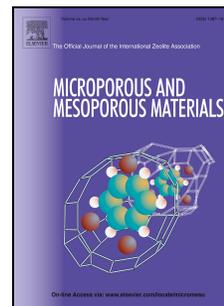


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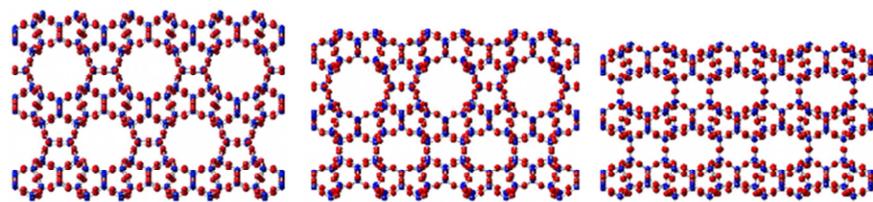
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IPC-2

IPC-6

IPC-4

ACCEPTED MANUSCRIPT

Nitric oxide production from nitrite by a series of zeolites produced via the ADOR route

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The nitric oxide (NO) production for a series of aluminosilicate zeolites, prepared using the ADOR method, was investigated. Al-UTL and Al-IPC-2, -4 and -6 were prepared and characterised to determine their elemental composition. Positive trends were found to exist between zeolite pore size and the rate and total amount of NO produced. A trend between the number of acid sites and the initial rate of NO produced by the zeolite was also discovered.

1. Introduction

Zeolites are routinely used for large-scale catalytic applications, including petroleum cracking and DeNO_x catalysis.^{1,2} More recently, these inorganic, microporous solids have been used for the storage and subsequent delivery of drugs and medically useful gases (e.g. nitric oxide).³⁻⁶ Based on the previous medical applications of zeolites, this study has focused on their potential to produce nitric oxide (NO) gas from bioavailable nitrite.

NO, although toxic in quantities exceeding 80 parts per million (ppm),⁷ is nonetheless a bio-active gas which acts as a signalling molecule⁸ in the body and possesses a variety of anti-thrombotic, anti-inflammatory and anti-mitogenic properties.⁹

Previous studies have shown this colourless, free radical is responsible for many biological processes with low NO concentrations (pico- to nanomolar) necessary for controlling vasodilation^{10,11} and inhibiting platelet adherence¹² whilst larger NO concentrations (micromolar) are necessary for antibacterial effects.¹³ In the future, zeolites capable of converting bioavailable nitrite into NO could be medically useful for targeted release, with possible applications including use as coatings for stents and catheters or in wound-healing products.^{14,15}

The ADOR (Assembly-Disassembly-Organisation-Reassembly) method is a novel approach that has enabled us to selectively control the pore size of the zeolite by altering the linkers between silicate layers.^{16,17} Unlike the traditional methods of zeolite synthesis this method allows us to produce a series of structurally similar zeolites with the same basic topological features but different pore sizes. This allows us to directly compare the effect of pore size on a process. Here we report just such a study where we describe the use of a series of ADOR-derived zeolites to convert nitrite to nitric oxide in amounts that are potentially of use in biology or medicine.

The assembly stage (A) of the ADOR process involves the synthesis of a 'parent' germanosilicate zeolite, which is then selectively disassembled (D) via hydrolysis. The exact structure of the disassembled species depends on the strength of the acid and timescale of the reaction.¹⁸ As germanium has a preference for being located in the double-4-ring (d4r) units of the UTL structure and these d4r units consist of Ge-O-Ge and Ge-O-Si linkages which are hydrolytically unstable, selective disassembly of UTL is possible. This results in the formation of an intermediate structure, often IPC-1P, which consists of UTL layers that can be organised (O) with the use of a structure directing agent or via self-organisation. The layered structure is reassembled (R) using calcination to form a 'daughter' zeolite. The 'parent' and descendent zeolites both possess the same layers, but the linkages between the layers differ. By altering the reagents and conditions used in the disassembly and organisation steps of the process, the linker between layers and therefore, the pore size of the structure is controlled.^{19,20} In zeolite UTL, the linkers located between layers are d4r units whilst the linkers in IPC-2 are single-4-rings (s4r) and in IPC-4 the layers are directly connected through an oxygen atom. Therefore, the pore size and accessibility of the zeolite structures decrease with decreasing size of the linker.

A source of aluminium was incorporated during the disassembly stage of the ADOR process, as outlined in a previous paper and ²⁷Al MAS NMR indicated that all measureable aluminium is tetrahedrally coordinated.²¹ This was necessary to produce the acid-form of the zeolite, as the production of NO from nitrite needs acid to proceed.

Here we will report the syntheses of the acid-forms of zeolites UTL (which is linked by d4r units), IPC-2 (s4r), IPC-4 (only oxygen links) and IPC-6 (s4r and oxygen) and discuss how altering the pore size of the zeolite affects

the rate and quantity of NO produced by the sample. The family of ADOR-derived IPC-n materials is interesting for these studies because the chemistry of the layers remains unchanged across the series, meaning that the variables are reduced only to pore size.

Experimental Section

Synthesis of zeolites UTL, Al-IPC-2, -4 and -6

All solvents and reagents necessary to prepare each of the products were sourced commercially (ACROS Organics, Alfa Aesar, Fisher and Sigma Aldrich) and were used without further purification. The formation of germanosilicate UTL and zeolites Al-IPC-2, -4 and -6 were prepared according to previous syntheses reported in the literature.^{20,21} The full details of these syntheses are included in the supporting information.

Formation of Al-UTL

A mixture containing calcined UTL (0.2 g) and aluminium nitrate (20 mL, 1 M) was stirred for 20 minutes then heated in an autoclave to 175 °C for 24 hours. The product was isolated by filtration, stirred with dilute hydrochloric acid (10 mL, 0.01 M) for 10 minutes, washed and calcined at 580 °C for 6 hours.²¹

Acid site formation of zeolite

Zeolite (0.5 g) and ammonium chloride (0.3 M, 10 mL) were stirred overnight at room temperature; the sample was then isolated by filtration and dried in air. This process of ion-exchange was repeated a further two times before the sample was calcined at 580 °C for 6 hours.

Characterisation of samples

Powder X-ray diffraction (PXRD) data was collected on a STOE STADIP diffractometer operating CuK α_1 radiation in Debye-Scherrer mode. Diffraction patterns were collected over an angle range of 3-50° 2 θ and all samples were ground to reduce the effects of preferential orientation of crystallites.

A Jeol JSM-5600 Scanning Electron Microscope (SEM) was used to record images of each sample. All samples were sputter-coated with gold using a Quorum Q150R ES coating system.

EDX analysis was performed using the SEM system which had an Energy Dispersive X-ray (EDX) system attached. Calculations were performed to determine the amount of aluminium in terms of μmol . This allowed the number of acid sites to be predicted for each sample.

Measurement of NO production

A sealed vial containing the acid-form of the zeolite (5 mg) and purified water (2.6 mL) was connected to the analyser. An injection of aqueous sodium nitrite (250 μL , 0.05 M, 0.0125 mmol) took place five minutes into the run. The run was terminated once NO production had returned to background levels. The nitrite to NO reaction therefore takes place in the presence of water. At all times the temperature was maintained at 25 °C.

The conversion of sodium nitrite to NO gas was determined by recording the total amount of NO produced by each zeolite sample using a Sievers 280i Nitric Oxide Analyser, which uses chemiluminescence to quantify the amount of NO in a gas stream.

Data were collected until the detected NO concentration measured background NO levels (~ 6 ppb). The time taken for each sample to return to background levels varies depending on the structure of the zeolite, and hence this is another indicator of the zeolites usefulness for medical applications. Results for each sample were recorded in triplicate (except for the Al-IPC-4, 1.02% aluminium sample where data were collected in duplicate), with the average NO production reported for each sample.

Thermogravimetric Analysis

TGA analyses were carried out in air, with samples placed in ceramic crucibles and heated to 250 °C (ramp rate of 10 °C min^{-1}). All results were recorded on a Netzsch TG 209 instrument. The dehydration was recorded for all samples, with the exception of the Al-IPC-4 zeolite containing 1.02% aluminium.

Results and Discussion

Characterisation of acid-zeolite samples

Zeolites Al-IPC-2, -4 and -6 were prepared using the ADOR method,^{18,20} as outlined in Figure 1, whilst the Al-UTL sample was prepared using a slightly different approach²¹ that involved reacting calcined UTL and aluminium nitrate solution (1M) in an autoclave for 24 hours.

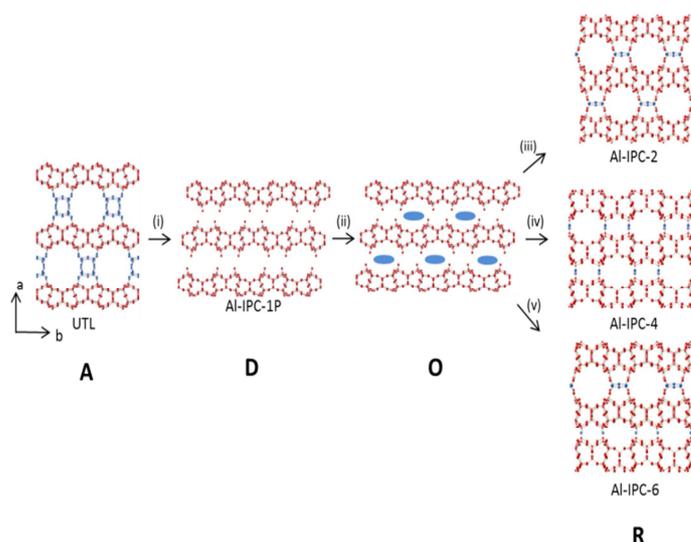


Fig. 1: ADOR method reaction scheme. Germanosilicate UTL was selectively disassembled using (i) a mixture of 1 M acid and 1-1.6 M aluminium nitrate to form the layered Al-IPC-1P structure. The layers were rearranged with the use of either (ii) octylamine or diethoxydiethylsilane. Using calcination at 580 °C, the layers are reassembled to form either (iii) Al-IPC-2, (iv) Al-IPC-4 and (v) Al-IPC-6. Note that the red atoms represent the common topology of each structure, whilst blue atoms represent the differing linkers.

PXRD analysis was performed on the as-made and acid-forms of the samples to confirm that each zeolite tested on the NOA was a crystalline, phase pure material. PXRD patterns of the calcined zeolites are shown in the supporting information. Analysis of the SEM images recorded for each zeolite and its UTL starting material revealed that the crystal morphology remained broadly unchanged throughout the process, although the surfaces of the crystals did reveal some damage (see supplementary information). This is to be expected during the ADOR process and the subsequent ion-exchange step. EDX analysis confirmed that the incorporation of aluminium during the disassembly step was successful, with the results of EDX analysis tabulated in the supporting information. Based on the percentage content of aluminium in the structure, an approximate calculation of the number of acid sites present in the zeolite was made assuming each aluminium ion produced one acid site.

Although the ADOR process was successfully applied to germanosilicate UTL, once doped to form Al-UTL the ADOR process was no longer applicable. Based on the results of EDX analysis it was noted that the germanium content decreased from 4.51% in UTL to 0.27% in the Al-UTL sample after the alumination of the sample. As hydrolytically unstable germanium was removed during the addition of aluminium, this meant the Al-UTL zeolite could not be disassembled to produce Al-IPC-2, -4 or -6. As a result, the D4R linkers in the Al-UTL structure are made predominantly of silicon and aluminium atoms, explaining why Al-UTL is no longer able to undergo the ADOR process.

Previous research has revealed that washing aluminium-doped samples with 0.01-0.1 M HCl removes all extra-framework aluminium, as does the ion-exchange process. The ion-exchange step was performed on each sample and in some cases samples were rinsed with dilute HCl, which is known to remove extraframework aluminium.^{23,24} The aluminium content ranged from 0.25% (Si/Al = 95.7) to 1.75% (Si/Al = 14.3) – see Table 1 for details.

The amount of water in the pores was calculated using thermogravimetric analysis (TGA). As the dry weight of the samples tested on the NO analyser could be determined, and the aluminium content of each sample was known, the maximum possible number of molar acid sites present in each zeolite sample was calculated. Based on the understanding that two neighbouring acid sites were necessary for the production of one molecule of NO,²² we calculated how many acid sites had reacted during the process and the percentage of acid sites that had reacted for each sample.

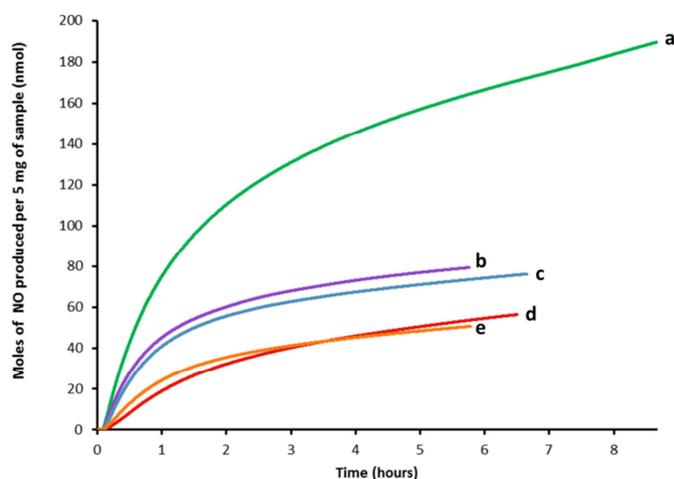


Figure 2: The total NO production of a) Al-UTL b) Al-IPC-2 c) Al-IPC-6 d) Al-IPC-4 containing 1.02% aluminium and e) Al-IPC-4 containing 0.25% aluminium were recorded with a clear trend arising between increasing pore size and NO production. Graphically, it is seen that as the pore-size of the zeolite species increases ($a > b > c > d = e$), the total production of NO gas and the rate of NO production increase. In comparison, NO production appears to vary little with the number of acid sites (d and e). The temperature of the measurements was 25 °C.

NO production from acid-form zeolite samples

It is clear from the graph in figure 2 that the NO production of the Al-UTL sample was greatest (193.0 nmol) whilst the Al-IPC-4 (1.02% Al) sample produced the lowest quantity of NO (56.5 nmol). Samples Al-IPC-2 and Al-IPC-6 produced 80.1 nmol and 77.7 nmol of NO, respectively. Of the samples investigated in this study, Al-UTL (14-12-R channels) had the largest channel size, whilst Al-IPC-4 had the smallest channel size (10-8-R). Al-IPC-2 (12-10-R) and Al-IPC-6 (12-10-R and 10-8-R) consisted of intermediately sized channels. Hence it is clear that the total NO production of the sample increases as channel size and therefore framework accessibility increases. It is likely that the nitrite ion can access acid sites in a larger pored zeolite that are structurally inaccessible in smaller pored zeolites.

A trend between pore size and rate of NO production is also clear from the graph shown in Figure 2, as the gradients of the NO production curves, and so the rates of NO production, increase with increasing channel size. This relationship arises as it is easier for the nitrite ion to enter and for the NO radical to leave from larger pore systems than smaller pore systems.

In order to establish whether the conversion of sodium nitrite to NO gas was controlled by the Brønsted acid site, a reference was recorded on the analyser. The sample used was a calcined but un-exchanged sample of high silica RHO that therefore contained no acid sites. When using this sample in the set-up, no NO gas was produced (see supporting information for release profile). This confirms that the reaction does not proceed without the acid sites. Although the acid sites control the reaction, no obvious trend between the concentration of acid sites and NO production of each sample was displayed when the results of the NO and EDX analysis were compared (table 1).

As discussed previously, EDX analysis was used to determine the number of μmol of aluminium atoms in the framework. Based on this result the number of acid sites was approximated for each structure. To determine whether the NO production varied only with pore size or with the number of acid sites as well, a second batch of Al-IPC-4 with a lower aluminium content (0.25% aluminium) was prepared.

By comparing the average NO production of the two Al-IPC-4 zeolites (figure 2; d and e), it is possible to see that the difference in total NO production is small (5.7 nmol). As the Al-IPC-4 (d) contains 1.02% aluminium whilst the other sample (e) contains just 0.25% aluminium, it was expected that a four-fold decrease in aluminium

content - and therefore acid site content - would result in a four-fold decrease in NO production, but this was not observed.

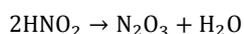
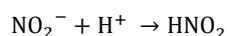
Although the total NO production appears to change little with aluminium (and acid site) content, the rate of NO release does. This can be seen by variations in the gradients of the two NO production curves (figure 2; d and e). As the Al-IPC-4 containing 0.25% aluminium (e) has a steeper gradient than the sample containing 1.02% aluminium (d), it appears that the rate of initial NO production is faster in samples with lower aluminium contents. This is because acid-site strength is inversely related to the number of acid sites (and aluminium concentration).

Zeolites which contain acid sites have the potential to be catalytic, depending on whether the acid site is able to be regenerated during some stage of the reaction. The catalytic potential of the acid-zeolites used to convert nitrite to NO gas was tested by injection of a second aliquot of sodium nitrite (250 μ L, 0.05 M) once the NO production of the Al-IPC-6 sample had returned below 6 ppb. Unfortunately, although there was a small spike in NO production (from 6 to 12 ppb) upon injecting more nitrite, the typical NO release curve for an acid-form zeolite was not observed. This suggested that the acid sites were not regenerated in the reaction and, as a result, turn over frequencies (TOF) of these samples could not be measured. This suggests that the process is currently stoichiometric and not catalytic in the present experiment.

Instead, the efficiency of the samples was compared in terms of the percentage of acid sites that had reacted. Looking at various mechanisms reported in literature, it seems most likely that the reaction proceeded as follows:²⁵

	Sample	Channel Size	NO release (nmol)	Si/Al ratio	Acid sites (μ mol)	Reacted acid sites (%)	Time of reaction (h)
a	Al-UTL	14-12-R	193.0	14.3	5.00	7.7	8.2
b	Al-IPC-2	12-10-R	80.1	52.9	1.55	10.4	5.8
c	Al-IPC-6	12-10-R, 10-8-R	77.7	28.7	2.66	5.8	6.7
d	Al-IPC-4 (1.02% Al)	10-8-R	56.5	315	2.55	4.4	6.6
e	Al-IPC-4 (0.25% Al)	10-8-R	50.8	97.1	8.13	12.5	5.8

Table 1: The average NO release, number of acid sites (molar quantities) and percentage of reacted acid sites are shown for each sample (a-d). The results in the table show how as pore size decreases (a>b>c>d=e), NO release decreases but no clear relationship is established between NO production and the number of acid sites. The listed time of reaction is the number of hours the NO measurement requires to reach background levels.



Other mechanisms²⁶ have been reported for this process, however these show regeneration of the acid site, which has been ruled out based on our observations. It has been possible to determine the percentage of acid sites which reacted in each sample using the stoichiometry of the proposed mechanism, the quantity of NO produced and the number of acid sites in each sample. Although 5 mg of each sample was tested on NO analyser, using TGA the dehydrated mass of the samples (with the exception of the Al-IPC-4 sample containing 1.02% aluminium) was calculated, hence the number of acid sites was calculated from the results of TGA and EDX analysis. Based on these calculations (shown in the supporting information), between 4.4% (Al-IPC-4, 1.02% Al) and 12.5% (Al-IPC-4, 0.25% Al) of the acid sites reacted to produce NO gas.

Future potential of acid-form ADOR zeolites:

Although the number of acid sites which reacted was low (4.4-12.5%), just 5 mg of each sample was necessary to produce a bioactive (nanomolar) quantity of NO. As a result, the incomplete conversion of acid sites has no detrimental effect on future biomedical applications of these zeolites. Indeed, increasing the dosage of NO too much risks provoking the toxic effects NO is well known for in larger amounts. Whilst NO production on a nanomolar scale controls vasodilation and platelet adherence, by simply increasing the amount of sample used, we can produce NO on a micromolar scale. On a micromolar scale, NO has antibacterial properties which are useful in wound healing; hence these zeolites have a range of possible biomedical applications.

Determining which sample is best suited for future applications requires further research. However, the Al-IPC-4 (1.02% Al) and Al-UTL samples appear to be the most interesting in terms of NO release. The Al-IPC-4 (1.02% Al) sample has the slowest rate of release, which could be important as too rapid a release of NO could cause cell death. However, the NO release of this sample was low (56.5 nmol) compared with other samples and lasted just 6.5 hours, with Al-UTL being discovered to have the most rapid and greatest NO release (193.0 nmol) that lasted just over 8.5 hours. The amount of NO released by these ADOR-derived zeolite is of the same order of magnitude as other H-zeolites, such as H-MOR and H-FER, but are at only 60% of the NO produced by H-SSZ-13 and H-ZSM-5.⁶

Conclusions

Aluminium was incorporated into the framework of zeolites UTL, IPC-2, IPC-4 and IPC-6, all of which share the same layered structure (UTL) but vary in terms of connectivity. The acid-forms of these zeolites were characterised and the NO production of each sample was measured quantitatively. Analysis of the NO production of each sample revealed a strong correlation between the rate and total amount of NO produced and the pore size of the zeolite (Al-UTL>Al-IPC-2>Al-IPC-6>Al-IPC-4). This relationship arises due to increased diffusion of sodium nitrite and NO gas throughout the structure as the pore size increases. Although the quantity of acid sites appears to have an effect on the rate and total amount of NO produced by the zeolite, this difference in NO production is too small (5.7 nmol) to draw many significant conclusions.

Each of the samples produce a biologically active quantity of NO, hence all show potential for future medical applications. As the rate and total amount of NO produced by each samples varies, the samples could be useful for a variety of different biomedical applications. There is scope for further development of these ADOR materials, especially for the slower delivery of small amounts of NO. As the samples do not produce NO catalytically, it is likely that these zeolites may be more suited to wound-healing, rather than as stent coatings where long-term release is required. Further work must now be carried out to ensure the zeolite samples are non-toxic and do not degrade in the body and to address any issues with scaling up the synthesis of these zeolites.

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The authors declare no conflicts of interest.

References

- 1 E. T. C. Vogt and B.M. Weckhuysen, *Chem. Soc. Rev.*, 44, (2015), 7342-7370.
- 2 Urea-SCR Technology for deNO_x After Treatment of Diesel Exhaust, ed. I. Nova and E. Tronconi, Springer, New York, 2014, iv.
- 3 A. Boës, B. Xiao, I. L. Megson and R. E. Morris, *Top. Catal.*, 52, (2008), 35-39.
- 4 R. Amorim, N. Vilaca, O. Martinho, R. M. Reis, M. Sardo, J. Rocha, A. M. Fonseca, F. Baltazar, I. C. Neves, *J. Phys. Chem. C*, 116 (2012), 25642–25650.
- 5 P. S. Wheatley, A. R. Butler, M. S. Crane, S. Fox, B. Xiao, A. G. Rossi, I. L. Megson and R. E. Morris, *J. Am. Chem. Soc.*, 128, (2006), 502–509
- 6 S. E. Russell, J. M. G. Carballo, C. Orellana-Tavra, D. Fairen-Jimenez and R. E. Morris, *Dalton Trans.*, 46, (2017), 3915-3920
- 7 B. Weinberger, D. L. Laskin, D. E. Heck and J. D. Laskin, *Toxicol. Sci.*, 59, (2001), 5-16

- 8 J. V. Espluges, *Br. J. Pharmacol.*, 135, (2002), 1079-1095.
- 9 D. S. Bredt, *Free Radical Res.*, 31, (1999), 577-596.
- 10 A. Butler and R. Nicholson, *Life, Death and Nitric Oxide*, The Royal Society of Chemistry, Cambridge, 2003.
- 11 M. R. Miller and I. L. Megson, *J. Pharmacol.*, 151, (2007), 305-321.
- 12 M. W. Radomski, R. M. J. Palmer and S. Moncada, *Biochem. Biophys. Commun. Rev.*, 148, (1987), 1482-1489.
- 13 J. O. Lundberg, M. T. Gladwin and E. Weitz, *Nat. Rev. Drug. Discov.*, 14, (2015), 623-641.
- 14 G. Dangas and F. Kuepper, *Circulation*, 105, (2002), 2586-2587.
- 15 M. Neidrauer, U. K. Ercan, A. Bhattacharyya, J. Samuels, J. Sedlak, R. Trikha, K. A. Barbee, M. S. Weingarten and S. G. Joshi, *J. Med. Microbiol.*, 63, (2014), 203-209.
- 16 W. J. Roth, P. Nachtigall, R. E. Morris, P. S. Wheatley, V. R. Seymour, S. E. Ashbrook, P. Chlubná, L. Grajciar, M. Položij, A. Zukal, O. V. Shvets and J. Čejka, *Nat. Chem.*, 5, (2013), 628-633.
- 17 M. Mazur, P. S. Wheatley, M. Navarro, W. J. Roth, M. Polozij, A. Mayoral, P. Eliasova, P. Nachtigall, J. Cejka and R. E. Morris, *Nat Chem*, 8, (2016), 58-62
- 18 S. A. Morris, G. P. M. Bignami, Y. Tian, M. Navarro, D. S. Firth, J. Cejka, P. S. Wheatley, D. M. Dawson, W. A. Slawinski, D. S. Wragg, R. E. Morris and S. E. Ashbrook, *Nat Chem*, 9, (2017), 1012-1018
- 19 P. Eliášová, M. Opanasenko, P. S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W. J. Roth, R. E. Morris and J. Čejka, *Chem. Soc. Rev.*, 44, (2015), 7177-7206.
- 20 P. S. Wheatley, P. Chlubna-Eliasova, H. Greer, W. Z. Zhou, V. R. Seymour, D. M. Dawson, S. E. Ashbrook, A. B. Pinar, L. B. McCusker, M. Opanasenko, J. Cejka and R. E. Morris, *Angew Chem Int Edit*, 53, (2014), 13210-13214
- 21 N. Žilková, P. Eliášová, S. Al-Khattaf, R. E. Morris, M. Mazur and J. Čejka, *Catal. Today*, 277, (2016), 55-60
- 22 P. Chlubná-Eliášová, Y. Tian, A. B. Pinar, M. Kubu, J. Čejka and R. E. Morris, *Angew Chem Int Ed Engl.*, 53, (2014), 7048-7052
- 23 M. Shamzhy, M. Opanasenko, Y. Tian, K. Konyesheva, O. Shvets, R. E. Morris and J. Čejka, *Chem. Mater.*, 26, (2014), 789-5798.
- 24 O. V. Shvets, N. Kasian, A. Zukal, J. Pinkas and J. Čejka, *Chem. Matter.*, 22, (2010), 3482-3495.
- 25 M. Mowbray, X. Tan, P. S. Wheatley, R. E. Morris and R. B. Weller, *J. Invest. Dermatol.*, 128, (2008), 352-360.
- 26 J. B. J. Hardwick, A. T. Tucker, M. Wilks, A. Johnson and N. Benjamin, *Clin. Sci.*, 100, (2001), 395-400.

Highlights

- ADOR synthesis of active Al-containing zeolites
- Demonstration of NO-production from nitrite substrate
- Relationship between pore size and reaction developed

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