

Stabilizing Low-Silica Zeolites through Aluminum Sulfate Assisted Cannibalistic Dealumination

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A versatile dealumination strategy was proposed to stabilize low-silica zeolites through cannibalistic interaction between the host framework AI (FAL) and the guest aluminum salt. It is possible to capture selectively the FAL and Na ions in NaY zeolite by employing a special external AI source such as aluminum sulfate as the dealuminating agent. This unique postmodification reduces the FAL amount efficiently and converts the chemically reacted AI species into a γ -alumina support for the catalytically active component of zeolite, which avoids wasting AI sources. Possessing greatly enhanced hydrothermal stability, newly generated intracrystal mesopores, as well as an optimized distribution of FAL, the resultant dealuminated Y zeolite catalysts can be used practically in heavy oil cracking.

Zeolite catalysts are widely utilized in the petrochemical and oil-refining industries of today and are expected to live vividly into the future, as there is increasing interest in new applications to biomass and the pyrolysis oils industry.^[1] Zeolites often suffer from the fatal shortcomings of easy coking and deactivation, especially at high operation temperatures, and thus, the catalytic activity must be recovered by burning off the coke formed at temperatures up to 800 °C.^[2] In this sense, zeolites with high framework Si/Al ratios (FSARs) are more favorable owing to improved thermal and hydrothermal stabilities.^[3] Among various low-silica zeolites, Y zeolite with the FAU topology has been proven to be the most useful and important catalyst for fluid catalytic cracking (FCC) and hydrocracking, which have contributed greatly to the petrochemical industry and the energy society in the past 60 years. Nevertheless, pre-dealumination is definitely needed, as Y zeolite is obtained only at a FSAR below 3 in direct hydrothermal synthesis.^[4] Post-dealumination increases the Si/Al ratio of the zeolite framework, which in turn brings about new benefits, for example, optimized distribution of framework AI (FAL), improved acid strength, and an optionally generated secondary mesopore system.^[3, 5]

In the past decades, extensive studies from the academic and industrial communities have established three chemical or physicochemical ways that can be used for the dealumination of Y zeolite: FAL extraction with complexing agents, steamingassisted hydrothermal dealumination, and isomorphous substitution of Si for FAL with external SiCl₄ or (NH₄)₂SiF₆.^[4] Complexing agents such as ethylenediaminetetraacetic acid and (NH₄)₂SiF₆ are toxic and costly, whereas solid-gas modification with SiCl₄ vapor needs harsh operating conditions. Thus, hydrothermal dealumination is currently the most used in industry. However, this method requires extremely high operating temperatures, and it is only applicable to NH₄NaY or HNaY zeolite but not NaY.^[6] Therefore, novel techniques characteristic of eco-efficient dealumination and mild operating conditions are still highly desirable for developing useful Y zeolite based FCC catalysts.

 AI^{3+} ions present in acid solution have been shown to be helpful for removing the extra framework aluminum (EFAL) in Y zeolite,^[7] but not for the dealumination of FAL. On the contrary, modification with external Al sources such as AlCl₃ and AlBr₃ usually results in insertion of Al into the zeolite frameworks.^[8] Herein, we communicate a unique chemical way to decrease the FAL in zeolites by using a suitable Al salt as the dealuminating agent. In the presence of Al₂(SO₄)₃ solution, the dealumination of FAL occurs effectively instead of alumination. Moreover, this method is vital for the direct modification of assynthesized zeolites in sodium form.

Commercially available NaY (Si/Al=2.4) was treated in $Al_2(SO_4)_3/H_2O/EtOH$ solution at 150 °C to give a cannibalistically dealuminated Y zeolite, denoted CDY. In this process, the external Al source interacts with the FAL species to generate a mineral natroalunite, which is readily converted into alumina by washing with aqueous ammonia solution; this results in the CDY-wash sample. For comparison, a hydrothermally dealuminated sample (USY) was also prepared by using the conventional steaming technique.^[9]

The X-ray diffraction (XRD) patterns explicitly verify that pristine NaY and the corresponding postmodified samples possess the FAU topology (Figure 1). Besides diffraction peaks due to Y zeolite, those attributable to the natroalunite phase (JCPDS card No. 41-1467) are also observed in the pattern of CDY (Figure 1 b). The scanning electron microscopy (SEM) images and analysis by energy-dispersive X-ray spectroscopy (EDX) consistently confirm the presence of natroalunite in CDY (Figure S1 in the Supporting Information). The apparent relative crystallinity (RC) of Y zeolite contained in CDY is approximately 56%. On the basis of the bulk amount of SO_4^{2-} , this calculation indi-

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 Supporting Information for this article can be found under http:// dx.doi.org/10.1002/cctc.201600211.



Figure 1. XRD patterns of a) NaY, b) CDY, c) CDY-wash, and d) control sample USY. The inset shows the [642] diffraction of FAU topology, which was calibrated by using pure silicon as an internal standard according to SH/T0339-92. The asterisks indicate the diffractions attributed to natroalunite.

cates that the as-made CDY sample contains approximately 39 wt% natroalunite as a physical mixture. Considering this diluting factor, the $Al_2(SO_4)_3$ treatment is considered to cause negligible damage to the crystalline structure of Y zeolite.

Relative to NaY, CDY shows high-angle shifted diffractions, which can be clearly identified by the [642] reflection in the enlarged region (2 θ = 26.5–28.5°) calibrated with pure silicon (Figure 1, inset). This is simply because the unit cell shrinks as a result of the decreased content of FAL. The FSAR increases from 2.4 for NaY to 4.1 for CDY (Table 1), as measured by XRD, $^{[10]}$ which indicates that $\mathsf{AI}_2(\mathsf{SO}_4)_3$ efficiently extracts the framework AI species. The FTIR spectrum of CDY shows that the asymmetric stretching vibrations shift to higher wavenumbers (Figure S2); this is consistent with the XRD investigation. By doubling the content of $AI_2(SO_4)_3$ in the treatment, the FAL species in NaY are further removed, which increases the FSAR to approximately 6. Moreover, the RC of Y zeolite decreases to 26%, as the coexisting natroalunite mixture accounts for approximately 60 wt% of the entire weight of the composite material.

In the $AI_2(SO_4)_3$ treatment process, part of the AI^{3+} ions in solution are hydrolyzed, and this leads to a pH value of 3–4. This low pH condition may lower the barrier of water inversion for the Si–O–Al linkages,^[11] which allows the FAL ions to be easily extracted. However, if NaY is modified by AlCl₃, Al(NO₃)₃,

or H_2SO_4 at the same pH value of 3–4, no crystalline natroalunite phase is formed, and the FSAR of the resultant Y zeolites remains in the low range of 2.5–2.8 (Figure S3). Thus, the formation of natroalunite is the key point for realizing cannibalistic dealumination by using aluminum salt sources. The possible reaction between the framework of the NaY host and the $Al_2(SO_4)_3$ guest is illustrated in Equation (1):

$$\begin{split} \text{Na}_{55}\text{AI}_{55}\text{Si}_{137}\text{O}_{384} + 27/2\,\text{AI}_2(\text{SO}_4)_3 + 54\,\text{H}_2\text{O} \rightarrow \\ \text{H}_6\text{Na}_{25}\text{AI}_{31}\text{Si}_{137}\text{O}_{336} + 17\,\text{Na}\text{AI}_3(\text{SO}_4)_2(\text{OH})_6 + 13/2\,\text{Na}_2\text{SO}_4 \\ \\ \Delta G = -4961.6\,\text{kJ}\,\text{mol}^{-1} \end{split}$$
(1)

 $Na_{55}Al_{55}Si_{137}O_{384}$ and $H_6Na_{25}Al_{31}Si_{137}O_{336}$ represent the chemical compositions of NaY and dealuminated Y zeolite, respectively, whereas $NaAl_3(SO_4)_2(OH)_6$ represents mineral natroalunite. The coefficient of $Al_2(SO_4)_3$ in Equation (1) depends on the degree of dealumination, that is, the FSAR of dealuminated Y, which is 4.4, as determined by ²⁹Si NMR spectroscopy. The detailed element balance of Equation (1) is given in Table S1. The strategy for cannibalistic dealumination of NaY by aluminum sulfate treatment is illustrated in Scheme 1.

The presence of natroalunite destroys the skeleton structure of the zeolite, as it decomposes to acidic aluminum sulfate or sulfur oxide by calcination at high temperatures. To achieve



Scheme 1. Strategy for cannibalistic dealumination of NaY by aluminum sulfate.

Table 1. Composition and textural properties of various Y zeolites. ^[a]											
Samples	RC ^[b] [%]	Fr. XRD	amework S IR _{tot} ^[c]	i/Al NMR	Bulk Si/Al ^[d]	SO ₄ ^{2-[d]} [wt %]	Na ₂ O ^[d] [wt %]	S_{BET} [m ² g ⁻¹]	S_{meso} [m ² g ⁻¹]	$V_{ m micro}$ [cm ³ g ⁻¹]	V_{total} [cm ³ g ⁻¹]
NaY	100	2.4	2.5	2.6	2.5	0.2	13.2	797	34	0.35	0.40
CDY	56	4.1	4.0	4.4	1.7	19.2	7.4	509	79	0.19	0.31
CDY-wash	72	4.2	4.1	4.5	1.7	0.1	3.3	681	142	0.24	0.59
USY	86	4.2	4.1	4.5	2.5	0.0	3.6	705	54	0.29	0.46
steamed CDY-wash ^[e]	46	50.2	73.7	-	1.7	0.1	0.1	492	127	0.16	0.50
steamed USY ^[d]	55	53.0	76.2	-	2.7	0.1	0.1	486	48	0.20	0.43

[a] S_{BET} = specific surface area (Brunauer–Emmett–Teller analysis), S_{meso} = mesopore surface area, V_{micro} = microspore volume, V_{total} = total pore volume. [b] Relative crystallinity (RC) for Y zeolite calculated by comparing the sum peak intensities of eight representative diffractions with that of NaY (SH/T 0340-92). [c] Calculated from the asymmetric stretching vibrations w_{TOT} by using IR spectroscopy. [d] Measured by ICP-AES analysis. [e] Steamed samples were tested on H-type Y zeolite with 100% water vapor at 800 °C for 17 h.

ChemCatChem 2016, 8, 1891 - 1895



stable dealuminated zeolite, natroalunite must be removed selectively. This can be realized by washing with alkali solution (e.g., NH₃·H₂O, NaOH, or Na₂CO₃) or ammonia vapor. Keeping this in mind, we employed ammonia solution to delete the natroalunite phase, as illustrated in Equation (2). In this reaction, produced Al(OH)₃ may be transformed into AlOOH through self-dehydration.

$$2 \text{ NaAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6 \text{ NH}_3 \cdot \text{H}_2\text{O} \rightarrow$$

$$Na_2SO_4 + 3 (NH_4)_2SO_4 + 6 AI(OH)_3$$
 (2)

$$\Delta G = -136.2 \text{ kJ mol}^{-1}$$

The natroalunite phase is effectively destroyed after washing with ammonia solution. As a consequence, the diffraction peaks corresponding to natroalunite disappear completely in the XRD pattern of the CDY-wash sample (Figure 1c). The aluminum hydroxide produced in the ammonia-washing process is not washed away but is deposited on the surface of the Y zeolite crystals, and it is further converted into the alumina phase by subsequent calcination. The CDY-wash sample exhibits a typical resonance of octahedrally coordinated EFAL for Y zeolite at $\delta \approx 0$ ppm together with a resonance of octahedral skeleton aluminum in the γ -alumina species at $\delta \approx$ 10 ppm in the ²⁷Al magic-angle spinning (MAS) NMR spectrum (Figure S4).^[12] The bulk Si/Al ratio of the CDY-wash sample, given by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, is lower than the FSAR of the pristine Y zeolite because of the co-existing γ -alumina phase. The concentrations of Al and Si in the filtrate for both the dealumination and ammonia washing steps are less than 20 ppm, which implies Si and Al all exist in the composite material. More than 98% of the Al ions from added aluminum sulfate are utilized. In fact, the molar ratio of Si/Al in the feeding mixture (NaY+aluminum sulfate) is approximately 1.7, which is the same as that of the CDY-wash sample.

The aluminum sulfate treatment not only dealuminates the zeolite framework, but it also effectively removes the Na⁺ ions within the cation sites of NaY. The Na₂O content of CDY (7.5 wt%) is much lower than that of NaY zeolite (13.2 wt%). Considering the fact that the natroalunite phase contains a part of sodium, the Y zeolite part in CDY should contain a lower Na₂O content. The ammonia washing destroys the natroalunite phase and removes the sodium therein, which further decreases the Na₂O content to 3.5 wt% for the CDY-wash sample.

The nitrogen adsorption/desorption profile of the CDY-wash sample shows characteristics of the combined features of types I and IV isotherms, clearly different from the type I isotherm of NaY (Figure 2); this indicates the presence of multilayer adsorption in the CDY-wash sample.^[13] The microspore volume of CDY-wash is 0.24 cm³g⁻¹ (Table 1), and apart from the coexisting physical mixture of nonporous alumina, the real microspore volume for the Y zeolite part is estimated to be as high as 0.30 cm³g⁻¹. CDY-wash has an external surface area of

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Figure 2. N₂ adsorption/desorption isotherms and adsorption pore-size distribution curves (inset) of a) NaY, b) CDY, c) CDY-wash, and d) steamed CDY-wash. P/P_0 =relative pressure, STP=standard temperature and pressure.

142 m²g⁻¹, which is much higher than that of NaY (32 m²g⁻¹) and that of conventionally prepared USY (54 m²g⁻¹). Nevertheless, a part of the external surface area in CDY-wash may have a contribution from the mesopores in coexisting γ -alumina (Figure S5). The high surface area provides open reaction spaces that are helpful for processing large molecules if CDYwash is employed as an oil-refining catalyst. On the other hand, the alumina, generated from the Al₂(SO₄)₃ source and the Al species coming out of the Y zeolite framework, is presumed to have no negative effect on the catalytic performance of the Y active component, but it is expected to serve as a matrix or even an active species in the catalytic cracking of bulk hydrocarbons.^[14]

The high-angle shift of the X-ray diffraction peaks is indicative of the removal of FAL, and this is further verified by ²⁹Si MAS NMR spectroscopy (Figure 3). The ²⁹Si MAS NMR spectrum of parent NaY demonstrates resonances at $\delta = -105$, -100, -94, and -89 ppm (Figure 3a), which can be reasonably assigned to the Si(0AI), Si(1AI), Si(2AI), and Si(3AI) building units, respectively. After modification by aluminum sulfate and ammonia, the resonances for all configurations are slightly shifted to higher magnetic field (Figure 3b).^[15] Moreover, the resonance of the Al-rich building units, Si(3AI), almost disap-



Figure 3. ²⁹Si MAS NMR spectra of a) NaY, b) CDY-wash, and c) control sample USY. The dashed lines represent the deconvoluted resonances, and the inserted numbers represent the percentages of Si(nAl) species (n=0-3).



pears, and that of the Si(2Al) units diminishes remarkably, whereas the proportion of the Si(OAI) units dramatically increases. The FSAR of USY prepared by conventional steaming dealumination is very similar to that of CDY-wash, but it exhibits different relative intensities of the Si(nAl) units (Figure 3 c). During the dealumination, the next nearest neighbor aluminum atoms in four-membered rings (NNN-AI) are more easily removed than isolated aluminum atoms with no neighbor aluminum atoms (0-NNN-AI).^[16] The removal of NNN-AI affirmatively results in a decreased amount of Si(nAl) ($n \ge 2$) units, whereas removal of 0-NNN-AI has a much lower chance of reducing these Al-rich units.^[16c] If different dealumination methods remove the same amount of FAL, the one with the higher selectivity for removal of NNN-Al may contain fewer Si(nAl) (n > 2) units.^[16c] Here, the proportion of Si(2AI) in CDY-wash is lower than that in USY, the reason for which may lie in the more selective removal of NNN-AI by the aluminum sulfate assisted dealumination approach. Lónyi and Evmiridis also independently reported that hydrothermal dealumination is less selective in removing NNN-AI in Y zeolite.^[17]

The acid strength of zeolites closely depends on NNN-Al, and removal of NNN-Al will increase the strong acid sites of Y zeolite.^[16b] The acidic properties of the proton-type samples (i.e., HCDY-wash, HUSY, and HY) were investigated by the temperature-programmed desorption of ammonia (NH₃-TPD) technique and IR spectroscopy analysis of the pyridine adsorption band (Figures S6 and S7 and Table S2). The samples possess both Brønsted acid sites and Lewis acid sites. HCDY-wash and HUSY have more strong acid sites than HY, probably because of extensive dealumination and removal of NNN-Al.^[16c] On the other hand, HCDY-wash possesses 22% more strong acid sites than HUSY, though they have comparable FSARs, and HUSY has a higher microspore volume. This difference is presumably ascribed to the greater amount of 0-NNN-Al units contained in HCDY-wash.

The stronger acid strength is helpful in giving a longer kinetic chain length, faster chain propagation, and higher overall rates for zeolite-processed reactions. HY, HCDY-wash, and HUSY were tested for the catalytic cracking of *n*-hexane at 400 °C (Table S3). HCDY-wash exhibits a *n*-hexane conversion of 14.8% and a hydrogen transfer index (HTI) of 4.3;^[18] both values are higher than the corresponding values of HY (8.6% conversion and HTI of 3.4) and those of HUSY (12.4% conversion and HTI of 3.7). This difference is in agreement with the order of strong acid sites for these three catalysts. To determine if the properties of stabilized Y are adequate for its practical use as a FCC catalyst, it must be tested after severe steam treatment.^[14,19] After hydrothermally treatment with 100% steam at 800°C for 17 h, the crystalline structure of HY completely collapses, but that of two dealuminated Y zeolites are well preserved (Figure S8). After steaming, CDY-wash and USY possess similar RC of Y zeolite (46–55%), and they maintain a high external surface area (127 and 48 m²g⁻¹, respectively). This verifies that aluminum sulfate assisted dealumination is highly effective as conventional steaming for stabilizing the framework of Y zeolite.

The two steamed dealuminated Y zeolites demonstrate Si(OAI) as the only building unit (Figure S9), and the number of strong and weak acid sites in their structures is extremely low as a result of the deep dealumination of FAL. As they both show almost no activity in *n*-hexane cracking at 400 °C, their catalyst activity was thus tested in the cracking of 1,3,5-triisopropylbenzene (TIPB) (Table S4). Steamed CDY-wash shows a TIPB conversion of 33.4% and a diisopropylbenzene (DIPB) yield of 16.4 wt%, the values of which are higher than those of steamed USY (27.0% and 12.0 wt%, respectively). The yields of benzene and cumene are similar for these two steamed catalysts. TIPB with a kinetic diameter of 9.4 Å is larger than the window opening of the microspores of Y zeolite,^[20] which first needs cracking on the external surface of the zeolite crystals and/or matrix-like alumina. Thus, the slightly higher cracking ability of steam CDY-wash can probably be attributed to co-existing γ -alumina.^[21] According to these results, steamed CDYwash is expected to possess higher activity for the conversion of long-chain hydrocarbons into smaller, more useful hydrocarbons.

We further investigated the practicality of using CDY as a FCC catalyst by comparing it to a commercial catalyst under reaction conditions close to the industrial process. HCDY-wash and HUSY were dry sprayed by mixing with kaolin clay and silica sol to prepare microsphere catalysts, which were further loaded with a poisoning metal (V and Ni) and steam aged at 800 °C for 17 h, which allowed the catalysts to experience the severe conditions in the actual processes. The XRD patterns and SEM images verify that the microsphere catalysts obtained are of good quality (Figures S10 and S11). The 20 wt% sprayed catalyst was blended with a Sinopec ShengLi FCC catalyst. The catalytic cracking performance was checked with a FCC microactivity testing unit (ACE Models R+MM) with Sinopec heavy vacuum oil as feedstock (Table S5). Detailed heavy oil cracking activities and product selectivities are shown in Table 2. The

Table 2. Heavy oil cracking activity and selectivities.											
Catalyst ^(a)		Conversion ^[b] [wt %]	Dry gas [wt %]	LPG [wt %]	Gasoline [wt %]	Diesel [wt %]	Bottoms [wt %]	Coke [wt %]	RON	MON	(RON + MON)/2
ShengLi 80% ShengLi + 20% sprayed catalyst	sprayed HCDY-wash ^[c] sprayed HUSY ^[c]	77.1 78.8 78.0	1.8 1.9 1.9	16.5 16.6 16.7	47.9 49.2 48.2	14.2 13.1 13.5	8.7 8.1 8.5	10.9 11.1 11.2	92.4 92.7 93.1	83.4 84.0 84.2	87.9 88.3 88.6
[a] Catalyst performance time: catalyst/oil = 8, time on stream: 90 s, reaction temperature: 500° C. [b] Conversion is defined as the sum of dry gas, LPG, gas-											



HUSY-containing sprayed catalyst shows catalytic properties similar to those of the ShengLi catalyst. The HCDY-containing sprayed catalyst, on the other hand, exhibits higher conversion (+0.8 wt%), higher gasoline (+1.0 wt%) yield, and lower bottoms (-0.4 wt%) and diesel (-0.4 wt%) yields than the sprayed HUSY-containing catalyst. Their coke, dry gas, and liquid petroleum gas (LPG) yields and RON and MON (the research and motor octane numbers, respectively) were at the same level. The higher conversion and higher gasoline yield on the sprayed HCDY-wash containing catalyst may result in great profits for the oil-refining industry.^[22] These preliminary laboratory results indicate that CDY-wash is promising for actual FCC applications.

This unique approach of using aluminum sulfate as a dealuminating agent has proven to be versatile to remove framework aluminum from other low-silica zeolites such as chabazite and mazzite (Figure S12). More research on the mechanism of dealumination by aluminum sulfate and exploitation of the practical utilization of the dealuminated zeolites are in progress.

Experimental Section

Commercially available NaY (410 g, dry base) was mixed with $AI_2(SO_4)_3$ - $18H_2O$ (285 g), H_2O (600 g), and EtOH (300 g) in a 2 L stainless-steel autoclave (pH 3–4), and the mixture was stirred at 150 °C for 6 h. Cannibalistically dealuminated Y zeolite (CDY, 50 g) thus obtained was further treated with 1 M ammonia solution (500 g) at 80 °C for 1 h followed by calcination at 550 °C for 6 h, which gave the CDY-wash sample. The preparation procedures of the control USY sample, sprayed FCC microsphere catalysts, and chabazite and mazzite zeolites are given in the Supporting Information.

The structures and crystallinities of the samples were verified by X-ray diffraction. The FSARs of the Y zeolites were tested by X-ray diffraction, IR spectroscopy, and ²⁹Si NMR spectroscopy. The natroalunite phase in CDY was confirmed by SEM images and EDX analysis. The adsorption isotherms were measured with a volumetric adsorption analyzer. The mesopores in CDY-wash were affirmed by TEM. The acidic properties were investigated by NH₃-TPD and IR spectroscopy of the pyridine adsorption. The bulk Si, Al, Na, and SO₄^{2–} contents were determined by ICP-AES.

The catalytic cracking of *n*-hexane or TIPB was performed on a fixed-bed reactor. The FCC cracking behaviors of sprayed microsphere catalysts were tested with a FCC microactivity testing unit (ACE Models R + MM) by using commercial heavy vacuum oil.

Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (NSFC) (21533002,

20925310), Ministry of Science and Technology (2012BAE05B02), Programs Foundation of Ministry of Education (2012007613000), and Shanghai Leading Academic Discipline Project (B409).

Keywords: acidity · cracking · dealumination · hydrothermal stability · zeolites

- a) K. Zhang, B. Eliasson, U. Kogelschatz, *Ind. Eng. Chem. Res.* 2002, *41*, 1462–1468; b) T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, G. W. Huber, *Science* 2010, *330*, 1222–1227.
- [2] H. S. Cerqueira, G. Caeiro, L. Costa, F. R. Ribeiro, J. Mol. Catal. A 2008, 292, 1–13.
- [3] J. Scherzer, Catal. Rev. Sci. Eng. 1989, 31, 215-354.
- [4] H. Beyer, in *Post-Synthesis Modification I, Vol. 3*, Springer Berlin-Heidelberg, 2002, pp. 203–255.
- [5] S. van Donk, A. H. Janssen, J. H. Bitter, K. P. de Jong, *Catal. Rev. Sci. Eng.* 2003, 45, 297–319.
- [6] M. B. Yue, T. Xue, W. Q. Jiao, Y. M. Wang, M.-Y. He, *Microporous Mesoporous Mater.* 2012, 159, 50–56.
- [7] F. Wang, X. Liu, Y. Du, M. Guan, CN Patent 101450319A, 2007.
- [8] C. D. Chang, C. T. W. Chu, J. N. Miale, R. F. Bridger, R. B. Calvert, J. Am. Chem. Soc. 1984, 106, 8143–8146.
- [9] G. T. Kerr, J. Catal. 1969, 15, 200-204.
- [10] a) W. Lutz, D. Heidemann, R. Kurzhals, G. Kryukova, Z. Anorg. Allg. Chem. 2010, 636, 1361–1367; b) G. Engelhardt, D. Michel, High-resolution solidstate NMR of silicates and zeolites, John Wiley & Sons, Chichister, New York, 1987.
- [11] S. Li, A. Zheng, Y. Su, H. Zhang, L. Chen, J. Yang, C. Ye, F. Deng, J. Am. Chem. Soc. 2007, 129, 11161 – 11171.
- [12] J. Jiao, J. Kanellopoulos, W. Wang, S. S. Ray, H. Foerster, D. Freude, M. Hunger, Phys. Chem. Chem. Phys. 2005, 7, 3221–3226.
- [13] J. C. Groen, L. A. A. Peffer, J. Perez-Ramirez, Microporous Mesoporous Mater. 2003, 60, 1–17.
- [14] W. C. Cheng, X. Zhao, P. S. Deitz, US Patent 6605207 B2, 2003.
- [15] W. Lutz, Adv. Mater. Sci. Eng. 2014, 2014, 724248.
- [16] a) R. Beaumont, D. Barthomeuf, J. Catal. 1972, 26, 218–225; b) R. J. Mikovsky, J. F. Marshall, J. Catal. 1976, 44, 170–173; c) B. Beagley, J. Dwyer, F. R. Fitch, R. Mann, J. Walters, J. Phys. Chem. 1984, 88, 1744– 1751.
- [17] a) K. S. Triantafillidis, A. G. Vlessidis, N. P. Evmiridis, Ind. Eng. Chem. Res. 2000, 39, 307–319; b) F. Lónyi, J. H. Lunsford, J. Catal. 1992, 136, 566– 577.
- [18] D. B. Lukyanov, J. Catal. 1994, 145, 54–57.
- [19] J. W. Ward, Y. L. Linda, Calif, US Patent 3929672, 1973.
- [20] P. Morales-Pacheco, J. M. Domínguez, L. Bucio, F. Alvarez, U. Sedran, M. Falco, Catal. Today 2011, 166, 25–38.
- [21] a) M. Falco, E. Morgado, N. Amadeo, U. Sedran, *Appl. Catal. A* 2006, 315, 29–34; b) Y. Lu, M. He, J. Song, X. Shu, Y. Lu, M. He, J. Song, X. Shu, *Stud. Surf. Sci. Catal.* 2001, 134, 209–217; c) G. T. Whiting, F. Meirer, M. M. Mertens, A. J. Bons, B. M. Weiss, P. A. Stevens, D. E. Smit, B. M. Weckhuysen, *ChemCatChem* 2015, 7, 1312–1321; d) X. Liu, *J. Phys. Chem. B* 1999, 103, 2647–2652.
- [22] a) Z. X. Qin, B. J. Shen, Z. W. Yu, F. Deng, L. Zhao, S. G. Zhou, D. L. Yuan, X. H. Gao, B. J. Wang, H. J. Zhao, H. H. Liu, *J. Catal.* 2013, *298*, 102–111;
 b) B. W. Wojciechowski, *Catal. Rev. Sci. Eng.* 1998, *40*, 209–328.

Received: February 22, 2016 Published online on May 24, 2016