Supplementary Information

Regeneration of Cu/SAPO-34(MO) with H_2O only: Too good to be true?

Jungwon Woo[a]*, Diana Bernin[a], Homayoun Ahari[b], Mark Shost[b], Michael Zammit[b] and Louise Olsson[a]*

[a]*Chemical Engineering, Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden*

[b]*FCA US LLC, 800 Chrysler Drive, Auburn Hills, MI 48326-2766, USA*

*jungwon@chalmers.se; *louise.olsson@chalmers.se

Figures

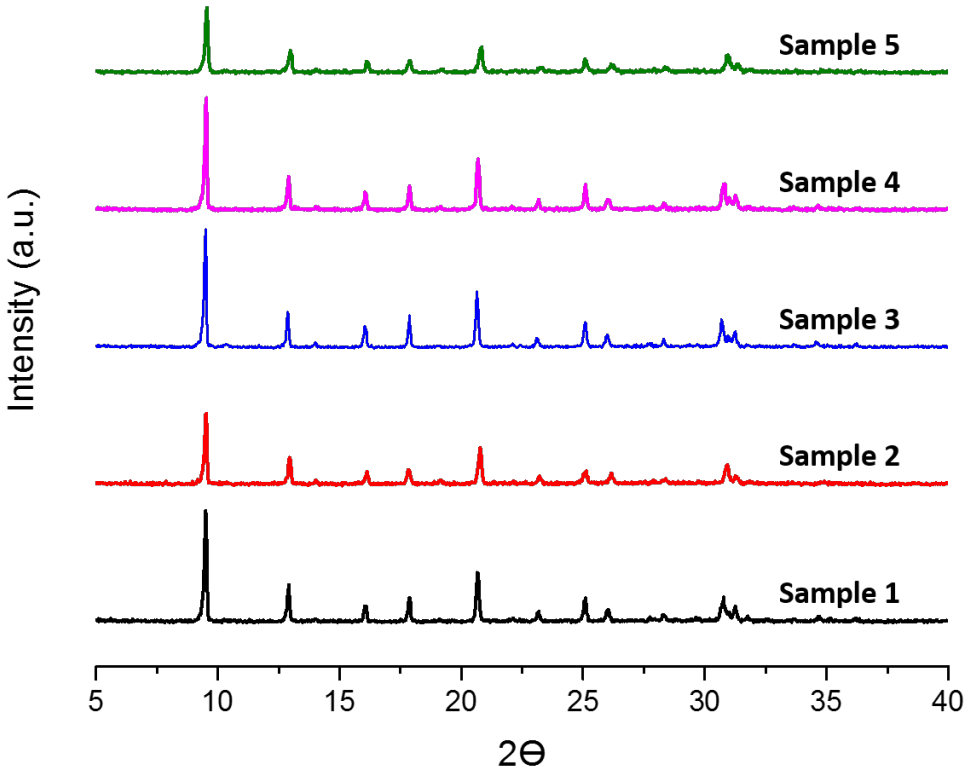

Figure S1. XRD patterns of Cu/SAPO-34(MO) after reaction experiments WEE-1, 2, 3, 4 (See Tables S1-4 for experimental conditions). Sample 5 is de-greened only.

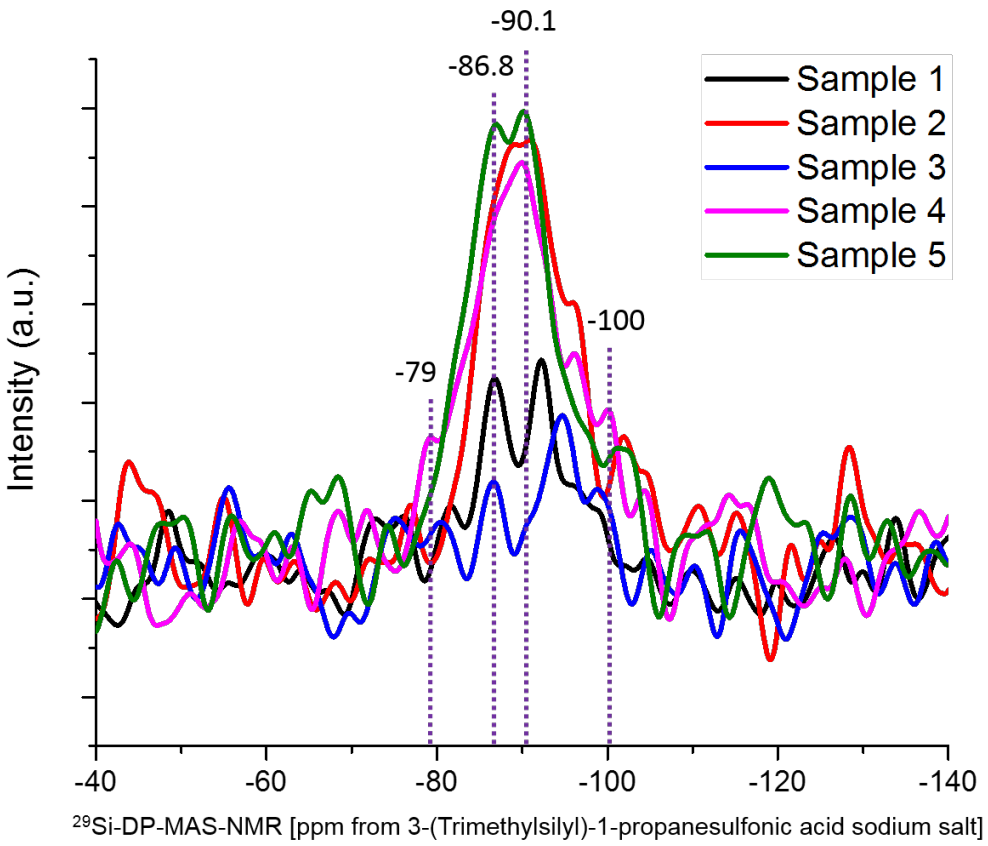

Figure S2. ^{29}Si CP MAS NMR spectra of Cu/SAPO-34(MO) after reaction experiments WEE-1, 2, 3, 4 (See Tables S1-4 for experimental conditions.) Sample 5 is de-greened only.

Tables

Table S1. Series of steps in water exposure experiment 1 (WEE-1): pre-treatment conditions and reaction temperatures for NH_3-SCR.

Series of experimental plans	Water exposure test (WT)	Temperature protocol (°C)
WEE1-Step 1 (S-1)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE1-Step 2 (S-2)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE1-Step 3 (S-3)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE1-Step 4 (S-4)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE1-Step 5 (S-5)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE1-Step 6 (S-6)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250

Table S2. Series of steps in water exposure experiment 2 (WEE-2): pre-treatment conditions and reaction temperatures for NH_3-SCR.

Series of experimental plans	Water exposure test	Temperature protocol (°C)
WEE2-Step 1 (S-1)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 2 (S-2)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 3 (S-3)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 4 (S-4)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 5 (S-5)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 6 (S-6)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 7 (S-7)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 8 (S-8)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE2-Step 9 (S-9)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250

Table S3. Series of steps in water exposure experiment 3 (WEE-3): pre-treatment conditions and reaction temperatures for NH_3-SCR.

Series of experimental plans	Water exposure test	Temperature protocol (°C)
WEE3-Step 1 (S-1)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 2 (S-2)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 3 (S-3)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 4 (S-4)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 5 (S-5)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 6 (S-6)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 7 (S-7)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 8 (S-8)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 9 (S-9)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE3-Step 23 (S-23)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250

Table S4. Series of steps in water exposure experiment 4 (WEE-4): pre-treatment conditions and reaction temperatures for NH_3-SCR.

Series of experimental plans	Water exposure test	Temperature protocol (°C)
WEE4-Step 1 (S-1)	8% O_2, 5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 2 (S-2)	8% O_2, 5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 3 (S-3)	8% O_2, 5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 4 (S-4)	8% O_2, 5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 5 (S-5)	8% O_2, 5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 6 (S-6)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 7 (S-7)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 8 (S-8)	8% O_2, 10% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 9 (S-9)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 10 (S-10)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 11 (S-11)	8% O_2, 7.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 12 (S-12)	8% O_2, 12.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 13 (S-13)	8% O_2, 12.5% H_2O at 70 °C for 5 hr	150, 200, 250
WEE4-Step 14 (S-14)	8% O_2, 12.5% H_2O at 70 °C for 5 hr	150, 200, 251
WEE4-Step 15 (S-15)	8% O_2, 12.5% H_2O at 70 °C for 5 hr	150, 200, 252
WEE4-Step 16 (S-16)	8% O_2, 12.5% H_2O at 70 °C for 5 hr	150, 200, 253

Table S5. In-situ H_2-TPR with consecutive H_2O exposure using the same monolith.

Series of experimental plans	Conditions	Temperature protocol (°C)
Degreening	400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O for 4 h	750
H_2-TPR-1	H_2 (2000 ppm) with Ar	70-750
NH_3-SCR-1	400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O	150, 200, 250
H_2O exposure-1	5 % H_2O and 8% O_2 for 5 h	70
H_2-TPR-2	H_2 (2000 ppm) with Ar	70-750
NH_3-SCR-2	400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O	150, 200, 250
H_2O exposure-2	7.5 % H_2O and 8% O_2 for 5 h	70
H_2-TPR-3	H_2 (2000 ppm) with Ar	70-750
NH_3-SCR-3	400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O	150, 200, 250
H_2O exposure-3	10 % H_2O and 8% O_2 for 5 h	70
H_2-TPR-4	H_2 (2000 ppm) with Ar	70-750
NH_3-SCR-4	400 ppm NH_3, 400 ppm NO, 8% O_2, 5% H_2O	150, 200, 250

Table S6. BET and micropore surface area, pore volume, and average pore diameter of Cu/SAPO-34(MO) treated with WEE-1, 2, 3, and 4.

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
Sample 1 (Treated with WEE-1)	591	0.32	21.7
Sample 2 (Treated with WEE-2)	522	0.26	19.7
Sample 3 (Treated with WEE-3)	529	0.27	20.1
Sample 4 (Treated with WEE-4)	605	0.30	20.0
Sample 5 (Only degreened)	528	0.27	20.7

Table S7. Distribution (%) of Al environments obtained from deconvoluted ^{27}Al MAS NMR spectra of Cu/SAPO-34(MO) treated with WEE-1, 2, 3, and 4.

	Al(IV)	Al(V)	Al(VI)
Sample 1	61.9	12.5	25.7
Sample 2	55.8	12.9	31.3
Sample 3	63.8	14.1	22.1
Sample 4	54.8	12.4	32.8
Sample 5	53.9	12.1	33.9

Further information about 1-year old sample that underwent structural collapse

We have earlier found (data not shown) that if Cu/SAPO-34(MO) is left in air for very long time the structure starts to collapse as evidenced by a significant drop in BET surface area. We therefore prepared a monolith using Cu/SAPO-34 that was left on the shelf for one year. We observed a significant drop in initial activity (after degreening) where the conversions at 150, 200, 250°C dropped to 4.8, 24.2, 40.4 %, respectively, from 24, 65, 75% in Figure 1. We confirmed the partial collapsed structure with XRD and BET (data not shown), where the BET decreased from 610m^2/g to 89 m^2/g, and this can explain the low activity of the 1-year old sample. We tried to also regenerate this sample using 10% H_2O, which was not possible since the structure had collapsed. Thus, the focus of this work is the regeneration of Cu/SAPO-34, when the zeolite structure is still maintained.