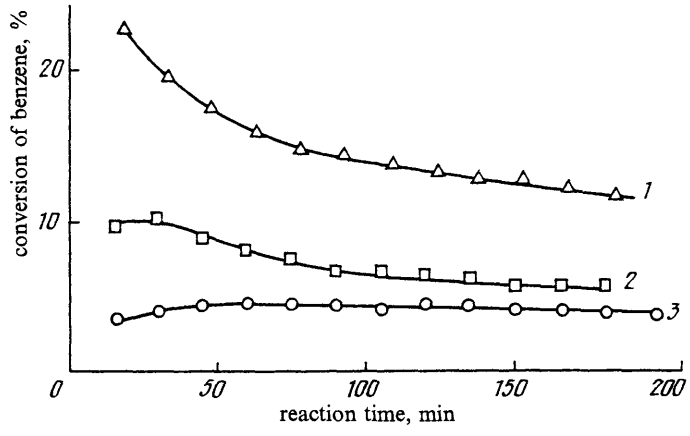


Figure 2. Dependence of the degree of conversion of benzene in the oxidation with nitrous oxide on the sodium content in the Fe(Al)-0.08 specimen (SiO_2/Al_2O_3 = 100; Fe_2O_3 = 0.08 wt.%). Na_2O content (wt.%): *1*, 0.06; *2*, 0.8; *3*, 1.1. Composition of the reaction mixture (mol%): C_6H_5—5, N_2O—20; He—75; T = 350 °C; contact time 2 s.

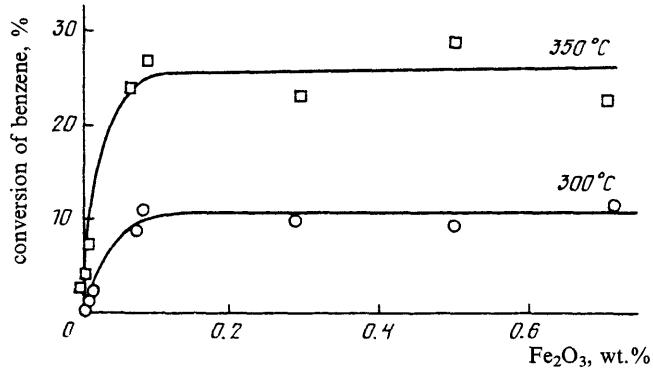


Figure 3. Dependence of the degree of conversion of benzene on the iron concentration in the Fe–Al–Si ZSM-5 zeolite specimens. The reaction conditions were the same as in Fig. 2.

Fig. 3 illustrates the dependence of the degree of conversion of benzene on the iron content in the Fe–Al–Si system plotted on the basis of the data of Panov et al.[64] Indeed, the Fe(Al)–0.004 and Fe(Al)–0.007 specimens, synthesised taking all possible precautions and virtually free of iron (0.004 and 0.007 wt.% Fe_2O_3 respectively), proved to be relatively inactive. With increase in the iron content to

0.1 wt.%, the degree of conversion of benzene increases appreciably but subsequently changes little. The Fe–Al–Si specimens containing 0.07–0.7 wt.% Fe_2O_3 exhibit such a high activity that they ensure a degree of conversion of benzene (X) at a level of 10% already at 300 °C with a selectivity with respect to phenol of 100%. At 350 °C, the degree of conversion reaches 25% for a selectivity of 95% and above on the best specimens. For higher values of X, the reaction selectivity falls owing to the further oxidation of phenol. Under these conditions, benzoquinone, catechol, hydroquinone, dibenzofuran, and cresol appear among the reaction products. The overall selectivity with respect to these substances can reach several per cent.[64]

The question of the catalytic properties of other metals is of considerable interest. Tests on specimens of the ZSM-5 zeolite containing V, Cr, Mn, Co, Ni, Cu, Ti, Zn, Sc, Pd, and Pt, which were introduced either during the synthesis of the zeolite[64] or by ion exchange,[54] showed that they are all inactive in the oxidation of benzene to phenol. It may be that iron is one of the few or even the only element capable of promoting this reaction with a high degree of efficiency. This question merits further careful study. One may note an analogy in the mechanism of the action of iron in the Fe-ZSM-5 composition and in cytochrome P-450 as well as certain artificial systems simulating its operation. These are systems which are also capable of effecting with a high degree of selectivity the oxidative hydroxylation of hydrocarbons, including the oxidation of benzene to phenol.[65]

2. The influence of aluminium

The iron introduced into the Al–Si matrix plays a decisive role in the catalytic properties of the ZSM-5 zeolite. The Fe–Al–Si specimens with the optimum iron content are greatly superior in their effectiveness to all other known catalysts, including ZSM-5 zeolites without specially added iron.[54–58] However, iron-containing zeolites with the same structure can be synthesised also in the absence of aluminium on a purely silicate base. Comparison of these two systems was of great interest from the standpoint of the influence of the chemical composition of the zeolite matrix on the catalytic properties of the added iron.

For this purpose, a study has been made[66] of a series of ZSM-5 zeolite specimens with an Fe–Si composition and a low content of the aluminium admixture (0.01–0.03 wt.% Al_2O_3) but with extensive variation of the iron content: from 0.003 to 4.8 wt.% Fe_2O_3. The formula Fe–N was used to designate these specimens. Fig. 4 shows that the influence of iron in this system is just as marked as in the Fe–Al–Si system. Thus, whereas in the presence of the Fe–0.003 specimen the oxidation of benzene with nitrous oxide occurs at a barely appreciable rate only at 500 °C, in the presence of specimens containing more than 2 wt.% Fe_2O_3 the degree of conversion of benzene reaches 25% already at 350 °C.

Although the relations illustrated in Figs. 3 and 4 are similar, attention should be drawn to the appreciable difference in the abscissa scales corresponding to the iron content. In order to represent the picture as a whole, the data concerning the influence of iron in the Fe–Si and Fe–Al–Si systems are presented in Fig.5 using logarithmic coordinates. Evidently, the relations in these two systems are appreciably displaced relative to one another in respect of the iron content. Thus, in order to attain the same degree of conversion in the case of the Fe–Si system, it is necessary to introduce 10–30 times more iron than in the Fe–Al–Si system. Conversely, for the same iron concentration, the activity of specimens containing aluminium is in many instances an order of magnitude or more higher than the activity of specimens without aluminium. Such a marked influence of aluminium suggests that the active centres for the reaction include not only Fe atoms but also Al atoms.

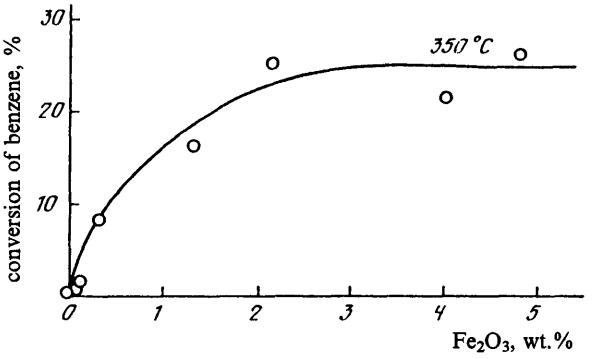


Figure 4. Dependence of the degree of conversion of benzene on the iron concentration in the Fe–Si ZSM-5 zeolite specimens. The reaction conditions were the same as in Fig. 2.

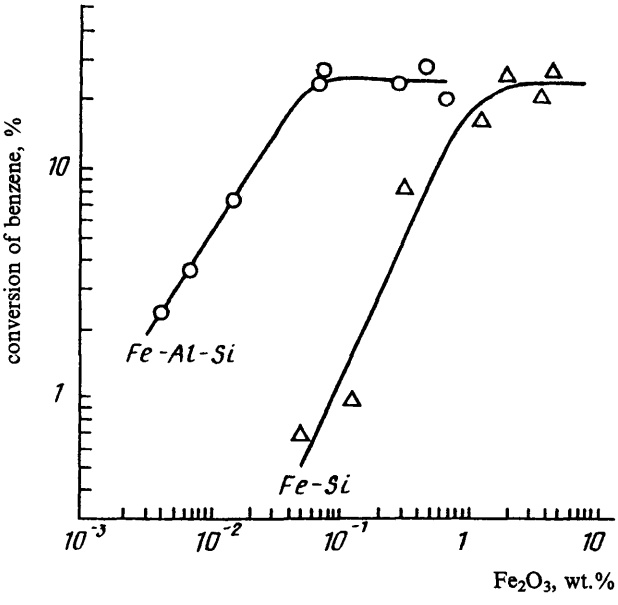


Figure 5. Dependence of the degree of conversion of benzene on the iron concentration in the Fe–Si and Fe–Al–Si ZSM-5 zeolite specimens at 350 °C. The reaction conditions were the same as Fig. 2.

This hypothesis was examined in a study[24] involving the analysis of the influence of iron on the catalytic activity of Fe-ZSM-5 specimens in the N_2O decomposition reaction. Direct comparison of

the concentration of the active centres (which can be reliably measured in these systems) with the concentration of the impurity Al atoms did not confirm this hypothesis. According to the above data,[24,66] the presence of aluminium does not affect the composition and catalytic properties of the iron-containing active centres but leads to their higher concentration as a consequence of the favourable effect of aluminium on the distribution of iron in the zeolite matrix.

V. Specific features of nitrous oxide as an oxidant. The mechanism of the hydroxylation of benzene

Iron oxide is known to exhibit a moderate activity in extensive oxidation reactions but it does not promote partial oxidation reactions.[16] The activity of the iron-containing zeolites in the oxidation of benzene to phenol therefore appears to be an extremely unexpected property of iron, manifested in the presence of nitrous oxide.

Table 4. The influence of the nature of the oxidant on the oxidation of benzene to phenol on Fe-ZSM-5 and Fe_2O_3 specimens.

Catalyst	N_2O oxidant		O_2 oxidant	
	X, %	*S*, %	*X*, %	*S*, %
Fe - 2.15	25.6	96.0	3.3	0.0
Fe(Al) - 0.08	27.0	99.0	0.0	-
Fe_2O_3	5.5	0.0	24.5	0.0

Note. Composition of the reaction mixture (mol%); C_6H_6 — 5; N_2O — 20; He — 75; T = 500 °C; contact time 2 s.

The specific features of nitrous oxide as an oxidant constitute one of the most interesting aspects of the study of the mechanism of the hydroxylation of benzene. These specific features are clearly seen on examining Table 4, which presents data for the oxidation of benzene on two typical Fe-ZSM-5 specimens with the Fe—Si and Fe—Al—Si compositions. Evidently, the replacement of nitrous oxide by molecular oxygen entails a sharp decrease in the rate of reaction. Whereas the degree of conversion of benzene on both specimens at 350 °C in the presence of N_2O is 25—27%, in the presence of O_2 and the ferrosilicate Fe—2.1 specimen it diminishes to 3% and on the ferroaluminosilicate Fe(Al)—0.08 specimen it diminishes to an infinitesimal value. [In the presence of O_2, the activity of the Fe(Al)—0.608 specimen is so low that the benzene oxidation reaction proceeds at a measurable rate only at 550 °C.] The fact that the reaction pathway changes completely under these conditions merits special attention. Instead of the formation of phenol with a selectivity of 96—99%, only total oxidation products are formed in the presence of O_2.

Such a marked influence of the nature of the oxidant justifies the hypothesis that this is associated with significant changes in the state of the surface oxygen. This stimulated a series of studies on the mechanism of the nitrous oxide decompositon reaction in the presence of the ZSM-5 zeolites,[23,24,67,68] because this particular reaction supplies oxygen to the catalyst surface. Such investigations established that the introduction of iron into the zeolite results in the formation of active centres (called α-centres), on which the decomposition of N_2O is accompanied by the formation of a new form of surface oxygen (the α-form), whose properties have been studied in detail.[23,24,67—70] The main features of this form of oxygen are that (1) it exists on iron-containing active centres of ZSM-5 but not on Fe_2O_3 and many other iron-containing specimens investigated, (2) the energy of the bond between this form of oxygen and the surface is anomalously low and close to the bond energy in the O_2 molecule, (3) is it thermally stable up to 300 °C, above which it undergoes irreversible desorption, (4) it is formed on decomposition of N_2O but not on adsorption of O_2, and (5) it is highly reactive—it participates in O_2 isotope exchange at room temperature and oxidises CO and CH_4.

α-Oxygen has been compared with the thoroughly investigated surface oxygen radical-ions O^- and O_2^-.[71] The reactivity of the α-form is close to that of the O^- radical-ion,[72—74] but it exhibits a number of significant differences which preclude the identification of these two forms of oxygen. According to Haber's classification,[26] the α-form should be regarded as an electrophilic state of surface oxygen. According to Sheveleva et al.,[66] the ability to form the α-form of surface oxygen actually accounts for the specific behaviour of N_2O as a benzene oxidant. The mechanism of formation of phenol with participation of the α-form (O) can be represented by the following stages:

(1) $N_2O + ( ) \rightarrow N_2 + (O)$,
(2) $C_6H_6 + (O) \rightarrow (C_6H_5OH)$,
(3) $(C_6H_5OH) \rightleftarrows C_6H_5OH + ( )$.

The formation of phenol is not observed in the presence of catalysts which do not contain α-oxygen. This is indicated both by the results, already mentioned, which were obtained in the presence of ZSM-5 zeolites containing different transition metals (other than iron) and the results of tests on oxide and metallic systems presented in Table 2. This is likewise confirmed by numerous unsuccessful attempts, undertaken by ourselves jointly with Krivoruchko and Skripchenko, to synthesise active catalysts by introducing iron into various non-zeolite matrices (Al_2O_3, SiO_2, TiO_2, MgO, and ZnO). Neither the existence of the α-form nor the formation of phenol were observed in any of these instances.

It has been shown[24] that the rate of decomposition of N_2O is determined by the concentration of the active centres which fix the α-form of surface oxygen, and is described by a single relation, involving direct proportionality, which is valid for all the specimens of the Fe—Si and Fe—Al—Si systems. If the mechanism of the oxidation of benzene represented by stages (1)—(3) is valid, then the above single relation should also hold for this reaction. Indeed, if the degree of conversion of benzene is represented by its dependence not on the concentration of iron (as was done in Fig. 5) but on the concentration of the active centres c_α, then we obtained a single relation for all the test specimens, which is illustrated in Fig. 6. In contrast to the decomposition of N_2O, this relation reaches a plateau at a high concentration of α-centres, which can be explained by the inhibiting effect of the reaction product—phenol.[66] Starting with a certain value of c_α, this inhibition becomes so significant that it virtually compensates for the further increase in the number of active centres.

A quantum-chemical model of the active centres, which makes it possible to account for the characteristics of α-oxygen on Fe-ZSM-5, has been described.[75]

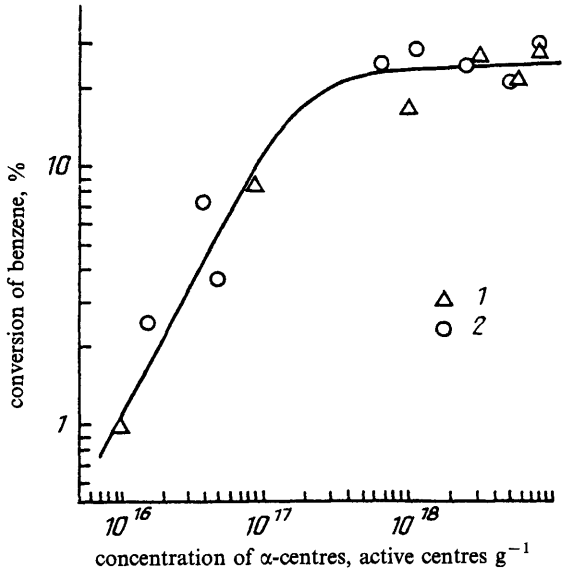


Figure 6. Dependence of the degree of conversion of benzene on the concentration of active centres on the Fe–Si and Fe–Al–Si ZSM-5 specimens at 350 °C. The reaction conditions were the same as in Fig. 2; *1*, Fe–Si; *2*, Fe–Al–Si.

Table 5. Prices of certain chemical products (USA, October, 1989).

Product	Price, U.S. dollars/tonne	Product	Price, U.S. dollars/tonne
Benzene	467	Catechol	4300
Nitrous oxide	507	Resorcinol	10000
Phenol	1091	Hydroquinone	4300

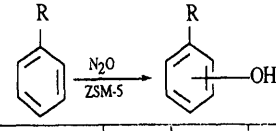
VI. Hydroxylation of benzene derivatives

The data published in the literature on the oxidation of benzene with nitrous oxide permit the conclusion that the best zeolite catalysts afford a yield of phenol up to 25–30% for a selectivity of 95–100%.[64,66] It must be admitted that, compared with numerous classical gas-phase oxidation processes, these results appear extremely modest. Thus in the oxidation of acrolein to acrylic acid[76] or of methanol to formaldehyde[77] in the presence of oxide catalysts, the yield of products reaches 95–98%. However, bearing in mind that this reaction is an alternative to the cumene process where the degree of convesion of the reactant in each of the three stages does not exceed 20–30%, the above parameters do not appear quite so bad.

According to the existing prices (Table 5), the expenditure on the raw material in the synthesis of phenol in terms of the above parameters should be 60–75% of the cost of the phenol, which can apparently ensure the competitiveness of the new process. This expenditure can be diminished somewhat by employing, instead of nitrous oxide of medical grade, a product with a lower degree of purification.

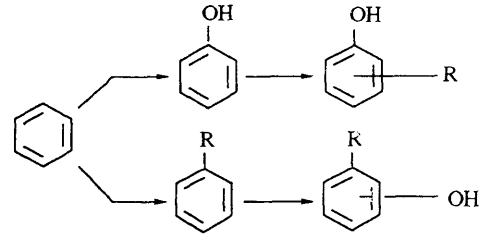
The question whether the given hydroxylation method is applicable to the preparation of more complex products which are more difficult to synthesise is important from the practical point of view. As can be seen in relation to dihydric phenols (Table 5), the cost of substituted phenols is much higher than that of phenol, so that the expenditure on nitrous oxide would no longer be significant in this case.

Table 6. Oxidative hydroxylation of benzene derivatives.



Initial compound	T, °C	X, %	S, %	Proportions of isomers, %			Refs.
				o	m	p	
Cl	330	6.7	100	58	$m \simeq p$		[54]
F	350	9.2	90.4	26.7	20.0	53.3	[55]
	400	11.0	90.4	31.1	22.7	46.2	
	450	15.2	85.3	24.4	23.7	51.9	
CH_3	350	48.1	22	$o \simeq m \simeq p$			[60]
OH	325	8.0	98	17	–	83	[60]
	350	11.5	92	18	–	82	

Two fundamentally different ways of synthesising benzene derivatives containing two substituents in the aromatic ring are possible:



These procedures differ in the sequence in which the functional groups are introduced. In view of the inadequate effectiveness of the existing hydroxylation methods, the first procedure is used nowadays in the vast majority of instances, i.e. phenol is synthesised initially and then the appropriate second group introduced with the aid of alkylation, halogenation, nitration, etc. processes.[46,47] In many cases, the processes in the second stage proceed non-selectively, require a large number of distillations, and afford a low yield of the product. For this reason, the search for effective aromatic ring hydroxylation methods, which would not involve the functional groups already introduced, is of considerable interest.

The hydroxylation of benzene derivatives with the aid of N_2O has so far been little investigated, although the possibility of such reactions in principle is not open to doubt. Table 6 presents the results of the oxidative hydroxylation of halobenzenes, toluene, and phenol. It is of interest to note that hydroxylation with the aid of nitrous oxide proceeds also when the aromatic ring contains deactivating substituents such as fluorine and chlorine, which (so far as we are aware) cannot be achieved in liquid-phase hydroxylation with the aid of peroxides.

In the oxidation of halobenzenes and toluene, hydroxylation takes place with formation of all three geometrical isomers, whereas in the oxidation of phenol, only the *o*- and *p*-isomers, i.e. catechols and hydroquinone (benzoquinone), are formed. The differences in the proportions of isomers may be associated both with the different nature of the substance oxidised and with the different chemical composition of the catalysts, the details of which are not reported in the patents.

VII. Conclusion

The earlier attempts in 1960–1970 to employ zeolites in oxidative catalysis did not yield positive results. This is because the transition metals introduced into the zeolite lose their ability to activate molecular oxygen. Although it has been possible in a number of instances to achieve effective parameters of the metal-containing zeolites, nevertheless they did not reach the level ensured by the best catalyst of the traditional type.

Studies carried out in the last decade led to a qualitative change in the situation. This was mainly promoted by two factors: the synthesis of high-silica zeolites of the type of pentasil and their metal-silicate analogues and the use of bound oxygen in the form of various oxygen-containing compounds.

The most effective among the oxygen-containing compounds proved to be H_2O_2 and N_2O. The results of the liquid-phase oxidation with hydrogen peroxide on titanosilicate zeolites are well known. They led to the development of a series of new methods for carrying out the reactions. In the present review, we attempted to draw attention to recent successes in the reactions involving gas-phase oxidation with nitrous oxide. The best parameters in this respect were achieved in the oxidation of benzene to phenol in the presence of iron-containing ZSM-5 zeolites. The uniqueness of this catalytic system is due to the existence of a specific form of surface oxygen formed on decomposition of the N_2O molecules.

Hydroxylation with the aid of nitrous oxide is particularly promising for the synthesis of complex compounds containing several functional groups in the aromatic ring. Studies on these lines are in an initial stage. The few, unfavourable data on the oxidation of benzene derivatives show that in this instance the reactions do not proceed quite so smoothly as in the oxidation of benzene itself and entail a reduced selectivity with respect to useful products. A faster deactivation of the catalysts is to be expected, although the existing patents to not report this.

Gas-phase reactions are known to have a series of important technological advantages over the liquid-phase version. However, analysis of the existing experimental data shows[78–80] that, when complex syntheses are carried out, these advantages may be lost as a consequence of the complications associated with the inadequate thermal stability of the reacting molecules and the difficulty of their desorption from the catalyst surface. Naturally, these complications must be taken into account in assessing the prospects of gas-phase oxidative hydroxylation. Nevertheless, the possibility of using an oxidant as readily available, safe, and cheap, as N_2O, which has considerable advantages over the oxidants used in the liquid phase, may significantly tip the scales in favour of this procedure. Furthermore, attention should be drawn to yet another important feature, namely the fact that the presence of deactivating substituents in the aromatic ring is not an obstacle to the introduction of a hydroxy-group with the aid of N_2O.

The importance of the search for new ways of hydroxylating aromatic compounds is so great that even the level of parameters already achieved is of practical interest. These parameters will undoubtedly be improved by a wide variety of methods for the modification of zeolites which permit a detailed adjustment of the most important characteristics of zeolites such as the chemical compositions of their internal and external surfaces, acidity, pore structure, steric selectivity, etc.[18,19,81–85] Hitherto, these procedures have not been used to optimise the catalysts of the oxidation with nitrous oxide.

An important step would also be to extend studies of this type to other classes of zeolites and zeolite-like materials, the number of which constantly grows by virtue of the advances in the adoption of new methods of their synthesis.[18,86,87] It may be hoped that further research will permit an appreciable increase in the effectiveness of this new method for the hydroxylation of aromatic compounds and probably its extension to other classes of organic substances.

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