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One-step oxidation of benzene to phenol with nitrous oxide over Fe/MFI catalysts

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Abstract

The one-step oxidation of benzene to phenol with nitrous oxide has been studied over a variety of Fe/MFI catalysts at 400 and 450 °C. The turnover frequency (TOF) is found to strongly increase with decreasing Fe loading in accordance with the model of mononuclear Fe sites. The TOF is highest for steamed H-MFI catalysts with an iron impurity of $\mathrm{Fe/Al} = 0.014$. A large increase in phenol yield upon steaming H-MFI at 650 °C indicates that Fe ions are transferred from lattice to extralattice positions. Treating such catalysts with H_2S results in a dramatic decrease of the selectivity to phenol, proving the crucial role of Fe ions. A small residual activity for phenol formation after sulfidation could indicate a different reaction path of low rate or regeneration of Fe sites by oxidation of sulfide groups. In general, three types of Fe sites have been identified in Fe/MFI catalysts: (1) mononuclear Fe, catalyzing phenol formation, (2) dinuclear, oxygen-bridged Fe oxo-ions, catalyzing NO_x reduction, and (3) Fe oxide nanoparticles, catalyzing deep oxidation.

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1. Introduction

The oxidation of benzene to phenol with nitrous oxide in one step has attracted much attention following the first paper by Iwamoto in 1983 [1] and numerous papers by the groups of Panov at Novosibirsk [2–10], Uriarte at Solutia [11], and others [12–16]. The nature of the active sites in Fe/MFI catalysts (the zeolite MFI is often called ZSM-5) and the reaction mechanism are subjects of intense debate. Brønsted and Lewis acids sites and mononuclear and dinuclear Fe sites have been proposed as the loci where phenol is formed. DFT calculations of a reaction path assuming mononuclear iron sites have recently been published by Kachurovskaya et al. [17]. In the present study Fe/MFI catalysts have been synthesized with a wide range of Fe/Al ratios by chemical vapor deposition, ion exchange from aqueous solution, and hydrothermal synthesis. The catalysts have been tested for benzene oxidation with nitrous oxide, both before and after treatment with H_2S which selectively poisons the Fe sites. For catalysts prepared by hydrothermal synthesis, including those which contain Fe only as an impurity, the effects of pretreatments have been studied that are known to transfer Fe ions from lattice to extralattice positions. Characterization techniques include FTIR and temperature-programmed oxidation of used catalysts.

2. Experimental

2.1. Catalyst preparation

The parent NaMFI was kindly provided by UOP LLC in Des Plaines (lot number 99499506001 $\mathrm{Si/Al} = 23$, $\mathrm{Na/Al} = 0.67$). The HMFI was prepared by ion exchange of NaMFI with NH_4NO_3 followed by calcination.

FeMFI (1) was synthesized by subliming $FeCl_3$ into HMFI for 5 min, followed by hydrolysis and calcination of the precursor at 500 °C [18].

FeMFI (2) was synthesized by controlled ion exchange of $FeCl_3$ into HMFI at room temperature for 24 h followed by hydrolysis and calcination of the precursor at 500 °C. As the proton is only partially exchanged by the iron, the Fe/Al ratio for Fe/MFI (1) and (2) from ICP should reflect the exchange percentage.

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FeMFI (3) was synthesized by hydrothermal synthesis [19]. A solution of the silica source (tetraethylorthosilicate, TEOS, Aldrich, 98%) and the template (tetrapropylammonium hydroxide, TPAOH, Fluka, 20% in water) was added to a mixture of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Aldrich, 99%) and iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Aldrich, 98.5%). The molar ratios between components were $H_2O/Si = 45$, $TPAOH/Si = 0.3$, $Si/Al = 36$, and $Si/Fe = 152$. The solution was transferred to a stainless-steel autoclave lined with Teflon lining and kept in a static air oven at 448 K for 5 days. The crystalline material was filtered and washed with deionized water. The as-synthesized sample, in which Fe(III) is isomorphously substituted in the zeolite framework, was calcined in air at 823 K for 10 h.

FeMFI (4) was synthesized by first exchanging NH_4NO_3 into NaMFI (replacing $\sim$ 80% of the Na ions), calcining at 550 °C, and then subliming $FeCl_3$ onto this precursor. This was followed by hydrolysis and calcination at 500 °C.

FeMFI (5), also called FeMFI (SUB), was synthesized by subliming $FeCl_3$ into HMFI until all Brønsted sites had been replaced; this was followed by hydrolysis and calcination of the precursor at 500 °C [18].

The chemical composition, determined by ICP, is listed in Table 1.

Table 1
Fe/Al and Si/Al of different Fe/MFI catalysts

Sample	Atomic ratio	
	Fe/Al	Si/Al
HMFI	0.014	23
Fe/MFI (1)	0.048	23
Fe/MFI (2)	0.18	23
Fe/MFI (3)	0.38	38
Fe/MFI (4)	0.83	23
Fe/MFI (5)	1.23	23

2.2. Catalyst testing

One-step oxidation of benzene to phenol was performed in a U-shaped fixed-bed quartz reactor with a mixture of C_6H_6/He (20 ml/min) and N_2O/He (60 ml/min) between 400 and 450 °C for 3 h at a pressure of 3 bar. The molar $C_6H_6/N_2O/He$ feed ratio is 1/3/36. The amounts 250 mg of finely powdered catalyst and 500 mg SiO_2 diluent were used. Before the reaction, the catalysts were normally treated in flowing O_2 (30 ml/min) while the temperature was increased from room temperature to 450 °C and held at 450 °C for 10 h. Then O_2 was replaced by H_2O/He (30 ml/min with a H_2O partial pressure of 2.9 kPa) (or O_2 30 ml/min) and the temperature was increased to 650 °C and kept there for 2 h. The catalyst was subsequently exposed for 0.5 h to a flow of N_2O in He (10%) at 400 °C. Some samples were further treated in a flow of H_2S/H_2 at 400 °C for 1 h and at 100 °C for an additional hour. The H_2S/H_2 mixture was produced by passing H_2 gas through a CuS bed heated at 400 °C. Products were analyzed by on-line gas chromatography (FID) with a 50-m capillary column of methyl silicone. The TOF was calculated from the ratio of produced phenol molecules and iron atoms in the catalyst.

2.3. Characterization of the catalyst

FTIR spectra were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer with a DTGS detector and were averaged with 32 scans at 2 cm^{-1} resolution. IR spectra of adsorbed species such as NO were obtained by subtracting the spectrum of the zeolite as background. The used catalysts were characterized by TPO. TPO was carried out with a 5% O_2/Ar flow of 40 ml/min and a temperature ramp rate of 8 °C/min. The evolution of CO_2, CO, and H_2O was monitored by mass spectroscopy (Dycor Quadruple Gas Analyzer).

3. Results

Fig. 1 shows the oxidation of benzene to phenol over a HZSM-5 catalyst, that contains Fe only as an impurity. The Fe/Al ratio of this sample is 0.014 and the Fe/Si ratio of 0.00061. When merely calcined in O_2 at 650 °C, this acid zeolite displays a low activity for benzene oxidation to phenol. However, upon treating this material in steam at 650 °C, the phenol yield rises dramatically; a phenol yield near 70% is achieved. This performance remains stable for the duration of the 3-h test. The dealumination process is evidenced by the IR spectra in Fig. 2. For the H-MFI samples pretreated in dry O_2 at 550 and 650 °C, Brønsted acid sites and silanol groups are apparent by the bands at 3610 and 3745 cm^{-1}, respectively [18]. After steaming, an additional band emerges at 3663 cm^{-1}; it is assigned to OH groups of highly dispersed Al_2O_3 inside zeolite channels [20]. During this dealumination, the intensity of the Brønsted acid site decreases. As Fe^{3+} ions in zeolite tetrahedra are less stable

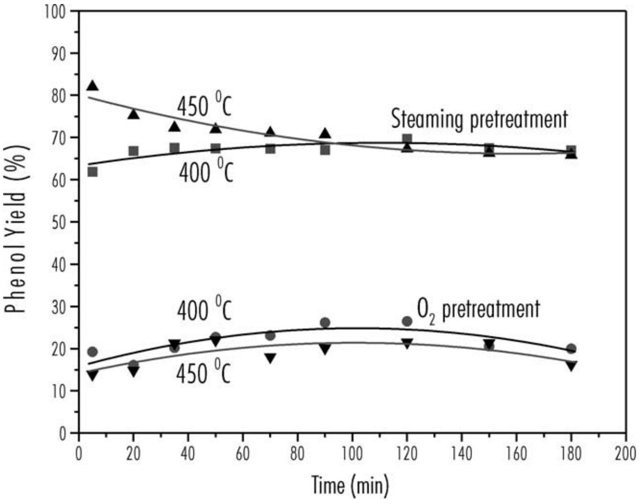
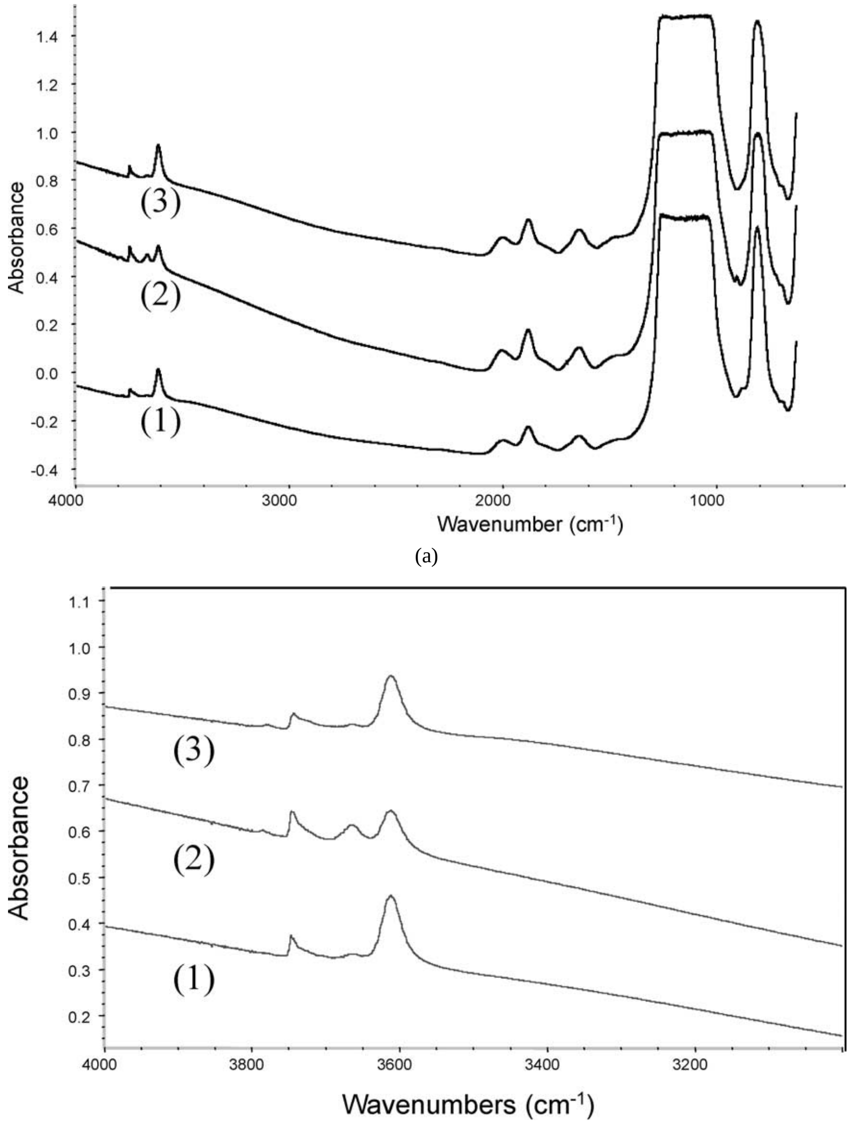


Fig. 1. One-step oxidation of benzene to phenol over HMFI (Fe/Al = 0.014) with steaming and O_2 pretreatment at 650 °C.



(a)

(b)

Fig. 2. (a and b) FT-IR spectra of HMFI with pretreatment of (1) in O_2 at 550 °C, (2) in steam at 650 °C, and (3) in O_2 at 650 °C.

than Al^{3+} ions, the Fe^{3+} ions will leave their positions in the zeolite lattice during this dealumination, as stated previously by Pirutko et al. [4].

This result lends credence to the model that Fe sites in extralattice positions are crucial for the benzene oxidation to phenol. We have, therefore, defined the turnover frequency (TOF), for this reaction as the number of moles of phenol formed per second and per Fe atom in the catalysts. Fe/MFI samples have been tested with widely differing Fe loadings, achieved by using catalysts that were prepared by hydrothermal synthesis, followed by steaming (HTS), or ion exchange from aqueous solution (WIE), or chemical vapor deposition by subliming $FeCl_3$ vapor onto H-MFI (SUB). The lowest Fe loading was present in the nominal Fe-free H-MFI with $Fe/Al = 0.014$; the highest Fe loading was obtained by CVD with $Fe/Al = 1.2$. These samples thus cover Fe/Al ratios of two orders of magnitude. All catalysts were probed in the same flow reactor at a total pressure of 3 bar; the reaction temperature being either 400 or 450 °C.

The results are presented in Fig. 3, where the TOF is plotted logarithmically against the Fe/Al ratio. From this figure it is evident that the TOF decreases by more than 3 orders of magnitude when the Fe loading is increased. The decrease is steepest in the area of low Fe/Al ratios.

To us, these results indicate that mononuclear Fe sites are crucial for the benzene oxidation to phenol.

Phenol is, of course, not the only reaction product of $C_6H_6 + N_2O$ over these catalysts. On acid sites carbenium ions can be formed from benzene and phenol; they can form carbonaceous deposits and react with N_2O to CO, CO_2, and N_2. To discriminate between the catalysis on the Fe ions and that on the acid sites, we have tried to selectively deactivate the Fe sites by exposing the catalysts to an $H_2S + H_2$ flow. The result of this strategy is shown in Fig. 4 for a catalyst

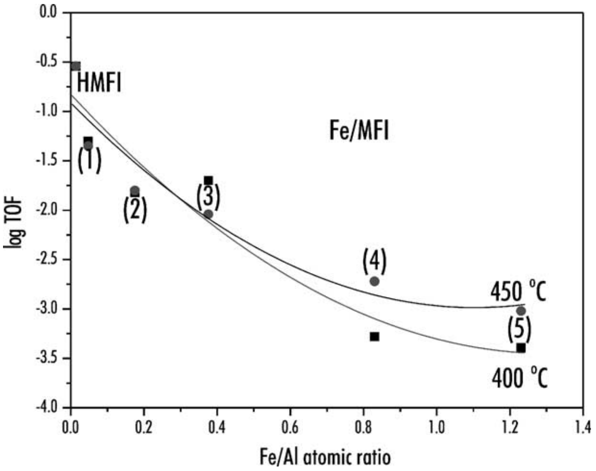


Fig. 3. Turnover frequency of benzene oxidation to phenol over FeMFI (with steaming treatment) catalysts at reaction time of 180 min.

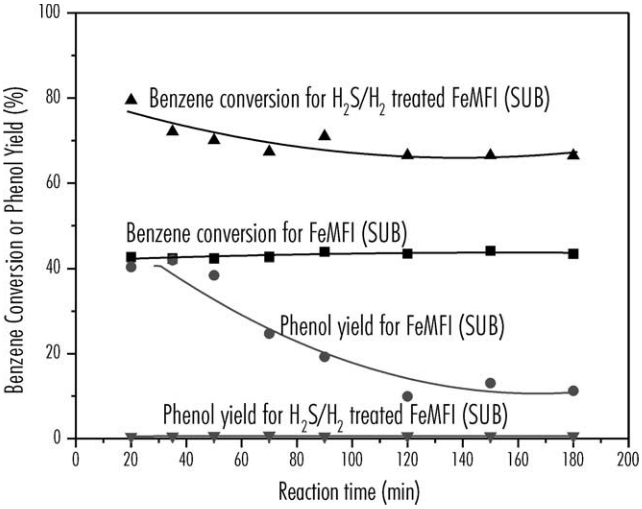


Fig. 4. One-step oxidation of benzene to phenol over FeMFI (SUB) and H_2S/H_2-treated FeMFI (SUB) catalysts at 450 °C (with steaming pretreatment).

prepared by CVD and in Fig. 5 for a steamed H-MFI catalyst. The data show that poisoning with H_2S has a very strong deactivating effect. In addition, it is noted that for the SUB catalyst with high Fe loading (Fig. 4) the benzene conversion is higher after poisoning the Fe sites. This could mean that some carbenium ions are converted over Fe sites to more strongly adsorbed entities that hinder the processes at the acid sites. This effect is absent on the H-MFI catalysts with a very low number of Fe sites. Another observation is that on the unsulfided SUB catalyst the reaction rate of phenol formation decreases with time on stream, indicating some poisoning of Fe sites by deposits.

The most interesting observation in the context of the present work is, however, that formation of phenol is very strongly suppressed by deactivation of the Fe sites. This suppression is almost 100% for the SUB catalyst with high Fe loading, and comparatively low concentration of acid sites, while a residual activity for phenol formation is recorded with the sulfided H-MFI catalyst with a much higher ratio of acid/iron sites. This could mean an authentic reaction path for benzene to phenol not requiring any transition metal ions or, alternatively, that some sulfided Fe ions are easily regenerated by oxidation of the sulfide groups with nitrous oxide.

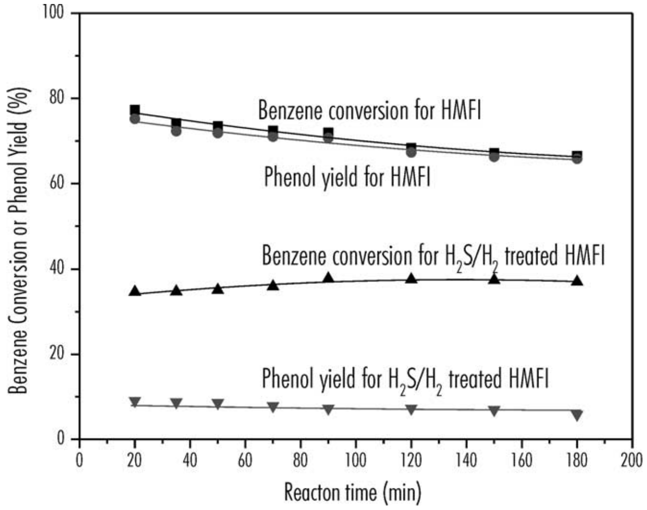


Fig. 5. One-step oxidation of benzene to phenol over HMFI and H_2S/H_2-treated HMFI catalysts at 450 °C (with steaming pretreatment).

The possibility of S^{2-} oxidation by N_2O has been addressed in the IR study of which Fig. 6 shows the result. The spectra were recorded with Fe/MFI (SUB) after different pretreatments. For a catalyst that was merely exposed to a H_2S/H_2 flow, no S–O groups are visible. Acidic sites (Al–OH) were not observed, but the Brønsted acid sites causing the well-known band at 3610 cm^{-1} recovered upon exposure to N_2O at 300 °C. No S=O groups were observed at this stage. After exposure to N_2O at a temperature above 450 °C, a band at 1380 cm^{-1} appears. It thus seems possible that the S^{2-} ions are oxidized to a S=O groups [21,22]. We imagine that H_2S/H_2 reacts with $[HO–Fe–O–Fe–OH]^{2+}$ (see [23]) at 300 °C to form $[HS–Fe–S–Fe–SH]^{2+}$. This ion will be oxidized to $[HO–Fe–S–Fe–OH]^{2+}$ by N_2O; at a temperature above 450 °C it will be oxidized to $[HO–Fe–(SO_4)–Fe–OH]^{2+}$. It is known that at 500 °C $Fe_2(SO_4)_3$ decomposes and SO_3 is released. This process will be facilitated if Fe^{3+} ions react with the Al_2O_3 nanoparticles inside the zeolite channels. In H-MFI, the Fe content is too small to follow the processes of sulfidation and reoxidation by IR. We also found that under our condition the H_2S does not deactivate the Brønsted acid sites in HMFI.

The question of site regeneration after sulfidation motivated us to follow the catalytic activity and selectivity for benzene oxidation with time on stream for a sulfided H-MFI catalyst. The results are shown in Fig. 7. The data indicate that the selectivity increases with time, while the conversion decreases. As the yield, per definition, is the product of conversion and selectivity, it changes little with time, as was shown in Figs. 4 and 5. The increase in selectivity from 60 to 90% seems to indicate some regeneration of selective iron sites by oxidation of sulfide groups.

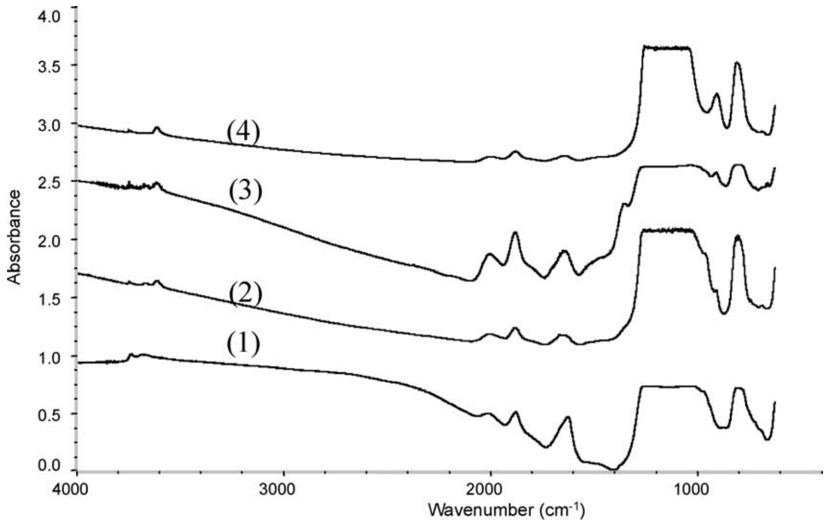


Fig. 6. FTIR spectra of FeMFI (SUB) after different pretreatments: (1) pretreated in H_2O/He at 650 °C, then in H_2S/H_2 at 400 °C; (2) pretreated in H_2O/He at 650 °C, then in H_2S/H_2 at 400 °C, and then in N_2O at 300 °C; (3) pretreated in H_2O/He at 650 °C, then in H_2S/H_2 at 400 °C, and then in N_2O at 450 °C; (4) pretreated in O_2 at 500 °C.

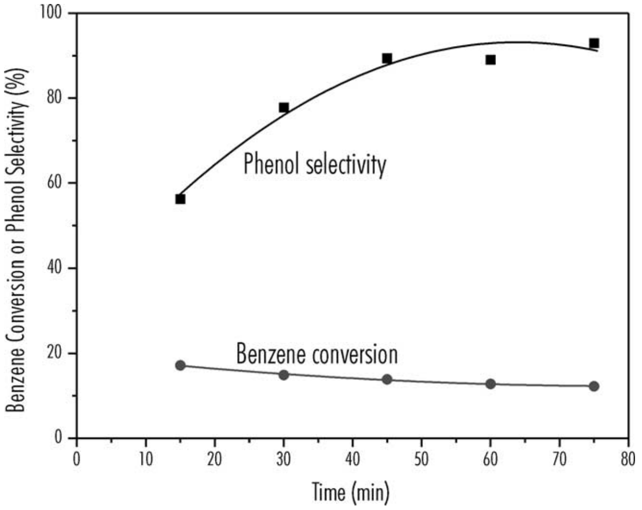


Fig. 7. Conversion and selectivity to phenol of presulfided HMFI catalysts as a function of time on stream.

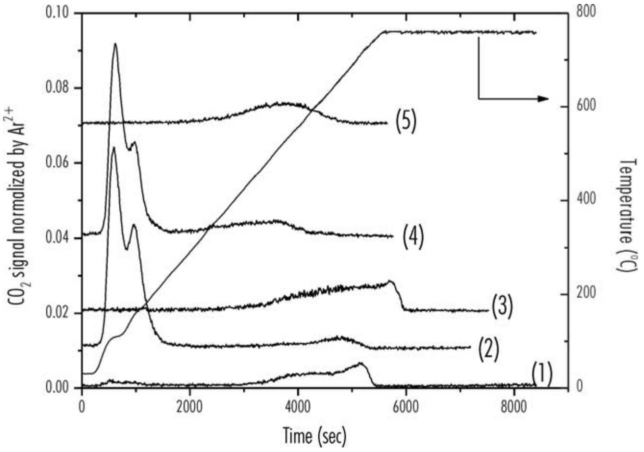


Fig. 8. TPO profiles of catalysts used for the oxidation of benzene to phenol at 450 °C: (1) HMFI pretreated in O_2 at 650 °C; (2) HMFI pretreated in H_2O at 650 °C; (3) HMFI pretreated in H_2O/He at 650 °C, then in H_2S/H_2 at 400 °C; (4) FeMFI (SUB) pretreated in H_2O at 650 °C; (5) FeMFI (SUB) pretreated in H_2O at 650 °C, then in H_2S/H_2 at 400 °C.

The effect of the Fe ions in exchange positions is further illustrated by the results in Fig. 8, which show the formation of CO_2 upon temperature-programmed oxidation (TPO) of used catalysts. Clearly, Fe has a very pronounced effect on

(1) the quantity of the CO_2, which is indicative for the amount of carbonaceous deposit on the catalysts after use, and
(2) the activation energy for the combustion of this coke during the TPO run.

The largest amounts of deposit are obviously formed on catalysts which have Fe ions in accessible positions and oxidize benzene to phenol. This is the case for the HMFI catalysts after steaming at 650 °C and for the Fe/MFI catalyst prepared by SUB. Much lower quantities of coke are present on the unsteamed HMFI and the sulfided catalysts. The iron is not only essential for the formation of this coke but also for its oxidation to CO_2. It is evident from Fig. 8, that this oxidation is almost complete at 150 °C for those catalysts which have Fe in accessible exchange positions, but oxidation of deposits requires a much higher temperature for the H-MFI catalysts which contains Fe inside the zeolite lattice. Likewise, sulfidation of Fe deactivates these sites as catalysts for coke combustion, shifting the temperature for this process upward by 400–500 °C.

4. Discussion

The discussion on the mechanism of the one-step oxidation of benzene with nitrous oxide to phenol focuses on two main questions:

(1) Are Fe ions required or can acid sites catalyze this oxidation in the absence of Fe?
(2) If Fe is required, are the selective Fe sites dinuclear as in some well-studied enzymes and the Fe/MFI catalysts used for NO_x reduction by hydrocarbon, or can mononuclear Fe catalyze benzene conversion to phenol?

An excellent discussion of these problems was recently published by Kubánek et al. in this journal [24]. This enables us to be brief in the present chapter. Panov et al. had argued that dinuclear Fe sites are most likely required for this catalytic reaction; the zeolite based Fe would thus be similar to the Fe groups in enzymes of the cytochrome group. Conversely, Suzuki et al. [25], Burch and Howitt [26], and Kustov and co-workers [27,28] argued that virtually Fe-free catalysts can catalyze this reaction; the amount of oxygen chemisorbed by dissociation of N_2O on these materials would exceed the number of Fe impurities. Kustov assumes that Lewis sites, such as Al, act as adsorption sites. A difficulty with that concept is, however, that the oxygen atom that is deposited on the surface by N_2O adsorption, followed by N_2 desorption, has only a sextet of outer electrons. As the Al Lewis site, likewise, has an incomplete octet, it does not recognize these O atoms as Lewis bases.

The present results show that selective poisoning of iron sites by sulfidation strongly suppresses the propensity of the catalyst to oxidize benzene to phenol. Even with the nominal H-MFI catalyst, having a ratio of acid sites to Fe sites > 70, the negative effect of sulfidation is very pronounced. These data clearly show the crucial role of Fe ions for the oxidation of benzene to phenol. Another important argument for this conclusion is the strong positive effect of treating low Fe catalysts with steam at high temperature. There is a wide consensus that such treatment will transport Fe from positions inside the zeolite lattice to more accessible positions. Pérez-Ramirez et al. have shown [29] that this treatment when applied to H-MFI zeolites with low Fe content, transfers Fe to extralattice positions and creates highly dispersed mononuclear sites. We are aware that this treatment will also have an effect on the transport parameters of the catalyst, because voids and mesopores will be formed, but in the present case it appears rather obvious that the creation of new sites is responsible for the drastic increase in catalytic activity.

After having stressed the crucial role of iron for benzene oxidation to phenol, it should be noted that the present data in Figs. 4 and 5 also show that after sulfidation a small residual activity has been identified. We, therefore, do not exclude that a parallel reaction path may exist which converts benzene to phenol without using Fe sites. If so, this path has a much lower rate constant than the predominant path using the Fe sites.

As noted, the steam treatment of H-MFI containing a small Fe impurity is known to generate highly dispersed mononuclear Fe sites. The catalyst prepared in this way displays the highest turnover frequency for benzene to phenol of all catalysts tested in this study. Our results, therefore, fully confirm the conclusions of Wichterlová's group, that for this catalysis mononuclear iron sites are required.

The TPO data show the important role of Fe both for the formation of carbonaceous deposits and for their oxidation to CO_2. Clearly, the activation energy for this oxidation is strongly reduced by iron ions in accessible positions, but gets lost when the Fe ions are encaged in zeolite tetrahedra or when they are deactivated by sulfur.

The role of Fe in coke formation may be a direct consequence of its catalytic selectivity for phenol formation. All catalysts under study expose Brønsted acid sites which form carbenium ions with aromatic molecules. The ionization potential of phenol, 8.51 V, is lower than that of benzene, 9.24 V. It thus makes sense to assume that phenol is an efficient precursor for carbenium ion reaction that ends up in the formation of carbonaceous deposits. Catalyst in which the function to form phenol is blocked will form less coke. This may be the reason for the observation in Fig. 4 that the catalysts prepared by chemical vapor deposition show a higher conversion, though a much lower phenol yield, after sulfidation than before sulfidation.

Within the group of Fe/MFI catalysts the optimal catalyst for benzene oxidation strongly differs from the best Fe/MFI catalysts for reduction of NO_x to N_2. As has been shown in numerous papers by our group and others [30–33] dinuclear oxygen-bridged Fe sites are required for the optimum NO_x reduction catalyst. We have routinely prepared catalysts for both processes and always found complementary behavior: high Fe load catalysts are required for NO_x reduction, low Fe loading is ideal for benzene oxidation to phenol. The present work shows that increasing the iron load from $Fe/Al = 0.014$ to 1.2 results in lowering the turnover frequency for phenol formation by three orders of magnitude. A common element of both classes of catalyst is that nanoparticles of iron oxide are deleterious for both phenol formation and NO_x reduction because they catalyze nonselective "deep" oxidation. The dominant Fe sites in Fe/MFI that are active in catalytic oxidation can thus be classified as follows:

(1) mononuclear Fe ions: catalyzing benzene oxidation with N_2O to phenol;
(2) dinuclear, oxygen-bridged ions such as $[HO–Fe–O–Fe–OH]^{2+}$ catalyzing NO_x reduction;
(3) iron oxide particles catalyzing combustion of organic molecules to $CO_2 + H_2O$.

The relative abundance of any of these sites depends not only on the Fe load of the zeolite, but also on the presence of acid sites in the same catalyst. Previously we have shown that contact of a base with Fe in MFI promotes the agglomeration of Fe oxo-ions to iron oxide nanoparticles; conversely acid groups promote redispersion of oxide particles to mono- or dinuclear (oxo-)ions [34]. It follows, that acidic groups coexisting with mono- or dinuclear Fe entities inside the same zeolite will be beneficial by protecting them against agglomeration to oxide particles that catalyze benzene combustion. This is in line with Notté's conclusion that coexistence of Fe sites and acidic groups is desirable for Fe/MFI catalysts for benzene oxidation to phenol [35].

In the pioneering work by Panov's group they stated that the "α-sites" on which benzene is oxidized to phenol are dinuclear. They based this conclusion on Mössbauer data and concluded that one atom of oxygen is deposited from N_2O onto a pair of Fe atoms; i.e., $O/Fe = 1/2$. In more recent work, however, this group states explicitly, that they no longer wish to rule out that the O/Fe ratio in "α-sites" could be $O/Fe = 1/1$ [10]. This is exactly the conclusion from the present results and those of Kubánik et al. for the sites responsible for the oxidation of benzene to phenol over Fe/MFI.

It appears that the sites which are deactivated by depositing sulfur can be regenerated to some extent by oxidizing the sulfide ions. Some reoxidation takes place during the standard catalytic tests because impinging N_2O molecules will oxidize sulfide ions. The formation of $S{=}O$ groups has been demonstrated by the IR band characterizing them; the concomitant increase in the catalytic selectivity to phenol is visible from Fig. 7.

5. Conclusions

(1) In Fe/MFI catalysts mononuclear sites catalyze benzene oxidation to phenol, dinuclear sites catalyze NO_x reduction with alkanes to N_2, and Fe-oxide nanoparticles catalyze combustion of organic molecules.

(2) Steam treatment at 650 °C of hydrothermally prepared Fe-H/MFI strongly enhances the catalyst selectivity for benzene oxidation to phenol, because Fe ions are expelled from the zeolite lattice.

(3) Poisoning of Fe sites by H_2S results in a dramatic decrease of the selectivity to phenol. This proves the dominant importance of Fe sites for phenol formation. However, a small residual selectivity of the sulfided catalysts might indicate an alternative reaction path of very low activity.

(4) The turnover frequency for benzene oxidation to phenol is highest for Fe/MFI catalysts with $Fe/Al = 0.014$; it decreases by three orders of magnitude to catalysts with $Fe/Al = 1.2$.

(5) Sulfidation of iron ions or their encagement inside zeolite tetrahedra substantially lowers the formation of carbonaceous deposits under catalytic test conditions. This might indicate the role of phenol as important "coke" precursor.

(6) Oxidation of sulfide ions in deactivated Fe/MFI catalysts restores part of the selectivity to phenol.

Acknowledgments

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