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Selective oxidation of aromatic compounds on zeolites using N_2O as a mild oxidant
A new approach to design active sites

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Abstract

Dehydroxylated ZSM-5 type zeolites are used for selective oxidation of aromatic compounds, including benzene, chlorobenzene, styrene, difluorobenzenes, phenol, alkylbenzenes into corresponding phenols and diphenols using nitrous oxide as a mild oxidant. In the case of benzene, the yield of phenol reaches 70–80%. Extremely high selectivity (~98–100%) in the case of benzene and ~85% in the case of difluorobenzenes and high regioselectivities are observed on the dehydroxylated HZSM-5 zeolite. The active sites are shown to be the strong Lewis acid–base pair sites formed upon dehydroxylation of the zeolites. The reaction mechanism that is alternative to the proposed iron-mediated mechanism is discussed. © 2000 Published by Elsevier Science B.V.

Keywords: Selective oxidation; Aromatic compounds; Zeolites

1. Introduction

Modified ZSM-5 zeolites are widely used as active and selective catalysts for redox-type reactions. Selective oxidation of aromatic hydrocarbons is of special interest, because it provides a way to mono- or diphenols that are valuable products or intermediates for synthesis of drugs, pesticides, polymers, etc. It was shown [1–7] that nitrous oxide may be used as a mild oxidizing agent for oxidation processes, in particular for benzene oxidation into monophenol or halogenated benzenes into corresponding halogenated phenols. These processes occur on acid-type zeolites (HZSM-5) that contain no noble metals or typical transition metals capable of oxidizing hydrocarbons (Cu, V, etc.). Trace amounts of specially introduced iron species were found to enhance the activity of the HZSM-5 zeolites.

Since the pioneering papers by Ono et al. [1], Panov et al. [2,3], and patents by Rhone-Poulenc [4,5], a lot of debates evoked in the literature related to the nature of the active sites and the mechanism of selective oxidation of benzene to phenol using N_2O as a mild oxidant. The idea of the proton-catalyzed reaction [8] did not survive, because no correlation was found between the activity and the concentration of protons. Later, the mechanism based on extra-framework iron species was put forward [2,3]. Though there is no direct correlation between the catalytic activity of the iron-containing zeolites and the total concentration of iron, there is no doubt that the iron-containing active centers, presumably extra-framework iron species, can activate N_2O molecules and generate

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monoatomic oxygen species, the so-called α-sites, which are responsible for the activity of HZSM-5 zeolite in benzene to phenol oxidation. However, the participation of the active sites of a different nature in N_2O activation and aromatics oxidation cannot be ruled out.

Earlier we studied the nature of Lewis acidity of zeolites, and their probable contribution to selective oxidation on zeolites became the subject of this paper. It was shown [6,7,9,10] that strong Lewis acid–base pair sites formed upon dehydroxylation of the HZSM-5 zeolite may take part in the processes of selective oxidation of different substrates by N_2O, because these centers are involved in the chemisorption and decomposition of N_2O occurring with the formation of chemisorbed oxygen atoms [Z–O]. The latter species exhibit strong oxidizing properties with respect to hydrocarbons, carbon monoxide, or molecular hydrogen.

2. Experimental

HZSM-5 zeolites (SiO_2/Al_2O_3=40–80) were prepared starting from the commercial (Nizhnii Novgorod plant) and laboratory samples of Na-ZSM-5 by decationization of the Na-forms with 1N aqueous solution of HCl. The crystallinity of the H-forms thus prepared was 97–99% and no extra-framework aluminum species were found by ^{27}Al MAS NMR spectroscopy. The content of iron impurities was 0.005–0.05 wt.%, i.e., no specially introduced iron was present in the catalysts. The preliminary activation (dehydroxylation) of all catalyst samples was carried out at temperatures of 820–1120 K either in an Ar flow or in an air flow for 6 h.

The oxidation of aromatic compounds was carried out in a flow catalytic setup at 600–720 K and atmospheric pressure, VHSV=0.3–3 h^{-1} (liquid), the oxidant-to-substrate ratio ranging from 1:2 to 4:1. The catalyst loading was typically 1 g (100 g in the bench-scale experiment). The contact time was 1–2 s.

The reaction products were analyzed by GC and MS–GC as described elsewhere [7]. DRIFT spectra were measured using a Protege Nicolet spectrophotometer. Molecular hydrogen adsorbed at 77 K and a pressure of 10–50 Torr was used as a probe for Lewis acid–base pairs. ESR spectra were recorded with an ERS-220 spectrometer (λ=3.2 cm) in order to control the presence and state of iron impurities.

3. Results and discussion

The analysis of the data presented below is not aimed at the comparison of the recently developed iron-containing HZSM-5 zeolite catalysts for benzene-to-phenol oxidation, which are already known as active catalysts for this process, with new zeolite systems, but is rather focused on the attempt to find new approaches to generate active sites, in particular by dehydroxylation of the HZSM-5 zeolite. In the future, a comparison of the two different types of the catalysts will be made.

The studied HZSM-5 samples contained a very low concentration of iron (<0.05 wt.%, the accuracy of the analyses was about 10–15%). The content of iron was determined both by chemical analysis (AAS) and by double integration of the corresponding ESR signals. The state of iron was controlled by monitoring characteristic ESR lines of iron species: a narrow line at g=4.3 (tetragonal iron species) and a broad ferromagnetic line at $g\sim2.0$ (the Fe_3O_4 phase). For the samples under study the intensities of these lines were negligible (below 10^{16}–10^{17} spin/g).

The active sites responsible for the generation of the active chemisorbed oxygen were earlier shown [6,9] to be the framework Lewis acid–base pairs (presumably, framework trigonal aluminum or silicon). The structure of these centers allows the accommodation of the N_2O molecule via a two-point mechanism resulting in polarization and activation of this molecule until its dissociation to produce molecular nitrogen and chemisorption of the singlet atomic oxygen species, which are the active sites for benzene oxidation analogous to the α-centers proposed for iron-containing catalysts.

The concentration and the distribution of the Lewis acid–base pair sites were controlled using the method based on IR-spectroscopic monitoring of the polarization of molecular hydrogen, which is adsorbed (77 K) via a two-point adsorption mechanism on the pair sites. The corresponding IR absorption bands are observed in the region of 3950–4050 cm^{-1} (the H–H bond stretching vibration in the polarized H_2 molecules) and are shifted to lower frequencies as compared to the gas-phase (4163 cm^{-1}). The concentration of strong Lewis acid–base pair sites was estimated by measuring volumetrically the amount of H_2 that is strongly held by the sample after evacuation at 77 K [6,9]. Thus, it was found [6,9] that the concentration of the active centers of this type increases with increasing calcination temperature from ~10^{17} centers g^{-1} for the zeolite pretreated under standard conditions (~770 K) to 3–5×10^{19} centers g^{-1} for the HZSM-5 zeolite dehydroxylated at 1170 K. Strong polarization occurs also in the case of N_2O adsorption on the centers of this type and the high-frequency shift (up to 40 cm^{-1}) of the N_2O band was observed with respect to the gas-phase frequency (~2240 cm^{-1}). According to our previous data and quantum-chemical calculations [6,9], the structure of the N_2O adsorption complex with a Lewis acid site, which is a precursor of the active oxidation site, i.e., atomic chemisorbed oxygen species, can be represented as follows:

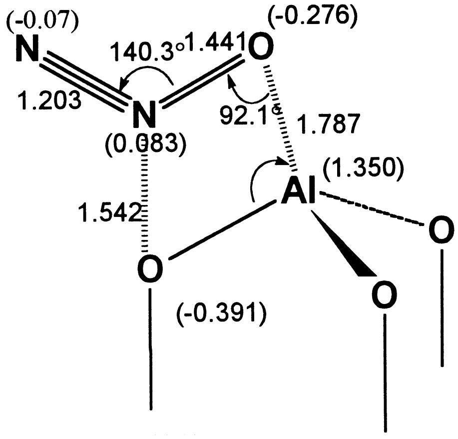


Table 1
Selective oxidation of benzene with nitrous oxide on HZSM-5 zeolites

Dehydroxylation temperature (K)	Reaction temperature (K)	Yield of phenol (%)	Selectivity to phenol (%)
Si/Al=20			
720	620	11.4	95
920		15.2	95
1120		27.8	96
1190		35.3	98
720	720	17.9	35
920		20.4	37
1120		36.7	68
1190		55.1	95
Si/Al=40			
820	620	2.0	100
920		13.0	100
1020		21.0	100
720	720	59.5	85
1020		67.5	90
1120		77.0	100

Despite strong Lewis acid–base pair sites, the dehydroxylated samples also contain the Broensted acid sites (bridging hydroxyl groups) that are the precursors of the Lewis sites and centers responsible for side reactions (phenol condensation and disproportionation of the condensation products). Therefore, the goal was to maximize the concentration of Lewis acid–base sites and minimize that of Broensted acid sites. Thus, the preliminary dehydroxylation of the HZSM-5 zeolite can solve two problems: (1) generation of strong Lewis acid–base pair sites and (2) removal of Broensted acid sites that catalyze undesirable side processes. Thus, the catalytic properties of ZSM-5 zeolites were studied as a function of the dehydroxylation temperature.

Benzene oxidation with N_2O on the HZSM-5 zeolites calcined under standard conditions (at 770 K) is characterized by the phenol yield of 10–15% with the selectivity decreasing with increasing reaction temperature. Dehydroxylation of the sample at T>970 K leads to a dramatic enhancement of the phenol yield (up to 70–75% for the sample calcined at 1170 K), whereas the selectivity is kept constant and high (98–100%) even at high reaction temperatures (720 K) (Table 1). The stability of the catalyst is also improved because of the suppression of the formation of side products. If the contact time increases, diphenols are also formed as products of consecutive reactions. Rather high regioselectivity is observed: the *o*-:*m*-:*p*-diphenol ratio reaches 1:1:3.

Thus, a good correlation seems to exist between the catalytic activity in selective oxidation with N_2O and the concentration of Lewis acid–base pairs. Noteworthy that the activity of the dehydroxylated HZSM-5 zeolite with the Si/Al ratio of 40 is higher than the activity of the sample with lower Si/Al ratio and thus, presumably, with a higher concentration of potential Lewis sites that might be generated from the bridged hydroxyl groups. This discrepancy can be explained by (1) the higher stability of the framework of the zeolite with higher Si/Al and partial amorphization of the zeolite with lower Si/Al, and (2) the higher stability of the catalytic activity of the former zeolite, because the amount of coke formed on the zeolite with a lower Si/Al ratio was about two to three times higher (5–6 wt.%) as compared to that formed on the high-silica analog, taking into account that the activity was measured 1 h after the start of the reaction.

An alternative mechanism of selective oxidation of aromatics with nitrous oxide can thus be proposed, which does not necessarily require the presence of iron ions. The most important step, which was studied by measuring volumetrically the amount of chemisorbed oxygen, is the generation of the singlet oxygen species which peaks at 520–620 K. The concentration of chemisorbed atomic oxygen reaches $5–7\times10^{19}\,g^{-1}$ for the HZSM-5 sample dehydroxylated at 1170 K, which agrees fairly well with the concentration of strong Lewis acid–base pairs ($\sim10^{20}\,g^{-1}$), but not with that of iron species ($<10^{17}\,g^{-1}$). At lower reaction temperatures, the concentration of chemisorbed oxygen species is low, since they are formed by the activated process: $Z + N_2O \rightarrow Z–O_{chem} + N_2$ (Z is LAS). At higher temperatures, the concentration of chemisorbed oxygen decreases because of the recombination reaction leading to the evolution of low-active molecular oxygen.

The reaction of selective oxidation of benzene with atomic chemisorbed oxygen leading to phenol starts at about 590 K and peaks at about 670 K. At higher temperatures, N_2O decomposition predominates and total oxidation leading to CO_2 starts to contribute to the overall process. An equally important factor, especially at low reaction temperatures is the rate of phenol diffusion and desorption from the zeolite channels. Most efficiently, phenol desorption proceeds at temperatures above 620 K, whereas at lower temperatures the process may be limited by the phenol diffusion.

The data on benzene oxidation at a large excess of benzene over nitrous oxide (7:1) on the dehydroxylated H-Beta and HZSM-5 zeolites (Table 2) show about the same performance of the dehydroxylated H-Beta zeolite and the phenol yield on the basis of N_2O reaches about 34% with a broad maximum at ∼730 K. The N_2O efficiency, the percentage of oxidant molecules converted into phenol vs. the total number of converted N_2O molecules, is extremely high (98%) even under conditions of an almost complete N_2O conversion (at 730 K, the N_2O conversion was 96%).

Table 2
Benzene oxidation with N_2O on the dehydroxylated H-Beta and HZSM-5 zeolites pretreated at 1170 K (N_2O:benzene=1:7, LHSV=$1.8\,h^{-1}$)

	Reaction temperature (K)			
	670	690	710	730
Phenol yield on the N_2O basis (%)				
HZSM-5	27.5	38.6	43.1	43.1
H-Beta	23.0	25.7	34.4	34.1

The bench-scale tests (Fig. 1) showed that the HZSM-5 catalyst provides a high level of activity and sufficient stability within 25 h of testing. Indeed, the phenol yield was stable for about 10 h of time on stream, and then decreased from ∼42 to 25% within additional 15 h. This stability plot shows clear advantages of the new catalyst (dehydroxylated HZSM-5 zeolite) in comparison with iron-containing catalysts: the iron-containing catalyst disclosed in the recent patent [12] demonstrated deactivation to a zero level within 20–22 h of testing, even though the catalyst was tested under conditions of an excess of benzene favoring the good stability.

Halogenated benzenes and other benzene derivatives (chloro-, difluorobenzenes, styrene, phenol, alkylbenzenes). Literature data on the oxidation of fluorobenzene and other aromatic hydrocarbons are scarce [5,11]. The maximum conversion of C_6H_5F attained 16% at 720 K and VHSV=$1.5\,h^{-1}$. The selectivity to phenols was about 90%.

The oxidation of difluorobenzene with nitrous oxide was studied under the same conditions as reported in [5,11]. Dehydroxylation of the HZSM-5 zeolite was found to have a remarkable effect on the catalyst performance: unlike the hydroxylated samples, which are characterized by the poor selectivities and yields of phenols, the samples containing strong Lewis acid sites exhibited much better activity and selectivity. For instance, in the oxidation of *o*-difluorobenzene (Table 3), the yield of difluorophenols reached 25–30% at the selectivity of ∼85%. High regioselectivity was observed and oxidation into the *para*-position predominated over other types of oxidation. Similar results were obtained in studying oxidation

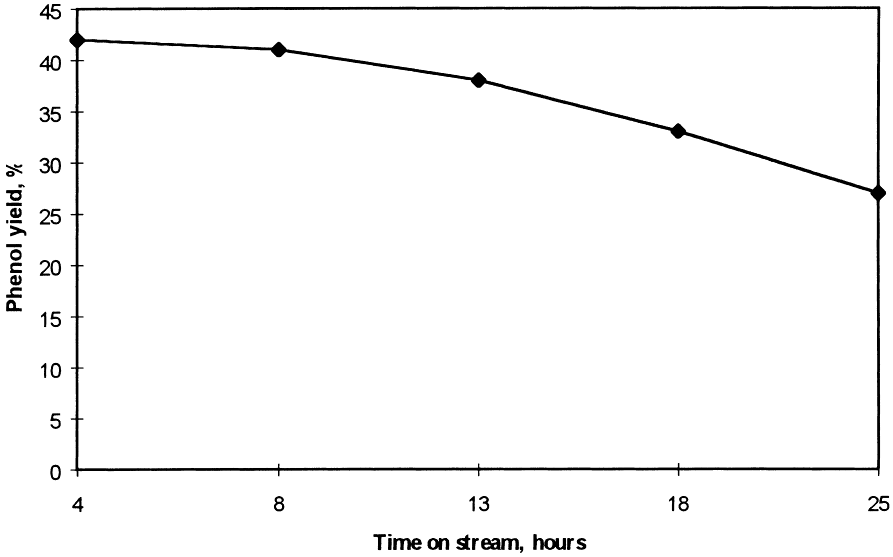


Fig. 1. Performance of the dehydroxylated HZSM-5 zeolite in benzene oxidation with N_2O (720 K, N_2O:C_6H_6=1:1, LHSV=0.88 h^{-1}).

of *m*- and *p*-difluorobenzenes into corresponding difluorophenols.

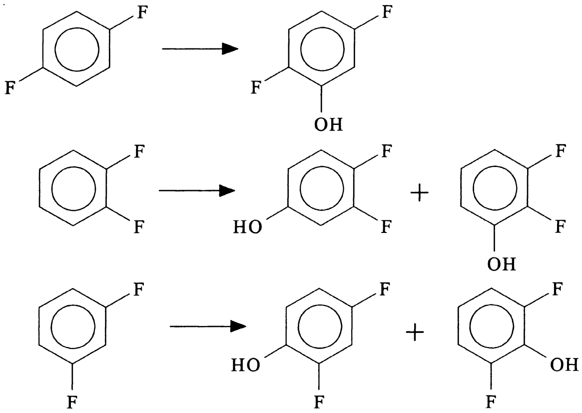
However, during the reaction, deactivation of the catalyst is observed due to poisoning of the active sites with coke precursors (tars and polycondensed aromatic hydrocarbons and phenols). Also, fluorination of the zeolite framework may occur to some extent. Nevertheless, the catalyst may be easily regenerated by purging the system with an air flow at 770 K.

The oxidation of difluorobenzene isomers on the high-silica HZSM-5 zeolite may proceed by two routes: (1) with difluorophenol formation, and (2) with monofluorophenol formation (Table 3). The conversions of *o*-, *m*-, and *p*-difluorobenzenes at 670 K are about 30%, i.e., by approximately 20% lower than in the case of monofluorobenzene. This is consistent with the strong mesomeric and inductive effects of fluorine atoms on the reactivity of the benzene ring toward oxidation with nitrous oxide. The decrease in the conversion of difluorobenzenes, as compared to monofluorobenzene, may be equally accounted for by the steric hindrances imposed by the HZSM-5 zeolite porous structure. The selectivity to phenols is close to 100%. In all the cases, the difluorophenol-to-monofluorophenol ratio in the reaction products is constant and equal to 4:1. This means that partial fluorination and thus destruction of the zeolite framework may occur during the oxidation of fluoroaromatics in consistency with decreasing activity of the HZSM-5 zeolite in repeated cycles including the reaction and regeneration. Further studies of the stability and reproducibility of the catalytic activity are necessary, including XRD measurements and ^{27}Al MAS NMR data. Thus, in the case of *p*-difluorobenzene, the only expected isomer (2,5-difluorophenol) is found without any other difluorophenols that may be formed

Table 3
Oxidation of difluorobenzenes on the dehydroxylated HZSM-5 zeolite

Substrate	*T* (K)	Conversion (%)	Selectivity to difluorophenol (%)	Selectivity to fluorophenol (%)
o-Difluorobenzene	670	30	84	16
m-Difluorobenzene	670	23	82	18
p-Difluorobenzene	670	30	79	21
	720	44	70	23

by isomerization or disproportionation, whereas in the case of *o*-difluorobenzene, mainly 3,4-difluorophenol with a small amount of 2,3-difluorophenol is produced. In the *m*-difluorobenzene conversion, predominantly 2,4-difluorophenol is formed (plus some 2,6-difluorophenol). The reaction network may be explained within the concept of the electrophilic substitution in the aromatic ring and the formation of a chemisorbed atomic oxygen species stabilized on strong Lewis sites (X=H, Cl, F, F_2, OH, alkyl):



Oxidation of other aromatic substrates (styrene, alkylbenzene, phenol) on dehydroxylated zeolites using N_2O was also studied in detail. It was shown that styrene can be easily oxidized to phenylacetic acid. In the case of alkylaromatic hydrocarbons, oxidation of the side groups interferes the main process thus leading to condensation (tar-like) products. Phenol oxidation, in agreement with [5], proceeds with the formation of two main isomers (*o*- and *p*-diphenols, ∼1:3).

Thus, the dehydroxylated zeolites as catalysts for the processes of oxidation of aromatic compounds into phenols using nitrous oxide as an oxidant exhibit the following advantages: (1) the benzene conversion approaches 50–75% at high selectivity (∼98–100%); (2) the selectivity of phenol production at a high reaction temperature (∼670–730 K) remains high (95–100%) at the phenol yield up to 70%; (3) the efficiency of N_2O utilization for the selective oxidation of benzene reaches 90–100%; (4) the stability and the life time of the catalyst are very good.

Acknowledgements

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