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Priority Communication

Extraframework Fe–Al–O species occluded in MFI zeolite as the active species in the oxidation of benzene to phenol with nitrous oxide

E.J.M. Hensen,* Q. Zhu, and R.A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB, Eindhoven, The Netherlands

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Abstract

Iron and aluminum are required for the formation of active sites in MFI-type zeolites for benzene oxidation to phenol by nitrous oxide. We propose that the active species are extraframework Fe–Al–O species. These species produce characteristic IR bands around 1625 and 1635 cm^{-1} after exposure to NO which are different from those found in Fe-substituted silicalite-1 and HZSM-5. While we only observe negligible benzene oxidation activities for these latter materials, a MFI zeolite containing Fe and Al shows good performance. Additionally, we found that postsynthesis dispersion of aluminum to Fe-substituted silicalite-1 offers an alternative preparation route to an active material.

Keywords: FeZSM-5; Benzene oxidation; Nitrous oxide; Active sites; Extraframework; Infrared spectroscopy

1. Introduction

Selective oxidation processes for the conversion of hydrocarbons to their oxygenates are much desired for replace existing environmentally stressing processes [1]. Iron-containing MFI-type zeolites have received their share of attention, because of their ability to hydroxylate aromatics with nitrous oxide as oxidant, a prime example being the transformation of benzene to phenol [2], which can replace the existing three-step process via cumene [3]. There is considerable divergence of opinion on the structure of the active sites for these zeolite-based catalysts. Most frequently, the importance of extraframework iron sites has been stressed, possibly with a binuclear structure in analogy with the enzyme methane monooxygenase [4]. These zeolite-occluded iron sites are capable of decomposing nitrous oxide leaving an extraframework oxygen atom which can be transferred to a hydrocarbon [2]. However, Brønsted acid sites [5,6] and EFAL (extraframework aluminum) Lewis acidic centers created by high-temperature activation [7–9] are among the alternative proposals for the active sites. It thus appeared worthwhile to prepare zeolites with an MFI structure containing either Fe or Al or a combination of both and to test such materials in the oxidation of benzene with nitrous oxide.

2. Experimental

Three zeolite samples were prepared by hydrothermal synthesis starting from tetraethylorthosilicate in order to avoid the iron and aluminum impurities in conventional silica precursors [10]. In short, the preparation consisted of the slow addition of an aqueous solution of metal nitrate(s) to a mixture of tetraethylorthosilicate (TEOS, Acros) and tetrapropylammonium hydroxide (TPAOH, 20% solution in water, Fluka). We carefully checked the iron contents of TEOS (< 0.00004 wt%), TPAOH (< 0.0001 wt%), and $Al(NO_3)_3 \cdot 9H_2O$ (Merck, < 0.002 wt%) and the aluminum content in $Fe(NO_3)_3 \cdot 9H_2O$ (Janssen Chimica, < 0.001 wt%). The resulting synthesis mixture was transferred into a PEEK-lined autoclave for hydrothermal synthesis (448 K, 5 days). After filtration and careful drying, the resulting materials were calcined. The calcined samples are denoted as [*Me*]MFI with $Me =$ Fe, Al, or Fe, Al. A portion of the calcined zeolites was further activated by a steaming treatment in a mixture of $O_2/H_2O/He$ (volume ratio $= 18/10/72$) at 973 K for 3 h. These samples are referred to as [*Me*]MFI-st.

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[*] Corresponding author.
E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

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All materials exhibit the typical powder XRD pattern of the MFI structure. No peaks related to iron oxide species were found in the calcined or steamed materials, showing that no strong aggregation of iron oxide particles occurred.

Moreover, we found that the textural properties of these materials are very similar. Another sample was prepared by mixing dehydrated [Fe]MFI with excess pure trimethylaluminum (Me_3Al, Aldrich) in a nitrogen-flushed glove box. After stirring for 24 h, excess Me_3Al was removed by evacuation. The sample was calcined ([Fe]MFI–Me_3Al) and subsequently steamed ([Fe]MFI–Me_3Al-st). A commercial HZSM-5 zeolite (Akzo Nobel) was used in its steamed form (HZSM-5-st) for comparison. The elemental composition of the zeolitic materials was determined by OES-ICP. Infrared spectra of self-supporting 10-mg catalyst wafers were recorded at room temperature on a Bruker IFS-113v Fourier transform IR spectrometer with a DTGS detector at a resolution of 4 cm^{-1}. Typically, a sample was pretreated in situ in oxygen at a temperature of 823 K for 1 h and cooled to room temperature in vacuo (pressure better than 10^{-6} mbar), followed by room temperature exposure to NO (purity > 99.9%, 5 mbar) for 30 min. Finally, the sample was evacuated and a spectrum was recorded at 298 K. Reaction data were collected in a single-pass atmospheric plug flow reactor. Typically, 100 mg of catalyst was diluted with an amount of SiC to obtain a catalyst bed of 2 cm in height. Gas-phase product analysis was performed by a well-calibrated combination of GC and MS. Prior to reaction, the catalyst was pretreated in a flow of 100 ml/min O_2/He (20 vol% O_2) while heating to 823 K at a rate of 1 K/min. Benzene oxidation was carried out by feeding a mixture of C_6H_6/N_2O/He (volume ratio = 1/4/96) at a flow rate of 100 ml/min at a reaction temperature of 623 K.

3. Results and discussion

The elemental compositions are given in Table 1. We succeeded in preparing [Fe]MFI (Fe-substituted silicalite-1) with an Al content lower than 0.005 wt% and [Al]MFI (HZSM-5) with an Fe content below 0.001 wt%. The phenol productivities for the various catalysts as a function of the reaction time are displayed in Fig. 1. The corresponding reaction data are condensed in Table 1. [Fe,Al]MFI-st is the preferred catalyst with an initial activity of 6.8 $mmol\,g^{-1}\,h^{-1}$. Deactivation is pronounced due to coke formation in the zeolite micropores [11], which is corroborated by the finding that the initial activity can be restored by a simple oxidative treatment. [Fe,Al]MFI shows a lower initial activity, but a similar deactivation behavior. While the benzene selectivities are very high for these two materials, the nitrous oxide selectivities tend to be lower due to oxidation of coke [12]. The activity of the two [Al]MFI materials is negligible. As acidic [Al]MFI is found to be inactive, we infer that strong Brønsted acid sites [5,6] cannot be the active sites. The present results also clearly contrast earlier claims [7–9] that Al Lewis sites obtained by dehydroxylation of zeolite Si–O–Al groups are the active sites for the title reaction, since [Al]MFI-st did not show any activity. ^{27}Al NMR spectra (not shown) of this latter sample indicate that approximately one-

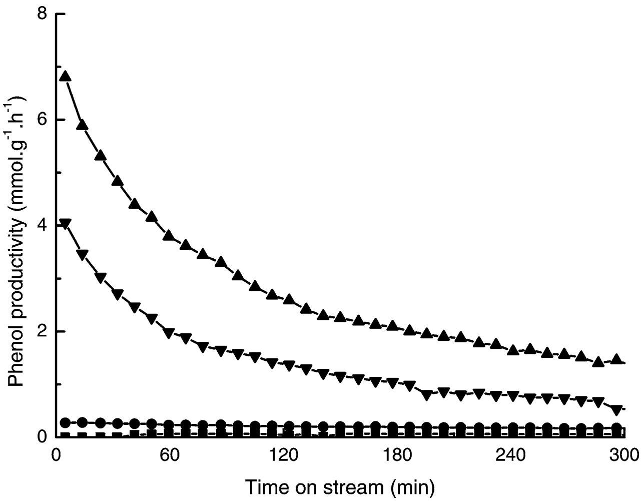

Fig. 1. Phenol productivities ($mmol\,g^{-1}\,h^{-1}$) as a function of the reaction time for (●) [Fe]MFI-st, (■) [Al]MFI-st, (▼) [Fe,Al]MFI, and (▲) [Fe,Al]MFI-st. The feed mixture consisted of 1 vol% C_6H_6, 4 vol% N_2O, and balance He at a total volumetric flow rate of 100 ml/min. The reaction temperature was 623 K.

Table 1
Elemental compositions and reaction data for the various zeolite materials

Sample	Fe	Al	Si	R_i	$t_R = 5$ min				$t_R = 5$ h			
	(wt%)	(wt%)	(wt%)		$X_{C_6H_6}$	$S_{C_6H_6}$	X_{N_2O}	S_{N_2O}	$X_{C_6H_6}$	$S_{C_6H_6}$	X_{N_2O}	S_{N_2O}
[Fe]MFI	0.55	< 0.005	40.6	0.23	9	9	1	30	2	5	< 1	2
[Fe]MFI-st	0.55	< 0.005	40.6	0.28	9	12	1	35	4	5	1	2
[Al]MFI	< 0.001	0.88	36.5	< 0.01	< 0.5	< 1	< 1	< 1	< 0.5	< 1	< 1	< 1
[Al]MFI-st	< 0.001	0.88	36.5	0.06	5	5	6	< 1	5	5	6	< 1
[Fe,Al]MFI	0.51	0.94	40	4.1	22	69	10	36	3	81	4	14
[Fe,Al]MFI-st	0.51	0.94	40	6.8	38	68	16	42	6	> 99	3	52
[Fe]MFI–Me_3Al	0.55	1.40	40.6	1.9	10	69	3	53	2	> 99	1	50
[Fe]MFI–Me_3Al-st	0.55	1.40	40.6	4.9	23	77	8	57	5	> 99	1	> 98
HZSM-5-st	0.024	2.01	36.5	5.4	31	61	5	93.5	9	> 99	2.3	> 98

The initial phenol productivities (R_i in $mmol\,g^{-1}\,h^{-1}$) and benzene conversions ($X_{C_6H_6}$), benzene selectivities to phenol ($S_{C_6H_6}$), nitrous oxide conversions (X_{N_2O}), and nitrous oxide selectivities to phenol (S_{N_2O}) after reaction times (t_R) of 5 min and 5 h are also given.

third of Al has been dislodged from the framework. Thus, we can firmly conclude that extraframework Al species are not solely responsible for the conversion of benzene to phenol with nitrous oxide. The deviant results of earlier reports most probably derive from the presence of considerable amounts of iron in the zeolitic starting materials [8,9]. This is further exemplified by the good performance of a steamed commercial HZSM-5 zeolite (Table 1) with an iron content of 0.024 wt%. On the other hand, the two [Fe]MFI zeolites also exhibit a much lower activity than [Fe,Al]MFI. Others have reported reasonable phenol productivities for [Fe]MFI [11, 13,14], the activities being generally somewhat lower than for [Fe,Al]MFI-type materials. While Selli et al. [14] prepared [Fe]MFI from sodium silicate which often contains an Al admixture, other authors [11,13] have reported the presence of considerable amounts of Al (∼ 0.03 wt%) in their samples. We thus interpret the present finding, i.e., the almost negligible activity of Fe[MFI]-st with an Al content below 0.005 wt%, as an indication that aluminum is a required element for the selective benzene oxidation with nitrous oxide. These data thus provide very strong indications for the proposal that Fe and Al are both important in the generation of catalytic sites for the oxidation of benzene with nitrous oxide.

Whereas it is more or less clear that Fe should be located at extraframework positions, the preferred position of Al has not been elucidated yet. Stabilization of iron complexes of low nuclearity on cation-exchange positions has been proposed [4,10], while others have pointed out the correlation between Al Lewis acidity and activity [7–9]. A general finding is that steam activation at moderate or calcination at high temperatures [4,10] is required to activate these catalysts. This has been described for [Fe,Al]MFI [10,15], despite the observation that already a significant fraction of iron has migrated from lattice positions during template removal [16]. We propose an alternative model where high-temperature activation is required to create EFAL sites which then form a mixed Fe–Al–O species. It is indeed well known that Si–O–Al framework bonds are stronger than Si–O–Fe ones. This view is further substantiated by the beneficial effect of high-temperature calcination and especially steaming on the decomposition of nitrous oxide [17,18] and benzene oxidation activity of sublimed Fe/ZSM-5 [12,19]. The important point to note is that, despite the fact that during sublimation virtually all Fe species are introduced at extraframework positions, steaming strongly increases the performance.

To obtain further insight into the nature of the extraframework species, we report preliminary results of an IR spectroscopic investigation of adsorbed NO. Fig. 2 presents the IR spectra of adsorbed NO. We note that the characteristic bands of reversibly adsorbed NO around 1880 cm^{-1} and in some cases those around 2130 cm^{-1} [20,21] were observed in the presence of gaseous NO but were absent after evacuation. What remains after evacuation are bands due to adsorption complexes of NO with extraframework oxygen atoms [21]. The spectrum of [Fe]MFI-st contains three bands. The strong band at 1613 cm^{-1} (band I) is assigned to NO$_2$ in interaction with Fe, which is close to the asymmetric stretch frequency of NO$_2$ at 1610 cm^{-1} [22]. The bands below 1600 cm^{-1} have been tentatively assigned to monodentate/bidentate nitrate groups [21,23], but at least one of them may also relate to nitrito groups (Fe–ONO) [21]. From the observation that the band at 1657 cm^{-1} (band IV) appears more strongly after steaming of [Al]MFI (spectrum of [Al]MFI not shown), we infer that it is related to a nitro group coordinating to Al. The weak features around 1600 cm^{-1} are then assigned to nitrate groups. The spectra for [Fe,Al]MFI and [Fe,Al]MFI-st are more complex. While in both samples a band at ∼ 1656 cm^{-1} similar to the one in [Al]MFI-st is visible with lower intensity, the band corresponding to NO$_2$ on extraframework Fe is only weakly found in [Fe,Al]MFI and cannot be distinguished in [Fe,Al]MFI-st. Clearly, the amount of Fe and Al sites that can form NO$_y$ complexes that are similar to those in [Fe]MFI-st and, respectively [Al]MFI-st is much lower. Moreover, the spectra contain two new bands around 1625 cm^{-1} (band II) and 1635 cm^{-1} (band III). These bands have been reported before for Fe/ZSM-5 samples [20,21,23]. Mul et al. [20] produced evidence for the attribution of the band at 1635 cm^{-1} to extraframework Fe–Al–O species. Its assignment to a mixed metal oxide species agrees with the present results, because we only observe this band in the [Fe,Al]MFI materials. Moreover, we find that the intensities of these two bands increase upon steaming, which tallies with their extraframework location. In our view, this derives from the additional extraction of Fe and especially Al from framework positions, resulting in the formation of more Fe–Al–O species. The presence of bands around 1625 and 1635 cm^{-1} in [Fe,Al]MFI and the intensity increase

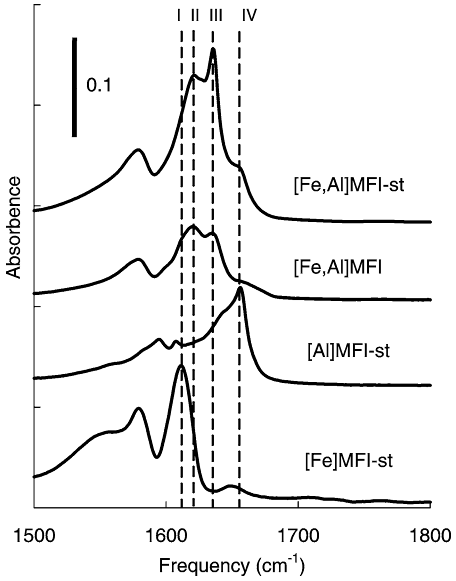

Fig. 2. IR spectra of the region 1500–1800 cm^{-1}. Catalyst samples were calcined at 823 K and cooled to room temperature in vacuo. Subsequently, they were exposed to 5 mbar NO for 30 min and evacuated. Spectra were recorded at 298 K.

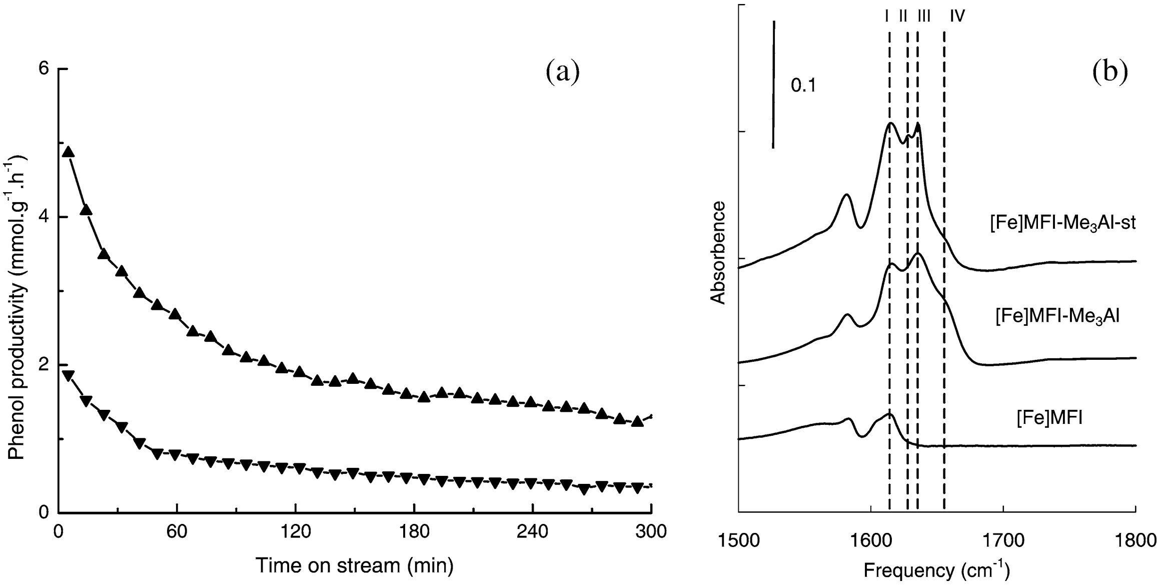

Fig. 3. Phenol productivities (mmol g^{-1} h^{-1}) as a function of the reaction time for (▼) [Fe]MFI–Me$_3$Al and (▲) [Fe]MFI–Me$_3$Al-st (a) and IR spectra after NO exposure and evacuation for [Fe]MFI, [Fe]MFI–Me$_3$Al, and [Fe]MFI–Me$_3$Al-st (b).

upon steaming correspond to the trends in phenol productivity, suggesting the relevance of the extraframework Fe–Al–O species in the selective benzene oxidation. We note in passing that we have found that the phenol productivity correlates to the intensity of these bands for a larger set of [Fe,Al]MFI samples with a wide range of Fe and Al contents.

Encouraged by these results, we reasoned along the following line: if the active species in [Fe,Al]MFI are extraframework Fe–Al–O species, the introduction of aluminum in [Fe]MFI should result in an active catalyst. Generally, introduction of aluminum in the micropores of zeolites is problematic due to acid attack of aluminum-containing solutions on the framework. Moreover, this would probably lead to the removal of a portion of the Fe species.

Alternatively, we make use of the reactivity of Me$_3$Al toward hydroxyl groups to introduce Al in an anhydrous manner. The resulting aluminum content is relatively high which is due to the partial deposition of trimethylaluminum on the external silanol groups. Fig. 3 combines the results for benzene oxidation of the resulting catalysts, [Fe]MFI–Me$_3$Al and [Fe]MFI–Me$_3$Al-st, and the corresponding IR spectra after NO adsorption. Clearly, the introduction of aluminum results in a much more active catalyst than the starting material [Fe]MFI. The effect is more pronounced after steaming. Tentatively, this is attributed to a higher degree of Fe extraction upon steaming, but it might also relate to the need for high temperatures or the presence of water vapor to create mixed oxide species. Despite the somewhat lower benzene conversion compared to the [Fe,Al]MFI materials, the nitrous oxide selectivity remains close to 100% for [Fe]MFI–Me$_3$Al-st for longer reaction times. We surmise that this is due to the large excess of Al which results in a low content of iron oxide nanoparticles which we have suggested to catalyze the oxidation of coke products [12]. The result of high nitrous oxide selectivity for HZSM-5-st, which also has a large Al/Fe ratio, is in line with this explanation. Furthermore, we observed that the addition of Me$_3$Al did not lead to the generation of Brønsted acid sites (no characteristic IR band at 3610 cm^{-1}). Importantly, the IR results in Fig. 3b show the appearance of bands around 1630 and 1636 cm^{-1} after introduction of Me$_3$Al and calcination. While in the calcined sample there is a band around 1656 cm^{-1} related to extraframework Al species, we observe that this band has largely disappeared after steaming. Steaming induces the increase of the band assigned to extraframework Fe species. Concomitantly, the bands related to Fe–Al–O species have increased.

The current findings warrant the conclusion that an extraframework Fe–Al–O species stabilized in the zeolite micropores is the active component in the benzene oxidation with nitrous oxide. Although we can only speculate on the structure of these species, it may very well be that they contain a dimeric Fe center [2,4] stabilized by an extraframework Al species. In conclusion, these investigations provide the important insight that Fe and Al are necessary components for the formation of active sites in benzene hydroxylation to phenol with nitrous oxide. We have produced strong indications that extraframework Fe–Al–O species stabilized in the micropores of the MFI zeolite are the active species. This knowledge explains several seemingly contradictory results in recent literature [2,4,7–9,12–15,24] on the catalytic role of iron and aluminum. This kind of fundamental understanding is also important for the molecular design of model clusters to further elucidate the active site structure and the improvement of existing oxidation catalysts.

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