

Direct hydroxylation of aromatics to their corresponding phenols catalysed by H-[Al]ZSM-5 zeolite

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Abstract

The direct hydroxylation of benzene and its derivatives with N_2O is studied using H-[Al]ZSM-5 zeolite as catalyst. The activity of the H-[Al]ZSM-5 zeolite is increased by hydrothermal treatment. This treatment dealuminates the zeolitic framework and creates Lewis acidic extra framework alumina (EFA) which controls the catalytic activity. It is shown by ^{27}Al MAS NMR and IR measurements that the degree of dealumination correlates with the amount of EFA species formed and the yield of phenol obtained. Simple calcination of the H-[Al]ZSM-5 zeolite for a longer time (18 h/550°C) increases the selectivity whereas conversion remains unchanged. Furthermore, benzene derivatives, naphthalene and biphenyl were used as substrates in the direct hydroxylation with N_2O . The selectivity to the corresponding phenols is lower than in the case of benzene because the functional groups participate in the reaction mechanism. No correlation is found between the activation or deactivation of the aromatic ring by the functional group and the yield of the corresponding hydroxylated product. In case of naphthalene and biphenyl the yield is limited by substrate decomposition. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The cumene process is widely used for phenol production [1]. The disadvantage of this three-step process is the low conversion at every step to keep the selectivity high. At the last step, the decomposition of cumene-hydroperoxide, equal molecular amounts of phenol and acetone are produced. The profitability of this process is

strongly dependent on the market price of the inevitable by-product acetone. Therefore, efforts to develop a new route to phenol are still of interest and investigations are undertaken for an one-step process from benzene. The direct oxidation of benzene with molecular oxygen fails as maleic acid is a main product in the liquid phase [1] and total oxidation appears producing CO_2 and water.

Alternative routes include the direct hydroxylation of aromatics with H_2O_2 in the presence of titanium silicate [2] and the direct hydroxylation N_2O .

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With a V_2O_5/SiO_2 catalyst, Iwamoto et al. [3] were the first to make phenol from benzene and N_2O , with a benzene conversion of about 11% and a selectivity towards phenol of 45%. Ono et al. [4] employed H-[Al]ZSM-5 zeolites as catalysts for the reaction. They achieved only a low yield of 9% but a very high selectivity of over 90% and noticed a strong catalyst deactivation due to coking.

Using H-[Al]ZSM-5 zeolites, Gubelmann and Tirel [5,6] attained a yield of 16% with a selectivity of higher than 95%. They postulated that Brønsted acid sites were the species affecting the reaction. Burch and Howitt [7,8] also believe in the necessity of Brønsted acid sites to catalyse the reaction. They found a correlation between the amount of Al atoms in H-[Al]ZSM-5 zeolites and the yield towards phenol. They achieved a yield of 27% and a selectivity of 98% while using a catalyst with high amount of aluminium ($SiO_2/Al_2O_3 = 33$).

By contrast, Panov et al. [9–23] found a correlation between the amount of iron in the ZSM-5 zeolite and the conversion of benzene with N_2O to phenol. They suggested that only the coordinatively-unsaturated iron atoms in extra framework iron hydroxide complexes, formed at the thermal treatment step after the synthesis of the zeolite (the so-called ‘ α -centres’), are responsible for the catalytic efficiency. The N_2O molecule decomposes on these ‘ α -centres’, producing molecular nitrogen and a kind of surface oxygen, the so-called ‘ α -oxygen’ which is adsorbed to the α -centres. The energy of adsorption is very low, causing the high reactivity of the α -oxygen which is able to oxidise CO and methane to CO_2 already at room temperature and even to react with benzene to phenol at room temperature.

Zholobenko [24] and Zholobenko et al. [25] confirmed the existence of adsorbed ‘ α -oxygen’ after the decomposition of N_2O on H-[Al]ZSM-5 zeolites. Their findings on the location of α -centres were in contradiction to the report of Panov et al. [15]. They noticed that a calcination of H-[Al]ZSM-5 zeolites at high temperatures

up to 850°C raises the activity for direct hydroxylation of benzene with N_2O to phenol. Hence, they proposed that structural defects in the zeolite framework created by severe calcination are the active centres that create the α -oxygen. Since coordinatively-unsaturated aluminium appears in these structural defects, there is a relationship with the active centres proposed by Panov et al. [15]. However, severe calcination leads to the collapse of the zeolite structure. Therefore, the loss of crystallinity due to structural collapse limits the increase of the conversion for the regarded reaction. The necessity of high crystallinity for the studied reaction was shown by Piryutko et al. [22] and Kharitonov et al. [23].

It was the aim of this work to create coordinatively-unsaturated extra framework aluminium through the mild steaming of H-[Al]ZSM-5 zeolites as active species and thereby avoiding the collapse of the zeolite structure. In this context, the issue whether direct hydroxylation of benzene derivatives might be an alternative route for the production of the corresponding phenols was also investigated.

2. Experimental

Three H-[Al]ZSM-5 zeolite samples were kindly provided by the companies Uetikon, Switzerland and Degussa, Germany. The zeolites were extrudated, calcined at 550°C for 5 h (zeolites A and B) and 18 h (zeolite C) and crashed into split 1–1.6 mm. The chemical composition of the zeolites are given in Table 1. Elemental analysis was done by ICP–AES using a Spectroflame D.

The steaming of the catalysts and the catalytic tests were done in the same apparatus. Three grams of the steamed catalyst was filled into a tubular reactor in the form of a coil with an i.d. of 6 mm and dried at 150°C under nitrogen. In case of hydrothermal treatment, the catalyst was steamed at 550°C and a water partial pressure of 300 mbar. The period of

Table 1
The chemical analysis of H-[Al]ZSM-5 zeolites

Sample		Si/Al	Na/Al	Fe/Al
A	KM 769 Degussa	14	0.027	0.020
B	KM 906 Degussa	16	0.027	0.004
C	Zeocat PZ-2/54 Uetikon	29	0.063	0.024

steaming varied in order to find a correlation between the steaming duration and the catalytic properties. After steaming, the reactor was cooled down and a sample of catalyst was taken for further analysis. For the reaction, 2 g of the catalyst were retained in the tube.

The reaction mixture contained 25 mol% aromatic substance and 75 mol% N₂O. The weight hourly space velocity (WHSV) based on the aromatic substance was 1 h⁻¹. In case of benzene the reaction temperature was 350°C but varied between 300°C and 550°C for the benzene derivatives. In both cases no inert gas was used. The products were collected in a cooling trap. Because of strong deactivation due to coking the first samples of products were taken already after 0.25 h time on stream (TOS). The time was measured after the first appearance of gaseous product in the trap.

The conversion is based on the aromatic substance reacted. The selectivity is defined as the molar ratio of the formed phenol to converted aromatic substance. The conversion of N₂O and the selectivity based on N₂O was not determined because N₂O was always used in excess. The mass balance during the sampling time was ≥ 95%.

The samples were analysed by a Siemens Sichromat RGC-202 Gaschromatograph using a 50-m Pona-HP-FS column. The product gas was collected in an air sack and analysed by an Fischer Gas Partitiometer Modell 1200. Under the employed reaction conditions no CO₂ was detected implying that no total oxidation appeared.

Two methods were used to measure the level of dealumination of the H-[Al]ZSM-5 zeolites after steaming: IR and ²⁷Al MAS NMR spectroscopy.

The IR spectra were recorded with a Nicolet FTIR 510 P spectrometer. The IR spectroscopy allows a qualitative estimation of the level of dealumination by the increase of the frequency of the structurally-non-sensitive asymmetrical T–O–T (T = Al or Si) stretching vibration at 1100 cm⁻¹ [26–28]. It is the most intensive peak in this area of the zeolite. H-[Al]ZSM-5 zeolites employed have a low content of aluminium. Therefore, the frequency shift of their T–O–T stretching vibration due to dealumination is small. This fact was considered by using a high resolution of 1 cm⁻¹ and analysing one sample several times. Furthermore, the amount of analysed sample was adjusted in such a way that a common transmittance of about 20–25% of any analysed peak was achieved.

Estimations about the aluminium distribution (framework–non-framework) were obtained by ²⁷Al MAS NMR spectroscopy, using a Bruker ASX spectrometer (resonance frequency 104 MHz, spinning speed 12 kHz). The external reference was Al(H₂O)₆³⁺. The samples were saturated with water over night. For dealuminated zeolites broad lines centred at around 30 ppm (Fig. 1) are usually attributed to non-framework tetrahedral and pentacoordinated aluminium [29–35]. The peak at 0 ppm corresponds to octahedrally-coordinated non-frame-

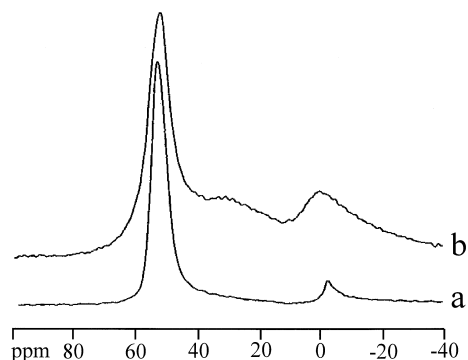


Fig. 1. ²⁷Al MAS NMR spectra of catalyst B calcined (5 h 550°C) (a) and subsequently steamed (7 h, 550°C, *p*_{H₂O} = 300 mbar) (b).

work aluminium. The sharp peak at about 55 ppm represents aluminium in tetrahedral environment. The ^{27}Al spectra were deconvoluted using Gaussian lines.

Non-framework tetrahedrally- and pentaedrally-coordinated aluminium exposes Lewis acidity [29,36,37].

To investigate the ratio of Lewis to Brønsted acidity the catalyst samples were adsorbed with pyridine and subsequently analysed by IR spectroscopy as presented elsewhere [38–40]. The qualitative evaluation of the peaks representing Brønsted and Lewis acidity occurred in accordance with the investigations of Khabtou et al. [41].

X-ray diffractometry (XRD) was done with a Siemens X-Ray Diffractometer D5000.

3. Results and discussion

Fig. 2 represents the frequency of the structurally-non-sensitive asymmetrical T–O–T stretching vibration for the catalysts A and B after 5 h calcination at 550°C and subsequent steaming at 550°C and a water partial pressure of 300 mbar.

Generally, the frequency shifted to higher wavenumbers due to steaming. For catalyst A, the frequency increased steadily up to 24 h steaming time. The shift to higher wavenumbers was negligible after 18 h of calcination at 550°C

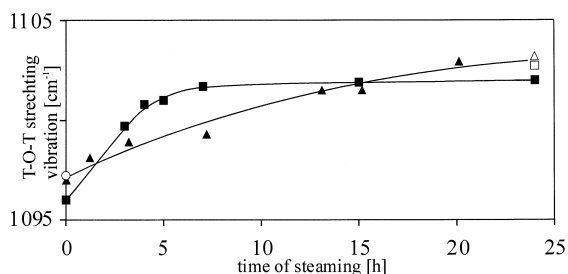


Fig. 2. Frequency of the structurally-non-sensitive asymmetrical T–O–T stretching vibration of catalyst A (\blacktriangle) calcined 5 h at 550°C (\circ , calcined 18 h at 550°C) and B (\blacksquare) calcined 5 h at 550°C for different steaming times at 550°C and a water partial pressure of 300 mbar (catalyst A (\triangle) and B (\square) steamed 600°C 24 h $p_{\text{H}_2\text{O}} = 450$ mbar).

without further steaming. Hence, no dealumination of the zeolite framework occurred due to longer calcination. In case of catalyst B, the stretching vibration increased only for a short time of steaming (5 h) and remained constant for a longer time of steaming. Furthermore, via increasing the steaming severity by raising the steam pressure to 450 mbar and the steaming temperature to 600°C, no significant further increase in the regarded vibration was observed. This implies that the catalysts cannot be further dealuminated under the applied conditions.

Table 2 shows the distribution of framework and extra framework aluminium of catalyst B for different steaming times. The distribution was determined by the deconvolution of ^{27}Al MAS NMR spectra using Gaussian lines and subsequent integration. After calcination, about 75% of the total Al content was tetrahedrally-coordinated. After 3 h of steaming, this amount decreased significantly to around 35%. Simultaneously there was an increase of the penta- and octahedrally-coordinated extra framework aluminium. A prolongation of the steaming time had minor effect on the distribution of the aluminium coordinated in different environments. The distribution of framework and extra framework aluminium for catalyst B as a function of steaming time was in agreement with the shift of the structurally-non-sensitive asymmetrical T–O–T stretching vibration (Fig. 2).

Fig. 3 displays typical FTIR spectra of pyridine adsorbed samples of catalyst B after different steaming times. The increase of the intensity of the band at 1455 cm^{-1} , which represents pyridine adsorbed at Lewis acid sites, could be seen clearly whereas the intensity of the 1545 cm^{-1} band, which represents Brønsted acid sites, remained rather unchanged. From these measurements, we derived a qualitative estimation about the ratio of the band intensities representing pyridine adsorbed at Lewis acid sites and pyridine adsorbed at Brønsted acid sites (Fig. 4).

This ratio increased with steaming time due to dealumination and the creation of Lewis

Table 2

The distribution of framework and extra framework aluminium for catalyst B by ^{27}Al MAS NMR

Aluminium distribution	Steaming time			
	Calcined	3 h	4 h	7 h
Octahedrally-coordinated extra framework aluminium	10%	24%	25%	27%
Penta- and tetrahedrally-coordinated extra framework aluminium	15%	41%	42%	43%
Tetrahedrally-coordinated framework aluminium	75%	35%	33%	30%

acidic EFA. After 3 h of steaming the Lewis-to-Bronsted ratio was more or less constant with only a slight decrease after 24 h of steaming. This slight decrease was probably caused by agglomeration of the extra framework aluminium to clusters, which expose less Lewis acid sites than numerous smaller EFA species. Such agglomeration was already observed as an effect of steaming [29,33,42,43]. XRD spectra (not presented here) showed that the zeolite structure did not collapse during steaming.

Finally, the calcined and steamed H-[Al]ZSM-5 zeolites were used as catalysts for the direct hydroxylation of benzene and N_2O to phenol. Figs. 5 and 6 present the results of conversion and selectivity for the catalysts A and B.

For catalyst A, the conversion increased from 12% up to 30% after around 10 h of steaming

and dropped to 20% after 24 h of steaming. A sharp increase in selectivity could be observed after simple calcination (18 h), whereas conversion remained unchanged. Short steaming times caused a similar increase in selectivity and for a longer period of steaming the selectivity remained rather constant. After calcination, catalyst B showed a conversion in the same range as catalyst A. For 5 h of steaming, the conversion increased from 15% to nearly 30%. In contrast to A, there was no decrease of conversion for a longer time of steaming. Further the selectivity increased up to 99% for 5 h of steaming and remained constant for longer steaming times.

For both catalysts, we can state that there was a significant increase of the conversion and selectivity towards phenol after hydrothermal treatment. Furthermore, only A showed a drop of conversion after a certain time of steaming. In case of catalyst A, longer calcination led to higher selectivity but resulted only to minor

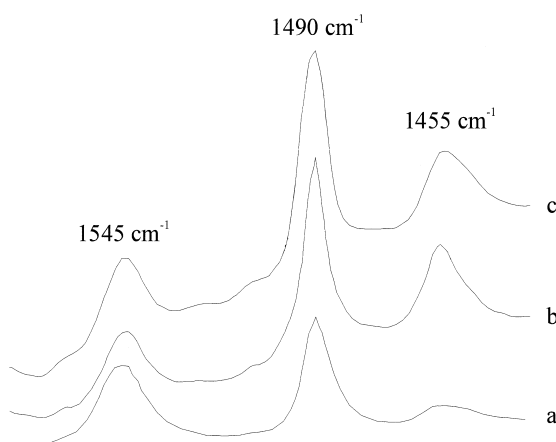


Fig. 3. The typical FTIR spectra of pyridine adsorbed samples of catalyst B after 5 h calcination at 550°C without steaming (a), calcination with 7 h (b) and 15 h (c) steaming at 550°C and a water partial pressure of 300 mbar.

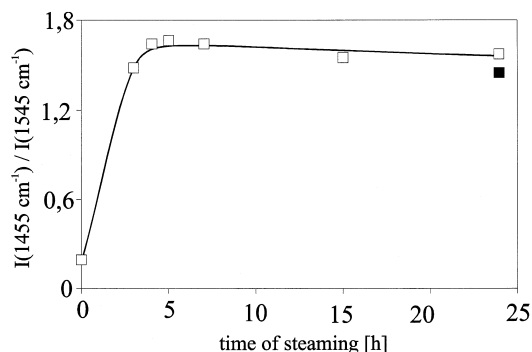


Fig. 4. The ratio of the band intensities representing pyridine adsorbed at Lewis acid sites (1455 cm^{-1}) and pyridine adsorbed at Bronsted acid sites (1545 cm^{-1}), respectively, of catalyst B as a function of steaming time (□: steamed 550°C, $p_{\text{H}_2\text{O}} = 300$ mbar) (■: steamed 600°C, $p_{\text{H}_2\text{O}} = 450$ mbar 24 h).

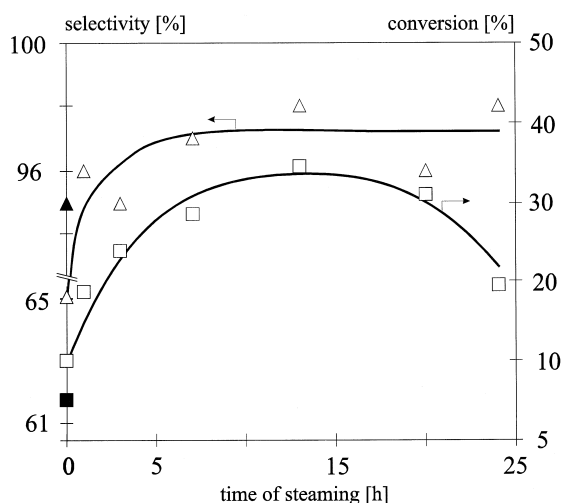


Fig. 5. The conversion (\square) and selectivity (Δ) to phenol obtained over the hydrothermally-treated catalyst A calcined 5 h at 550°C (conversion (\blacksquare) and selectivity (\blacktriangle) of A after 18 h calcination at 550°C).

effects in the conversion. More severe steaming conditions (catalyst B, 24 h, 600°C, $p_{\text{H}_2\text{O}} = 450$ mbar) did not lead to further enhanced catalytic activity.

The increase of the conversion as a function of steaming time can be explained with an increase of EFA species formed by dealumination. The increasing amount of EFA seems to be responsible for the increase of the intensity of the 1455 cm^{-1} band representing Lewis acidity in pyridine adsorption measurements (Fig. 3). This Lewis acidity enhances the catalytic activity of the H-[Al]ZSM-5 compared to the unsteamed sample.

For catalyst B there is a direct correlation between the level of dealumination (Fig. 2), the amount of EFA created (Table 2) and the conversion observed (Fig. 6). This correlation is not so straightforward for catalyst A. Nevertheless, we think that there is a dependency between the amount of EFA and the conversion of benzene to phenol. When steaming for a longer time causes no further dealumination (Fig. 2), agglomeration of the EFA species might be predominant. Then the amount of Lewis acid sites decreases and this could be responsible for the

observed drop of conversion for a longer time of steaming. The agglomeration of EFA species due to steaming is more pronounced for catalyst A than for B. So far, we have no explanation why there should be less agglomeration for B than for A.

The chemical analysis of the employed H-[Al]ZSM-5 zeolites (Table 1) shows that the content of iron is in a similar range of the H-[Al,Fe]ZSM5 zeolites used by Kharitonov et al. [13]. The authors found an increase of conversion from $\sim 7\%$ to $\sim 20\%$ with an increase of Fe content from 0.015 to 0.1 wt.% Fe in {Fe,Al}ZSM5-zeolites. If the amount of iron alone is responsible for the catalytic activity than catalyst A should give a significant better catalytic performance than catalyst B because of its higher iron content (catalyst A, 0.18 mass-% Fe_2O_3 ; catalyst B, 0.03 mass-% Fe_2O_3). Our results show no significant difference in the conversion of the unsteamed sample A and B but a difference in selectivity. Therefore, it can be concluded that beside the iron content the extra framework aluminum plays a significant role.

The good results of Panov et al. with H-[Al,Fe]-ZSM-5 and H-[Fe]ZSM-5 zeolites are probably caused by the easiness to dislodge iron from the zeolite framework only by thermal treatment [44–46] thereby creating Lewis acidic

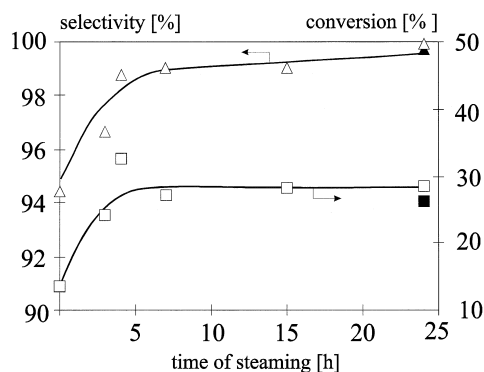


Fig. 6. The conversion (\square) and selectivity (Δ) to phenol obtained over the hydrothermally-treated catalyst B calcined 5 h at 550°C (conversion (\blacksquare) and selectivity (\blacktriangle) of B after 24 h steaming at 600°C with a water partial pressure of 450 mbar.

extra framework iron. Significant dealumination of the H-[Al]ZSM-5 is not possible with thermal treatment (Fig. 2). Only hydrothermal treatment dislodges aluminium from the framework. The thermal dislodgement of iron is particularly significant for H-[Al,Fe]ZSM-5 zeolites [46]. This might explain the better results obtained by Panov et al. [9,12] and Kharitonov et al. [13] with H-[Al,Fe]ZSM-5 zeolites rather than with H-[Fe]ZSM-5 zeolites. A direct comparison of the catalytic tests by Panov et al. to the tests of this work is not appropriate because of the different reaction conditions. In this work, no inert gas was used whereas Panov et al. employed N₂.

Concerning a possible reaction mechanism, the propositions of Panov et al. [18], Filatov et al. [47] and Zholobenko et al. [24,23] can be supported by our own results. The existence of a single electron pair allows N₂O to participate in a donor–acceptor interaction with Lewis acid centres. These authors also assume that after decomposition of the N₂O molecule the resulting oxygen remains as very active surface oxygen on Lewis acidic coordinatively-unsaturated aluminium (or iron species in the case of Panov et al.) in the framework or extra framework (as in the case of Zholobenko et al.).

In contrast to H-[Fe]ZSM-5 zeolites longer calcination of H-[Al]ZSM-5 zeolites did not ef-

fect significant demetallation. Therefore, no significant improvement of catalyst activity was achieved by calcination. The easiness to create extra framework iron only by calcination of H-[Fe]ZSM-5 zeolites explains the activity in contrast to the H-[Al]ZSM-5 catalysts which become more active after steaming.

4. Benzene derivatives, naphthalene and biphenyl

Benzene and several benzene derivatives with different functional groups were used in the direct hydroxylation with N₂O. Anisole, aniline and toluene represent substances with an activated aromatic ring for electrophilic attack whereas benzonitrile, benzaldehyde and nitrobenzene have a deactivated aromatic ring system. Chloro- and fluorobenzene are only weakly activated if at all.

Table 3 shows the conversion and selectivity of different benzene derivatives with zeolite C as catalyst. The zeolite was calcined for 18 h at 550°C prior use and not steamed. The conversion of benzene was 22% with a selectivity of 98% to phenol.

The conversion of anisole was 53% with nearly no selectivity to the desired hydroxylated

Table 3
The conversion of benzene derivatives to the corresponding phenols

Aromatic substance	Temperature (°C)	Conversion (%)	Selectivity (%)	Isomer distribution (%)		
				Ortho	Meta	Para
Benzene	350	22	98	–	–	–
Anisole	350	53	~ 1	~ 25	~ 25	~ 50
Aniline	500	13	29	65	2	33
	550	15	12	54	22	24
Toluene	350	24	27	52	32	16
Chlorobenzene	350	23	58	28	72	–
Fluorobenzene	350	19	68	32	19	49
Nitrobenzene	350	5	0	–	–	–
Benzonitrile	350	12	76	64	26	11
Benzaldehyde	300	12	0	–	–	–
Benzene mixed with nitrobenzene	350	4	~ 100 ^a	–	–	–

Reaction conditions: catalyst C (not steamed), $m_{\text{cat.}} = 2 \text{ g}$, $\text{WHSV} = 1 \text{ h}^{-1}$, $n_{\text{N}_2\text{O}}/n_{\text{aromate}} = 3$, $p = 1 \text{ bar}$, $\text{TOS} = 0.25 \text{ h}$.

^aOnly phenol was found.

product. Instead, phenol, cresol and cresol methyl ether were formed. Also only a small yield of aminophenols was found in the product mixture after hydroxylation of aniline with N_2O . At reaction temperatures under 450°C the NH_2 group of the aniline is usually adsorbed on the acid centres of the zeolite and hence no activation of N_2O at acid sites can occur. Therefore, higher reaction temperatures seem to be necessary to facilitate desorption. However at high temperatures the reaction mixture decomposed more easily to CO_2 and water. At 500°C and 550°C , the conversions of 13% and 15%, respectively, were rather low with poor selectivities of 29% and 12%. Beside CO_2 , the main by-products were phenazine, *N*-phenylbenzamine.

Toluene was converted to cresol with a conversion of 24% and a rather poor selectivity of about 27%. Besides some higher molecular aromatics the product mixture consisted of benzene, xylene and phenol.

Although anisole, aniline and toluene are more susceptible to electrophilic attack than benzene the yield of the corresponding hydroxylated products is always lower than that of benzene. This is due to poor selectivities because of decomposition of the reaction mixture or because of blocking the acid sites by the functional groups. In case of anisole the methoxy group is preferentially attacked.

For chlorobenzene and fluorobenzene the conversion to the corresponding phenols was similar to the conversion of benzene with a selectivity of about 70%. In both cases phenol was the major by-product. F and Cl atoms are

substituents which have almost no influence on the aromatic ring. This might be the reason why the conversion is similar to that of benzene.

Benzaldehyde was exclusively converted to benzene, phenol and benzoic acid. No corresponding hydroxyproduct was formed. In the case of benzonitrile, the conversion was 12% with a selectivity of 76%.

The direct hydroxylation of nitrobenzene yielded no nitrophenol at all. The by-products were benzene, phenol and aniline. Maybe the nitrogroup with its Lewis basic character occupies the acid centres so that the activation of the N_2O is not possible and only the nitrogroup participates in the reaction. In a mixture of benzene and nitrobenzene even benzene was almost not converted to phenol anymore. This is a hint that nitrobenzene blocks the Lewis acid centres.

To sum up, no influence due to the activating or deactivating character of the functional group at the aromatic ring is found. In spite of longer calcination for 18 h, which yields a high selectivity in case of benzene, only poor selectivities are observed. Instead the conversion is presumably lowered by blocking of the active Lewis acid centres or the selectivity is very poor because of an wide range of by-products.

Naphthalene or biphenyl without functional group might be more promising substrates for direct hydroxylation. At reaction temperatures below 450°C β -naphthol was the only product for the hydroxylation of naphthalene (Table 4). The low selectivity under 50% was exclusively caused by total oxidation. The formation of only β -naphthol underlines the shape selective prop-

Table 4
The conversion of naphthalene to naphthol

Temperature ($^\circ\text{C}$)	Conversion (%)	Selectivity (%)	Isomer distribution	
			α (%)	β (%)
300	~ 1	~	0	100
350	1	43	0	100
450	6	0	—	—

Reaction conditions: catalyst C (not steamed), $m_{\text{cat.}} = 2$ g, $WHSV = 1$ h $^{-1}$, $n_{N_2O}/n_{\text{aromate}} = 3$, $p = 1$ bar, TOS = 0.25 h.

Table 5
The conversion of biphenyl to hydroxybiphenyl

Temperature (°C)	Conversion (%)	Selectivity (%)	Isomer distribution		
			2- (%)	3- (%)	4- (%)
350	6	70	13	44	43
400	11	19	71	9	20
450	13	16	100	0	0

Reaction conditions: catalyst C (not steamed), $m_{\text{cat.}} = 2$ g, $\text{WHSV} = 1 \text{ h}^{-1}$, $n_{\text{N}_2\text{O}}/n_{\text{aromate}} = 3$, $p = 1$ bar, $\text{TOS} = 0.25$ h.

erties of the H-[Al]ZSM-5 zeolite because the formation of the bulky α -naphthol is suppressed. At higher reaction temperatures only total oxidation occurred.

At 350°C, biphenyl was converted to hydroxybiphenyl (Table 5) with a conversion of 6% and with a selectivity of 70%. At higher reaction temperatures the conversion increased because of significant total oxidation.

For hydroxylation of naphthalene and biphenyl total oxidation becomes an important side reaction so that the selectivity towards the corresponding phenols is lowered. Nevertheless even at lower temperatures at which less total oxidation occurs the yield is very poor.

5. Conclusions

It is shown that dealumination of H-[Al]ZSM-5 zeolites by steaming increases their activity for direct hydroxylation of benzene with N_2O to phenol. The Lewis acidity exposed by EFA species is probably necessary to improve the conversion with a very high selectivity. A correlation between the amount of EFA and yield of phenol depending on the period of steaming is found. A drop of conversion after a longer time of steaming might be caused by agglomeration of the Lewis acidic EFA species.

Benzene derivatives as well as naphthalene and biphenyl show less conversion to the corresponding phenols than benzene itself. In case of naphthalene and biphenyl formation of the corresponding phenols is limited by decomposition. The best results are achieved by chloro- and

fluorobenzene. Nevertheless no influence is found on the yield of the hydroxylated product in dependence of the activating or deactivating character of the functional group. Substituents with a basic character seem to block the Lewis acid sites of the zeolite. Therefore a higher temperature has to be employed which unfortunately favours side reaction.

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References

- [1] K. Weissermehl, H.J. Arpe, Industrielle Organische Chemie, VCH, Weinheim, 1988.
- [2] W.F. Hölderich, in: L. Guzi et al. (Ed.), New Frontiers in Catalysis, Elsevier, Amsterdam, 1993, p. 127.
- [3] M. Iwamoto, J. Hirata, K. Matsukami, S. Kagawa, J. Phys. Chem. 87 (1983) 903.
- [4] Y. Ono, K. Tohmori, S. Suzuki, K. Nakashiro, E. Suzuki, in: M. Guisnet et al. (Ed.), Heterogeneous Catalysis and Fine Chemicals, Elsevier, Amsterdam, 1988 p. 75.
- [5] M. Gubelmann, P. Tirel, EP 0341165, Rhone-Poulenc-Chimie, 1988.
- [6] M. Gubelmann, P. Tirel, US 5001280, Rhone-Poulenc-Chimie, 1988.
- [7] R. Burch, C. Howitt, Appl. Catal. A Gen. 86 (1992) 139.
- [8] R. Burch, C. Howitt, Appl. Catal. A Gen. 103 (1993) 135.
- [9] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, J. Mol. Catal. 61 (1990) 85.
- [10] V.I. Sobolev, G.I. Panov, A.S. Kharitonov, V.N. Romanikov, A.M. Volodin, Kinet. Catal. 34 (1993) 797.
- [11] V.I. Sobolev, O.N. Kovalenko, A.S. Kharitonov, G.I. Panov, Mendeleev Commun. 1 (1991) 29.

- [12] G.I. Panov, G.A. Shevela, A.S. Kharitonov, V.N. Romanikov, L.A. Vostrikova, *Appl. Catal. A Gen.* 82 (1992) 31.
- [13] A.S. Kharitonov, G.A. Sheveleva, G.I. Panov, V.I. Sobolev, Y.A. Paukshtis, V.N. Romannikov, *Appl. Catal. A Gen.* 98 (1993) 33.
- [14] A.S. Kharitonov, G.I. Panov, K.G. Ione, V.N. Romannikov, G.A. Sheveleva, L.A. Vostrikova, V.I. Sobolev, *US* 5,110,995 (1992).
- [15] G.I. Panov, A.S. Kharitonov, V.I. Sobolev, *Appl. Catal. A Gen.* 98 (1993) 1.
- [16] V.I. Sobolev, A.S. Kharitonov, Y.A. Paukshtis, G.I. Panov, *J. Mol. Catal.* 84 (1993) 117.
- [17] G.I. Panov, V.I. Sobolev, A.S. Kharitonov, E.A. Paukshtis, Meeting Phoenix 1994, poster No. 20.
- [18] V.I. Sobolev, O.N. Kovalenko, A.S. Kharitonov, Y.D. Pankratiev, G.I. Panov, *Mendeleev Commun.* 1 (1991) 29.
- [19] V.I. Sobolev, G.I. Panov, A.S. Kharitonov, V.N. Romanikov, A.M. Volodin, K.G. Ione, *J. Catal.* 139 (1993) 435.
- [20] A.S. Kharitonov, T.N. Aleksandrova, G.I. Panov, V.I. Sobolev, G.A. Sheveleva, E.A. Paukshtis, *Kinet. Katal.* 35 (2) (1994) 296.
- [21] A.M. Volodin, V.A. Bolshov, G.I. Panov, *J. Phys. Chem.* 98 (1994) 7548.
- [22] L.V. Piryutko, O.O. Parenago, B.V. Lunina, A.S. Kharitonov, L.G. Okkel, G.I. Panov, *React. Kinet. Catal. Lett.* 52 (1994) 275.
- [23] A.S. Kharitonov, V.B. Fenelonov, T.P. Voskresenskaya, N.A. Rudina, V.V. Molchanov, L.M. Plyasova, G.I. Panov, *Zeolites* 15 (1995) 253.
- [24] V. Zholobenko, *Mendeleev Commun.* 3 (1993) 28.
- [25] V. Zholobenko, I.N. Senchenya, L.M. Kustov, V.B. Kazansky, *Kinet. Catal.* 32 (1991) 132.
- [26] U. Lohse, E. Alsdorf, H. Stach, *Z. Anorg. Chem.* 447 (1978) 64.
- [27] E. Löffler, Ch. Peuker, H.G. Jerschke, *Catal. Today* 3 (1988) 415.
- [28] E.M. Flanigen, in: J.A. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, ACS Monograph, 1976, p. 80.
- [29] A.G. Ashton, S. Batmanian, J. Dwyer, I.S. Elliot, F.R. Fitch, *J. Mol. Catal.* 34 (1986) 73.
- [30] P.B. Bodart, J.B. Nagy, G. Debras, Z. Gabelica, P.A. Jacobs, *J. Phys. Chem.* 90 (1986) 5183.
- [31] G.J. Ray, A. Samoson, *Zeolites* 13 (1993) 410.
- [32] W.A. Buckermann, C.B. Huang, F. Fajula, *Zeolites* 13 (1993) 448.
- [33] D. Coster, A.L. Blumenfeld, J.J. Fripiat, *J. Phys. Chem.* 98 (1994) 6201.
- [34] J.P. Gilson, G.C. Edwards, A.W. Peters, K. Rajagopalan, R.F. Wormsbecher, T.G. Roberie, M.P. Shatlock, *J. Chem. Soc. Chem. Commun.* (1987) 91.
- [35] M.C. Cruickshank, L.S. Dentglessler, S.A.I. Barri, I.J.F. Poplett, *J. Chem. Soc. Chem. Commun.* (1986) 23.
- [36] P.A. Jacobs, R. von Ballmoos, *J. Phys. Chem.* 86 (1982) 3050.
- [37] N.P. Rhodes, R. Rudham, *J. Chem. Soc. Faraday Trans.* 89 (1993) 2551.
- [38] P.A. Jacobs, B.K.G. Theng, J.B. Uytterhoeven, *J. Catal.* 26 (1972) 191.
- [39] L.M. Parker, D.M. Bibby, G.R. Burns, *J. Chem. Soc. Faraday Trans.* 87 (1991) 3319.
- [40] S. Jolly, J. Saussey, J.C. Lavalley, *J. Mol. Catal.* 86 (1994) 401.
- [41] S. Khabtou, T. Chevreau, J.C. Lavalley, *Microp. Mater.* 3 (1994) 133.
- [42] L.D. Fernandes, P.B. Bartl, J.L.F. Monteiro, J.G. da Silva, S.G. de Menezes, M.J.B. Cardoso, *Zeolites* 14 (1994) 533.
- [43] J. Dwyer, F.R. Fitch, G. Qin, J.V. Vickermann, *J. Phys. Chem.* 86 (1982) 4574.
- [44] P. Ratnasamy, R. Kumar, *Catal. Today* 9 (1991) 329.
- [45] A. Brückner, R. Lück, W. Wieker, B. Fahlke, *Zeolites* 12 (1992) 380.
- [46] A. Hagen, F. Rössner, I. Weingart, B. Spliethoff, *Zeolites* 15 (1995) 270.
- [47] M.J. Filatov, A.G. Pelmeshnikov, G.M. Zhidomirov, in: L. Guzi (Ed.), *New Frontiers in Catalysis*, Elsevier, Amsterdam, 1993, p. 311.