# **Supporting Information**

# Synthetic Ferripyrophyllite: Preparation, Characterization and Catalytic Application

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### **Experimental Section**

## Materials:

SBA-15 was synthesized according to our reported work.<sup>1</sup> Furfural acetone was synthesized according to literature.<sup>2</sup> Cyclohexene, acetophenone, benzaldehyde, 4-methylbenzaldehyde, 4-fluorobenzaldehyde and 4-phenyl-3-buten-2-one were commercially obtained and used directly without further purification. Fe powder was purchased from Aldrich (12310-1KG-R), and deionized water was used in all cases. The model catalyst (MgFe<sub>2</sub>O<sub>4</sub>) for ammonia synthesis was synthesized according to literature.<sup>3</sup> For comparison, a multi-promoted state of the art industrial catalyst for ammonia synthesis was used, which consists mainly of Fe<sub>3</sub>O<sub>4</sub> with small amounts of different promoters.

#### Justification for the usage of excess iron in the synthesis procedure

For synthesis of iron silicate, excess Fe powder was applied with  $n_{Fe}:n_{Si} = 1:1.4$  (instead of theoretical  $n_{Fe}:n_{Si} = 1:2$ ) in order to promote more conversion of SBA-15:

Much more unreacted  $SiO_2$  was obtained (before purification process) if less Fe powder was added as starting material (e.g. 30 mg, 20 mg, 10 mg and even 5 mg instead of 64.5 mg, corresponding TEM images are shown in Figure S1). In contrast, not much difference was observed from TEM analysis in the following two conditions:

- 1) Much excess Fe powder was used as starting material (e.g. 200 mg instead of 64.5 mg);
- 2) freshly obtained iron silicate was further treated with Fe powder (30 mg) in water (5 mL) at 100 °C under air in an autoclave for 24 h. After drying, the obtained powder was treated with Fe powder (30 mg) one more time. A little bit more straight nanosheets were obtained from high-resolution TEM images (Figure S2 and TEM-EDX analysis based on 12 sampling areas gave the chemical formula of FeSi<sub>2.0</sub>O<sub>5.5</sub>).

#### Materials characterization

Obtained composite materials were characterized by elemental analysis, transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) and scanning transmission electron microscopy (STEM), Mössbauer spectroscopy, electron paramagnetic resonance (EPR), pair distribution function (PDF) analysis, Fourier-transform infrared spectroscopy (FTIR), in situ diffuse reflectance infrared fourier spectroscopy (DRIFT), SQUID measurement, thermogravimetric analysis–mass spectrometry (TG–MS), sorption isotherms (N<sub>2</sub>-BET), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

*Elemental analysis:* The quantitative analysis of Fe and Si succeeds by application the closed vessel pressure microwave assisted digestion procedure (ETHOS plus 2, MLS). Three accurately weighed samples (about 5 mg) were decomposed in 3 mL aqua regia + 100 µL HF at a temperature of 135 °C for 10 min and additional at 155 °C for 10 min. The solution were transferred into volumetric flasks (50 mL) and filled up with ultrapure water. The solutions were measured against a matrix matched calibration series with inductively coupled plasma -optical emission spectrometry (ICP-OES 5100 SVDV, Agilent). The O content was determined with the carrier gas hot extraction method (TCH 600, LECO). TEM and TEM-EDX were used to investigate the structural features with a Hitachi HF-2000 instrument. The EDX measurements were performed with an S-3500N Hitachi Scanning Electron Microscope. The EDX detector used is designated Si (Li) Pentafet Plus Oxford Instruments GmbH. STEM-EDX mapping was performed on a Hitachi HD-2700 electron microscope (Cs-corrected, 200 kV, Cold FEG, EDAX Octane T Ultra W 200 mm<sup>2</sup> SDD TEAM-Software). Mössbauer data were recorded on a conventional spectrometer operating in alternating constant-acceleration mode. A constant sample temperature was maintained with an Oxford Instruments Variox cryostat. EPR measurements were performed on a Bruker E500 ELEXSYS spectrometer equipped with the Bruker dual-mode cavity (ER4116DM) and an Oxford Instruments helium flow cryostat (ESR 900). The microwave bride was the high-sensitivity bridge Super-X from Bruker (ER-049X) with integrated microwave frequency counter. The magnetic field controller (ER032T) was externally calibrated with a Bruker NMR field probe (ER035M). Magnetic susceptibility data were measured from powder samples of solid material in the temperature range 2-300 K by using a SQUID susceptometer with a field of 0.1 T (MPMS-7, Quantum Design, calibrated with standard palladium reference sample, error <2%). PDF (pair distribution function) data were collected in-house, in glass and kapton capillaries Mo-radiation Qmax  $\sim 16$ Å-1. FT-IR spectra were recorded at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna 550). *Pyridine-FTIR spectra* were recorded at room temperature with a resolution of 4 cm<sup>-1</sup> and 128 scans for a single spectrum using a Nicolet iS50 spectrometer with MCT detector. Selected samples were pressed into self-

supporting wafers (ca. 10 mg cm<sup>-2</sup>) and in-situ activated at 450 °C for 4 h under vacuum. Adsorption of pyridine (3 mbar) was carried out at 150 °C for 20 min. Physisorbed pyridine was removed by evacuation for 20 min at 150°C under high vacuum. Desorption was also carried out at 250 °C in order to investigate the strength of the acid sites. The bands at 1545 and 1450 cm<sup>-1</sup> were selected for a semiguantitative characterization of the Brønsted (BAS) and Lewis acid sites (LAS), respectively. In situ DRIFT was investigated in a Nicolet Magna-IR 560 spectrometer equipped with a MCT detector. Samples were heated in the range of 100-250 °C under argon conditions. Spectra at different temperatures were recorded with a resolution of 2 cm<sup>-1</sup> (250 scans). Nitrogen sorption experiments at 77K were performed either on a Quantachrome Nova 3200e instrument or on a Micromeritics 3Flex instrument. CO<sub>2</sub> sorption experiments at 273 K were performed on a Micromeritics 3Flex instrument. Prior to sorption analyses, the samples were activated under vacuum at 200 °C for 10 h. The in situ Xray powder diffraction experiments have been performed under reaction conditions in a XRK900 reaction chamber (Anton Paar) mounted on a X'Pert Pro diffractometer (PANalytical) in Bragg-Brentano geometry. All data were collected using  $Cuk\alpha_{1,2}$  radiation, a secondary monochromator and a position sensitive strip detector. All samples have been prepared on a MARCOR sample holder. The reaction chamber is attached to a gas supply system and the gas flow parameters can be adjusted for each sample. The ex situ X-ray powder patterns for qualitative phase analysis were collected on a Stoe STADIP transmission diffractometer using Mo radiation (0.7093 Å). The instrument is equipped with a primary Ge (111) monochromator (MoK $\alpha_1$ ) and a position sensitive Mythen1K detector. For the measurements, the samples were filled into glass capillaries ( $\emptyset$  0.5 mm). The measured patterns were evaluated qualitatively by comparison with entries from the ICCD PDF-2 powder pattern database and by comparison with simulated data (crystal structure data were taken from the ICSD database). In addition, ex situ XRD measurements were performed on a X'Pert Pro diffractometer (PANalytical) in Bragg-Brentano geometry. All data were collected using Cuk $\alpha_{1,2}$  radiation, a secondary monochromator and a position sensitive strip detector. XPS measurements were performed with a Kratos spectrometer with a hemispherical analyzer. The monochromatized Al Ka X-ray source (E=1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, an analyzer pass energy of 40 eV was applied. The hybrid mode was used as lens mode. The base pressure during the experiment in the analysis chamber was  $4 \times 10^{-7}$  Pa. To account charging effects, all spectra have been referred to C 1s at 284.5 eV.



Figure S1. TEM images of iron silicate produced with less amount of Fe powder.



Figure S2. TEM image of iron silicate produced from SBA-15 with excess Fe powder.

Reaction conditions: 100 mg SBA-15, 64.5 mg Fe in 5 mL H<sub>2</sub>O, 100 °C, 24 h in an autoclave under air, followed by centrifugation, washing and drying  $\rightarrow$  obtained powder, 30 mg Fe in 5 mL H<sub>2</sub>O, 100 °C, 24 h in an autoclave under air, followed by centrifugation, washing, drying  $\rightarrow$  obtained powder, 30 mg Fe in 5 mL H<sub>2</sub>O, 100 °C, 24 h in an autoclave under air, followed by centrifugation, washing, drying  $\rightarrow$  obtained powder, 30 mg Fe in 5 mL H<sub>2</sub>O, 100 °C, 24 h in an autoclave under air, followed by centrifugation, washing, drying  $\rightarrow$  obtained powder, 30 mg Fe in 5 mL H<sub>2</sub>O, 100 °C, 24 h in autoclave under air, followed by centrifugation, washing, drying  $\rightarrow$  obtained powder, 30 mg Fe in 5 mL H<sub>2</sub>O, 100 °C, 24 h in autoclave under air, followed by centrifugation, washing, drying.



Figure S3. TEM images of iron silicate synthesized from scale-up production (in 500 mL autoclave with 6 g SBA-15 as starting material, 100 °C, no  $H_2$ ).



Figure S4. SEM-EDX mapping images of iron silicate synthesized from scale-up production (in 500 mL autoclave with 6 g SBA-15 as starting material, 100  $^{\circ}$ C, no H<sub>2</sub>)



**Figure S5.** TEM images of iron silicate synthesized from MCM-41 as an alternative silica source under the same reaction condition.



Figure S6. SEM-EDX of iron silicate with MCM-41 as silica source.



**Figure S7.** TEM images of aluminum containing iron silicate obtainable by using AlSBA-15 (Al: 6 wt%) as silica source.



Figure S8. SEM-EDX of iron silicate with AlSBA-15 (Al: 6 wt%) as silica source



Figure S9. TEM images of iron silicates obtainable by using aerosil as silica source.



Figure S10. TEM images of iron silicate with different scale bars synthesized from reaction's temperature of 220  $^{\circ}$ C and H<sub>2</sub> pressure of 100 bar.



Figure S11. SEM-EDX mapping images of iron silicate synthesized from reaction's temperature of 220  $^{\circ}$ C and H<sub>2</sub> pressure of 100 bar.



Figure S12. Thickness determination of the iron silicate nanosheets via TEM analysis.



Figure S13. CO<sub>2</sub> adsorption isotherm (273 K) of the iron silicate ( $p_0 = 34.85$  bar).



Figure S14. XPS spectrum showing the Si 2p signal from the surface of the iron silicate.





Figure S15. XPS spectra of the Fe 2p (upper) and 3p (bottom) signals from the surface of the iron silicate.



**Figure S16.** Mössbauer spectra of <sup>57</sup>Fe in iron silicate at 297 K (top) and 80 K (bottom). The red lines are the results of a fit with Gaussian distributions of Lorentzian quadrupole doublets shown in green and dotted blue. The corresponding Mössbauer parameters are\*:

| Temp. / Value | δ [mms <sup>-1</sup> ] | $\Delta E_Q [mms^{-1}]$ | $\Gamma_{\rm L}$ [mms <sup>-1</sup> ] | $\Gamma_{\rm G} [{\rm mms}^{-1}]$ | rel. Intensity |
|---------------|------------------------|-------------------------|---------------------------------------|-----------------------------------|----------------|
| 80 K green    | 0.45                   | 0.79                    | 0.29                                  | 0.46                              | 93 %           |
| blue          | 0.50                   | 2.10                    | 0.2                                   | 1.61                              | 7 %            |
| 293 K green   | 0.36                   | 0.80                    | 0.35                                  | 0.43                              | 93 %           |
| blue          | 0.45                   | 2.10                    | 0.20                                  | 1.60                              | 7 %            |

\*)  $\delta$ : Isomer shift;  $\Delta E_Q$ : quadrupole splitting;  $\Gamma_L$  Lorenztian line width;  $\Gamma_G$  width of Gaussian distribution

The small isomer shift and small quadrupole splitting of the major component (in green) is typical of Fe(III) highspin, whereas the wider splitting of the minor component (in blue) indicates more asymmetric local environment as for the (bulk) material. The occurrence of quadrupole spectra (instead of magnetically split spectra) and the absence of additional broadening at 80 K indicates fast magnetic relaxation at both conditions, as it is expected for superparamagnetic relaxatin of very small magnetic domains, or truly paramagnetic material. SAMP QIA-QD-005-07 TITL 'x118060538 QIA-QD-005-07, 10K'

/Users/ye/SL/Data/Eview/x118060538.pdf CMNT meterial at 10K

| 9.62583<br>0.10<br>2.00<br>10.00   | GHz<br>mW<br>G<br>K                  | m.wfreq.<br>m.wpower<br>mod. amplitude<br>sample temperat  | 1 |
|--|--------------------------------------|--|---|
| $\begin{array}{c}1&0&0&0&.&0&0\\&0&.&0&2\\1&0&0&.&0&0\\&1&.&0&0\\3&5&0&0&0&0\\6&0&0&0&.&0&0\\6&0&0&0&.&0&0\\8&1&.&9&2\\&2&.&0&0\\1&0&2&4&.&0&0\end{array}$ | s<br>deg<br>st<br>G<br>g<br>ms<br>ch | receiver gain<br>time constant<br>mod. frequency<br>mod. phase<br>harmonic<br>center field<br>sweep<br>ADC conv. time<br>number scans<br>nchan |   |



**Figure S17. X-band** EPR spectrum of iron silicate recorded at 10 K and 9.6258 GHz with 0.1 mW power and 0.2 mT modulation at 100 kHz. The broad, featureless line is typical of ferromagnetic resonance of (small) magnetic domains.<sup>4</sup>



**Figure S18.** Magnetization curves of the iron silicate under ZFC (Zero-Field Cooled, left ) and FC (Field Cooled, right) conditions.



**Figure S19.** Quantification of water built during ammonia synthesis. The iron silicate was treated in a flow of hydrogen and nitrogen in a temperature window between room temperature and 500 °C. (The release of ammonia during the first six hours is caused by desorption of an ammonia solution which was applied for sample purification, i.e. dissolution of unreacted SBA-15).



Figure S20. Pair distribution function (PDF) analysis of the iron silicate compared to simulated PDFs for  $Fe_2O_3$  and  $FeSiO_4$ .



Figure S21. ATR-IR spectra of SBA-15, iron silicate, physical mixtures of  $Fe_2O_3$  and SBA-15 after manual grinding and balling milling.



**Figure S22.** ATR-IR spectra of SBA-15, iron silicate, and iron silicate after drying under vacuum in the 4000-2500 cm<sup>-1</sup> and 1700-400 cm<sup>-1</sup> region.

The peak at 1443 cm<sup>-1</sup> disappeared after heating to 300 °C because of the decomposition of FeOOH, the additional peak for the decomposed product  $Fe_2O_3$  at 533 cm<sup>-1</sup> was overlapped with the peak centered at 445 cm<sup>-1</sup>, which further proves the trace amount of FeOOH in the obtained iron silicate.



**Figure S23.** FTIR spectra of hydroxyl (a) and pyridine vibration regions (b) after pyridine adsorption on the iron silicate. (BA: before adsorption).

#### Temperature-programmed NH<sub>3</sub> desorption (NH<sub>3</sub>-TPD).

The sample (ca. 70 mg, sieved in the size range of 0.3-0.4 mm) were first treated in situ to remove physisorbed water by heating in flow of He (25 mL min<sup>-1</sup>) to 400 °C (heating rate of 5 °C min<sup>-1</sup>) and maintaining the final temperature for 1 h. Afterwards, the sample was cooled down to 150 °C and a flow of 10%NH<sub>3</sub>/He (25 mL min<sup>-1</sup>) was admitted and maintained at the same temperature for 30 min to ensure saturation of the sample with ammonia. Next, the gas was switched to He (25 mL min<sup>-1</sup>) and the loosely bound ammonia was swept from the surface of the sample for 2 h at the adsorption temperature. Finally the sample was cooled down to 100 °C (initial temperature for the desorption step) and then the temperature linearly increased to 800 °C (10 °C min<sup>-1</sup>) while monitoring the release of ammonia using a TCD detector. A relevant desorption baseline trace was determined for each sample by repeating the experiment with a fresh sample aliquot, following the same experimental procedure though using He instead of 10%NH<sub>3</sub>/He during the adsorption step. Such profile was used to correct the NH<sub>3</sub>-TPD profile for the release of water at temperatures above that used to dry the sample in situ, e.g. due to dehydroxylation phenomena.

As reference materials:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by stagnant air-calcination of high-purity pseudo-boehmite (Disperal P2), provided by Sasol, in a muffle oven. A series of silico-alumina (ASA) materials with 5-40 wt% SiO<sub>2</sub> (nominal as indicated by supplier) were obtained by stagnant air-calcination of high-purity hydrous silicoalumina materials provided by Sasol (Siral series), in a muffle oven. An additional SiO<sub>2</sub>-rich ASA material (12 wt% Al<sub>2</sub>O<sub>3</sub>-88 wt% SiO<sub>2</sub>) was used as received from Sigma-Aldrich (grade 135). A high-purity, amorphous SiO<sub>2</sub> sample (Grace) was also studied to confirm a reliable baseline in the TPD profiles. A commercial zeolite H-Y was purchased from Sigma-Aldrich (Si/Al=2.5). A commercial zeolite H-beta was provided by Süd Chemie (today Clariant) (H-BEA 35, Si/Al=18). All zeolite samples were used in H<sup>+</sup>-form as received from the supplier.





**Figure S24:** Mass-normalized NH<sub>3</sub>-TPD profiles for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (ASA) and SiO<sub>2</sub> samples with various Si/Al ratios. TPD profile (black trace), blank baseline profile (gray trace), baseline-subtracted profile (blue trace).



**Figure S25:** Mass-normalized NH<sub>3</sub>-TPD profiles for selected commercial zeolite samples. TPD profile (black trace), blank baseline profile (gray trace), baseline-subtracted profile (blue trace).



**Figure S26:** Mass-normalized NH<sub>3</sub>-TPD profiles for iron silicate. TPD profile (black trace), blank baseline profile (gray trace), baseline-subtracted profile (blue trace).



**Figure S27.** Comparison of all samples in terms of acid site density (as derived from the integral intensity of the  $NH_3$  desorption profiles) and acid strength (assuming the peaking temperature of the  $NH_3$  desorption profile a suitable measure of the acid strength). Error bars correspond to the standard deviation as determined from three analysis on the ASA sample with 40 wt% SiO<sub>2</sub>.



**Figure S28.** Temperature-dependent X-ray diffraction (XRD) measurements of iron silicate under synthetic air between 25 and 850 °C as well as after cool-down to 25 °C (CuK $\alpha_{1,2}$  radiation, Bragg-Brentano geometry).



**Figure S29.** X-ray diffraction (XRD) measurements of the iron silicate before and after drying (CuK $\alpha_{1,2}$  radiation, Bragg-Brentano geometry).



**Figure S30.** DRIFT spectra of iron silicate: a) after drying at 100 °C for 12 h and *in-situ* activated at 100 °C for 150 min, b) after drying at 100 °C for 12 h, c) after drying at 300 °C for 3 h and *in-situ* activated at 100 °C for 150 min and d) after drying at 300 °C for 3 h.

Bands at ~3500 cm<sup>-1</sup> (broad) and ~1615 cm<sup>-1</sup> are ascribed to the presence of physisorbed H<sub>2</sub>O in the samples without activation. After heating the system at 100 °C, both bands start to decrease as it can be observed in the Figure S30a and S30c. The band at 3739 cm<sup>-1</sup> is characteristic of isolated/terminal silanols, while the broad band between 3700-3400 cm<sup>-1</sup> can be assigned to Fe(OH)Si entities. The broadness of the band indicates a large distribution of different Fe(OH)Si groups, which consists well with the conclusion that Fe(III) centers are randomly oriented. Furthermore, the band ascribed to Si–O–Si vibrations at 1216 cm<sup>-1</sup> shifted a little bit to higher wavenumbers proving slight structure change after heating to 300 °C.



**Figure S31.** Mössbauer spectra of in the iron silicate after drying at 100 °C for 12 h at 297 K (left) and 80 K (right).



Figure S32. Mössbauer spectra of the iron silicate after drying at 300 °C for 3 h at 297 K (left) and 80 K (right).



**Figure S33.** Nitrogen sorption isotherms of the iron silicate before (upper) and after (bottom) heating it at 600 °C for 3 h under synthetic air.



**Figure S34.** TEM images of iron silicate after heating the sample at 1000 °C for 3 hours under synthetic air at two different magnifications.



**Figure S35.** XRD pattern of the iron silicate after heating it at 1000 °C for 3 hours under synthetic air. The simulated XRD patterns of haematite, and epsilon  $Fe_2O_3$  are given for comparison (MoK $\alpha_1$  radiation, Transmission geometry).



**Figure S36.** Temperature-dependent X-ray diffraction (XRD) measurements of iron silicate under nitrogen atmosphere between 25 and 850 °C as well as after cooling to 25 °C (CuK $\alpha_{1,2}$  radiation, Bragg-Brentano geometry).



**Figure S37.** In situ XRD pattern of iron silicate after heating to 850 °C under nitrogen atmosphere and then cool down to 25 °C under N<sub>2</sub>. The XRD patterns of magnetite and Fayalite are given for comparison (CuK $\alpha_{1,2}$  radiation, Bragg-Brentano geometry).



Figure S38. TG-DSC-MS analysis of iron silicate under synthetic air with heating rate of 10 K min<sup>-1</sup>

(The TG-DSC measurement shows two endothermal signals in the temperature ranges from room temperature to 200 °C and from 200 to 375 °C, going along with relative weight losses of about 4.7 and 4.0 wt%. Upon further heating to 1000 °C, an additional weight loss of about 2.2 wt% is observed. All endothermic reactions are associated with a loss of water as indicated by mass spectrometry. The mass signal with m/z of 18 is caused by water molecules. The mass loss above 425 °C is likely associated with condensation of surface hydroxyl groups to water molecules that are released over a rather wide temperature range. The residual mass of the material at 100 °C is 88.9 wt%.)



Figure S39. TG-DSC-MS analysis of iron silicate under argon with heating rate of 10 K/min.

(The TG-DSC measurement shows two endothermal signals in the temperature ranges from room temperature to 200 °C and from 200 to 425 °C, going along with relative weight losses of about 8.0 and 6.0 wt%. Upon further heating to 1000 °C, an additional weight loss of about 1.7 wt% is observed. All endothermic reactions are associated with a loss of water as indicated by mass spectrometry. The mass signal with m/z of 18 is caused by water molecules. An additional mass signal with m/z of 32 is observed in parallel to the water signal. That mass signal indicates that  $O^{2-}$  anions either from the silicate or from adsorbed water get oxidized to release molecular  $O_2$  during these processes. The mass loss above 425 °C is likely associated with condensation of surface hydroxyl groups to water molecules that are released over a rather wide temperature range. The residual mass of the material at 1000 °C is 85.3 wt%.)

| run            | Conv./% | Yield/% |                         |  |
|----------------|---------|---------|-------------------------|--|
|                |         |         | $\overset{d}{\bigcirc}$ |  |
| 1              | >99     | 93      | 6                       |  |
| 2              | >99     | 97      | 2                       |  |
| 3              | 98      | 96      | 1                       |  |
| 4              | 99      | 97      | 1                       |  |
| 5              | 91      | 90      | 1                       |  |
| 6              | 41      | 40      | <1                      |  |
| 7 <sup>a</sup> | 54      | 53      | <1                      |  |

Table S1. Reusability of 3 wt% Pd/iron silicate for benzylidene acetone hydrogenation.

Reaction conditions: 3% Pd/iron silicate (10 mg), benzylidene acetone (5 mmol), no solvent, H<sub>2</sub> (20 bar), 120 °C, 3 h. <sup>a</sup> benzylidene acetone (2.5 mmol).

Additional experimental details for catalyst recycling experiments:

After cooling and depressurizing the autoclave, acetone (2 mL) was used to dissolve the organic part. The inner part of the autoclave was further cleaned with acetone (1 mL x 2). The combined liquid fraction was mixed and transferred into a 15 mL centrifuge tube. After centrifugation (4 k, 10 min), the powder was further washed with acetone (1.5 mL), separated by centrifugation (4 k, 10 min) for two times and finally dried in an oven. After that, the powder was transferred back into the glass inlet. After further addition of a certain amount of benzylidene acetone and 20 bar  $H_2$ , the next run starts.

The reduced conversion from run 5 onwards seems to be caused mainly by an incomplete catalyst recovery rather than its deactivation. For example, in run 3 the catalyst amount was already reduced from 10 to 6 mg.



Figure S40. Activity measurement of iron silicate in ammonia synthesis at 325-500 °C.



Figure S41. STEM-EDX mapping of iron silicate after ammonia synthesis.

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