Evaluation of Cu/SAPO-34 Catalysts Prepared by Solid State and Liquid Ion Exchange Methods for NO$_x$ removal by NH$_3$-SCR

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Supplementary Material
Table S1. Elemental composition of samples prepared by SSIE at different temperatures.

| SSIE temperature, °C | Composition wt., % | Si | Al | Fe | Mg | Ca | Na | P  | O  | Cu |
|----------------------|-------------------|----|----|----|----|----|----|----|----|----|
| H-SAPO-34            | -                 | 4.5| 19.4| 0.6| 0.1| 0.1| 0  | 18.2| 57.0| -  |
| 500                  |                   | 5.7| 20.1| 0.6| 0.1| 0.8| 0  | 18.6| 49.9| 4.3|
| 600                  |                   | 5.4| 20.3| 0.6| 0.1| 0.7| 0  | 18.7| 49.9| 4.3|
| 650                  |                   | 5.1| 20.1| 0.6| 0.1| 0.6| 0  | 18.9| 50.0| 4.2|
| 700                  |                   | 5.3| 20.3| 0.6| 0.1| 0.7| 0  | 18.9| 50.0| 4.2|
| 750                  |                   | 5.1| 20.2| 0.6| 0.1| 0.6| 0  | 18.9| 50.0| 4.2|
| 800                  |                   | 5.2| 20.2| 0.6| 0.1| 0.6| 0  | 18.9| 49.9| 4.4|

Table S2. Elemental composition of samples prepared by LIE and SSIE with different copper loading.

| Preparation method | Nominal Cu loading, % | Cu | Si | Al | P  | Na | Fe | O  |
|--------------------|-----------------------|----|----|----|----|----|----|----|
| H-SAPO-34          | -                     | -  | 4.5| 19.4| 18.2| 0.1| 0.6| 57.0|
|                    | 1                     | 1.1| 4.9| 21.4| 20.0| 0.4| 0.6| 51.3|
|                    | 2                     | 1.7| 4.9| 21.2| 19.9| 0.3| 0.6| 51.0|
|                    | 4                     | 2.2| 4.9| 21.0| 19.7| 0.3| 0.6| 50.8|
|                    | 10                    | 3.6| 4.8| 20.7| 19.4| 0.2| 0.6| 50.3|
| LIE                | 2                     | 1.9| 5.2| 21.6| 19.2| 0  | 0.6| 50.9|
|                    | 4                     | 3.7| 5.1| 20.7| 19.0| 0  | 0.6| 50.1|
| SSIE               | 6                     | 5.8| 4.9| 20.0| 18.3| 0  | 0.6| 49.1|
|                    | 8                     | 7.9| 4.9| 19.4| 17.8| 0  | 0.6| 48.3|
|                    | 10                    | 9.8| 5.0| 18.8| 17.0| 0  | 0.5| 47.5|
| Catalyst | T, °C | X_NO, % | $-\frac{\Delta T_{NO}}{mol}$ NO s$^{-1}$ mol Cu$^{-1}$ | Ea, kJ mol$^{-1}$ Cu ions | TOF, s$^{-1}$ Cu ions |
|----------|-------|---------|-------------------------------------------------|--------------------------|-----------------------|
| SSIE 500 °C | 230   | 6.66    | 1.76 10$^{-3}$                                  |                          |                       |
|          | 240   | 7.36    | 1.96 10$^{-3}$                                  |                          |                       |
|          | 250   | 8.33    | 2.24 10$^{-3}$                                  |                          |                       |
|          | 260   | 9.48    | 2.57 10$^{-3}$                                  |                          |                       |
|          | 270   | 10.33   | 2.81 10$^{-3}$                                  |                          |                       |
|          | 280   | 11.62   | 3.18 10$^{-3}$                                  |                          |                       |
|          | 290   | 13.13   | 3.61 10$^{-3}$                                  |                          |                       |
|          | 300   | 14.51   | 4.01 10$^{-3}$                                  |                          |                       |
| SSIE 600 °C | 180   | 5.68    | 1.63 10$^{-3}$                                  | 7.40 10$^{-3}$            | 9.04 10$^{-3}$        |
|          | 190   | 6.62    | 1.90 10$^{-3}$                                  | 8.62 10$^{-3}$            | 1.05 10$^{-2}$        |
|          | 200   | 7.90    | 2.26 10$^{-3}$                                  | 1.03 10$^{-3}$            | 1.26 10$^{-2}$        |
|          | 210   | 10.56   | 3.03 10$^{-3}$                                  | 1.38 10$^{-2}$            | 1.68 10$^{-2}$        |
|          | 220   | 12.31   | 3.53 10$^{-3}$                                  | 1.60 10$^{-2}$            | 1.96 10$^{-2}$        |
|          | 230   | 14.67   | 4.20 10$^{-3}$                                  | 1.91 10$^{-2}$            | 2.34 10$^{-2}$        |
| SSIE 650 °C | 180   | 6.42    | 1.87 10$^{-3}$                                  | 6.69 10$^{-3}$            | 7.49 10$^{-3}$        |
|          | 189   | 7.46    | 2.18 10$^{-3}$                                  | 7.77 10$^{-3}$            | 8.70 10$^{-3}$        |
|          | 201   | 9.49    | 2.77 10$^{-3}$                                  | 9.88 10$^{-3}$            | 1.11 10$^{-2}$        |
|          | 210   | 12.58   | 3.67 10$^{-3}$                                  | 1.31 10$^{-2}$            | 1.47 10$^{-2}$        |
|          | 220   | 16.39   | 4.59 10$^{-3}$                                  | 1.64 10$^{-2}$            | 1.83 10$^{-2}$        |
| SSIE 700 °C | 170   | 8.59    | 2.25 10$^{-3}$                                  | 6.44 10$^{-3}$            | 6.83 10$^{-3}$        |
|          | 180   | 10.80   | 3.13 10$^{-3}$                                  | 8.94 10$^{-3}$            | 9.49 10$^{-3}$        |
|          | 190   | 11.99   | 3.48 10$^{-3}$                                  | 9.93 10$^{-3}$            | 1.05 10$^{-2}$        |
|          | 200   | 15.49   | 4.49 10$^{-3}$                                  | 1.28 10$^{-2}$            | 1.36 10$^{-2}$        |
| SSIE 750 °C | 180   | 7.11    | 2.08 10$^{-3}$                                  | 6.70 10$^{-3}$            | 7.69 10$^{-3}$        |
|          | 190   | 8.34    | 2.44 10$^{-3}$                                  | 7.86 10$^{-3}$            | 9.02 10$^{-3}$        |
|          | 200   | 10.22   | 2.98 10$^{-3}$                                  | 9.63 10$^{-3}$            | 1.11 10$^{-2}$        |
|          | 210   | 13.00   | 3.80 10$^{-3}$                                  | 1.22 10$^{-2}$            | 1.41 10$^{-2}$        |
|          | 220   | 16.02   | 4.68 10$^{-3}$                                  | 1.51 10$^{-2}$            | 1.73 10$^{-2}$        |
| SSIE 800 °C | 190   | 6.58    | 1.87 10$^{-3}$                                  | 8.11 10$^{-3}$            | 1.10 10$^{-2}$        |
|          | 200   | 7.45    | 2.11 10$^{-3}$                                  | 9.17 10$^{-3}$            | 1.24 10$^{-2}$        |
|          | 210   | 10.49   | 2.96 10$^{-3}$                                  | 1.29 10$^{-2}$            | 1.74 10$^{-2}$        |
|          | 220   | 13.35   | 3.76 10$^{-3}$                                  | 1.63 10$^{-2}$            | 2.21 10$^{-2}$        |
|          | 230   | 15.53   | 4.10 10$^{-3}$                                  | 1.78 10$^{-2}$            | 2.41 10$^{-2}$        |
Table S4. Apparent activation energy ($E_a$) and turnover frequency (TOF) values calculation in differential regime for LIE catalysts with different copper loading. (W/F$_{NO}$=51250 g mol s$^{-1}$)

| Catalyst      | $T$, °C | $X_{NO}$, % | $-\dot{r}_{NO}$, mol NO s$^{-1}$ mol$_{Cu}^{-1}$ | $E_a$, kJ mol$^{-1}$ | TOF, s$^{-1}$ |
|---------------|---------|-------------|---------------------------------------------|----------------------|-------------|
|               |         |             |                                             |                      | Cu ions     |
| 1.1% Cu/SAPO-34 | 190     | 4.93        | 4.85$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               |         |             |                                             |                      | Cu$^{2+}$ ions |
|               | 200     | 5.06        | 4.98$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 210     | 5.85        | 5.87$\cdot$10$^{-3}$                       | 19                   | Cu$^{2+}$ ions |
|               | 220     | 6.14        | 6.19$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 230     | 7.00        | 7.14$\cdot$10$^{-3}$                       |                      | Cu$^{2+}$ ions |
| 1.7% Cu/SAPO-34 | 190     | 5.18        | 3.56$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               |         |             |                                             |                      | Cu$^{2+}$ ions |
|               | 200     | 6.09        | 4.19$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 210     | 7.51        | 5.17$\cdot$10$^{-3}$                       | 42                   | Cu$^{2+}$ ions |
|               | 220     | 9.75        | 6.72$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 230     | 12.21       | 8.41$\cdot$10$^{-3}$                       |                      | Cu$^{2+}$ ions |
| 2.2% Cu/SAPO-34 | 190     | 4.65        | 2.53$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               |         |             |                                             |                      | Cu$^{2+}$ ions |
|               | 200     | 5.41        | 2.95$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 210     | 7.17        | 3.91$\cdot$10$^{-3}$                       | 47                   | Cu$^{2+}$ ions |
|               | 220     | 10.13       | 5.52$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 230     | 14.78       | 6.42$\cdot$10$^{-3}$                       |                      | Cu$^{2+}$ ions |
| 3.6% Cu/SAPO-34 | 190     | 6.58        | 2.23$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               |         |             |                                             |                      | Cu$^{2+}$ ions |
|               | 200     | 7.66        | 2.59$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 210     | 9.37        | 3.171$\cdot$10$^{-3}$                      | 47                   | Cu$^{2+}$ ions |
|               | 220     | 12.42       | 4.21$\cdot$10$^{-3}$                       |                      | Cu ions     |
|               | 230     | 17.46       | 5.91$\cdot$10$^{-3}$                       |                      | Cu$^{2+}$ ions |
Table S5. Apparent activation energy (E<sub>a</sub>) and turnover frequency (TOF) values calculation in differential regime for SSIE catalysts with different copper loading. (W/F<sub>NO</sub>=51250 g mol s<sup>-1</sup>)

| Catalyst        | T, °C | X<sub>NO</sub>, % | r<sub>NO</sub>, mol NO s<sup>-1</sup> mol<sub>Cu</sub><sup>-1</sup> | Ea, kJ mol<sup>-1</sup> | TOF, h<sup>-1</sup> |
|-----------------|------|------------------|--------------------------|------------------|-----------------|
|                 |      |                  |                          |                  | Cu ions | Cu<sup>2+</sup> ions |
| 1.9% Cu/SAPO-34 | 170  | 6.86             | 4.38·10<sup>-3</sup>     |                  |       | 1.15·10<sup>-2</sup> | 1.33·10<sup>-2</sup> |
|                 | 180  | 7.89             | 5.04·10<sup>-3</sup>     |                  |       | 1.33·10<sup>-2</sup> | 1.53·10<sup>-2</sup> |
|                 | 190  | 9.27             | 5.92·10<sup>-3</sup>     | 37               |       | 1.56·10<sup>-2</sup> | 1.80·10<sup>-2</sup> |
|                 | 200  | 11.98            | 7.65·10<sup>-3</sup>     |                  |       | 2.01·10<sup>-2</sup> | 2.32·10<sup>-2</sup> |
|                 | 210  | 15.63            | 9.98·10<sup>-3</sup>     |                  |       | 2.63·10<sup>-2</sup> | 3.03·10<sup>-2</sup> |
| 3.7% Cu/SAPO-34 | 170  | 8.67             | 2.88·10<sup>-3</sup>     |                  | 38    | 8.22·10<sup>-3</sup> | 1.15·10<sup>-2</sup> |
|                 | 180  | 10.39            | 3.45·10<sup>-3</sup>     |                  |       | 9.84·10<sup>-3</sup> | 1.38·10<sup>-2</sup> |
|                 | 190  | 12.94            | 4.29·10<sup>-3</sup>     |                  |       | 1.23·10<sup>-2</sup> | 1.72·10<sup>-2</sup> |
|                 | 200  | 16.65            | 5.52·10<sup>-3</sup>     |                  |       | 1.58·10<sup>-2</sup> | 2.21·10<sup>-2</sup> |
| 5.8% Cu/SAPO-34 | 170  | 7.34             | 1.56·10<sup>-3</sup>     |                  | 34    | 8.19·10<sup>-3</sup> | 8.65·10<sup>-3</sup> |
|                 | 180  | 8.75             | 1.85·10<sup>-3</sup>     |                  |       | 9.76·10<sup>-3</sup> | 1.03·10<sup>-2</sup> |
|                 | 190  | 11.12            | 2.36·10<sup>-3</sup>     |                  |       | 1.24·10<sup>-2</sup> | 1.31·10<sup>-2</sup> |
|                 | 200  | 13.05            | 2.7710<sup>-3</sup>      |                  |       | 1.46·10<sup>-2</sup> | 1.54·10<sup>-2</sup> |
|                 | 210  | 16.20            | 3.4310<sup>-3</sup>      |                  |       | 1.81·10<sup>-2</sup> | 1.91·10<sup>-2</sup> |
| 7.9% Cu/SAPO-34 | 170  | 7.13             | 1.12·10<sup>-3</sup>     |                  | 36    | 6.19·10<sup>-3</sup> | 7.96·10<sup>-3</sup> |
|                 | 180  | 8.94             | 1.40·10<sup>-3</sup>     |                  |       | 7.77·10<sup>-3</sup> | 9.99·10<sup>-3</sup> |
|                 | 190  | 10.91            | 1.71·10<sup>-3</sup>     |                  |       | 9.48·10<sup>-3</sup> | 1.22·10<sup>-2</sup> |
|                 | 200  | 13.39            | 2.09·10<sup>-3</sup>     |                  |       | 1.16·10<sup>-2</sup> | 1.50·10<sup>-2</sup> |
| 9.9% Cu/SAPO-34 | 190  | 3.93             | 4.90·10<sup>-4</sup>     |                  | 32    | 2.88·10<sup>-3</sup> | 3.77·10<sup>-3</sup> |
|                 | 200  | 5.08             | 6.32·10<sup>-4</sup>     |                  |       | 3.72·10<sup>-3</sup> | 4.86·10<sup>-3</sup> |
|                 | 210  | 5.88             | 7.33·10<sup>-4</sup>     |                  |       | 4.31·10<sup>-3</sup> | 5.64·10<sup>-3</sup> |
|                 | 220  | 6.77             | 8.44·10<sup>-4</sup>     |                  |       | 4.96·10<sup>-3</sup> | 6.49·10<sup>-3</sup> |
|                 | 230  | 7.85             | 9.78·10<sup>-4</sup>     |                  |       | 5.75·10<sup>-3</sup> | 7.53·10<sup>-3</sup> |
Figure S1. Evolution of NO conversion with catalyst particle size and total flowrate for evaluating internal and external mass transfer resistances.

The experiments to evaluate the internal mass transfer resistance were carried out with 0.4 g of Cu/SAPO-34 catalyst and a gas stream composition of 660 ppm NO, 660 ppm NH₃ and 6% O₂ with a total flow rate of 2600 ml min⁻¹ at 300 °C. The absence of internal mass transfer resistance can be assured for particle sizes lower than 0.3-0.5 mm.

On the other hand, the experiments to evaluate the external mass transfer resistance were carried out varying the total flow rate and catalyst mass in order to maintain a constant W/FAD, i.e. 5220 g min mol⁻¹. The composition of the gas stream was 660 ppm NO, 660 ppm NH₃ and 6% O₂. Total flow rates above 2000 ml min⁻¹ assured the absence of external mass transfer resistance.
Figure S2. XRD diffraction patterns of Cu/SAPO-34 samples prepared at different SSIE temperatures along with a physical mixture of CuO/H-SAPO-34 and the bare H-SAPO-34 zeolite.

All the samples calcined below 700 °C presented the typical chabazite structure. Two peaks located at 36° and 38° were observed for Cu/SAPO-34 catalysts, which were assigned to CuO based on the XRD data of the physical mixture of CuO and SAPO-34. The detection of CuO reveals that the SSIE method is not able to achieve a complete dispersion of the original CuO nanoparticles to obtain exchanged copper ions.

On the other hand, the catalysts calcined at 750 and 800 °C presented an additional peak located at 21° assigned to silicon oxide (SiO₂). Thus, it can be concluded that the structure of the SAPO-34 zeolite starts to collapse for calcination temperatures above 700 °C, leading to some silicon segregation from the zeolite framework.
As can be observed in Figure S3, perfect cubic crystals were observed irrespective of the calcination temperature. The size of those crystals was rather homogeneous, in the range 2-5 µm. The number and size of copper aggregates was progressively reduced while increasing calcination temperature. Only for the highest calcination temperature, i.e. 800 °C, some bigger CuO aggregates were observed due to aggregation effects.
Figure S4. UV-vis spectra of CuO, H-SAPO-34 and Cu/SAPO-34 catalysts prepared at different SSIE temperatures.

The H-SAPO-34 exhibited a broad band located at around 240 nm which can be assigned to a charge transfer (CT) band of the zeolite. The broad band located around 300-800 nm was attributed to the presence of CuO, as evidenced by the physical mixture of CuO and H-SAPO-34 (WO/C) and also by the bulk CuO sample. The bands at 355 and 456 nm are assigned to the charge transfer bands of O-Cu-O and Cu-O-Cu complexes, respectively. The broad absorption band at 600-800 nm is assigned to the electron d-d- transitions of Cu$^{2+}$ in distorted octahedral coordination surrounded by oxygen in dispersed CuO particles.

Increasing the SSIE temperature up to 700 °C results in a progressive diminution of the absorption intensity. This fact is related to the progressive dispersion of the CuO nanoparticles in order to form small copper clusters or copper ions. However, SSIE temperatures of 750 and 800 °C presented higher absorption intensity around 350-600 nm due to the formation of copper aluminate, which is favored at high temperatures due to the collapse of the zeolite framework.
All samples prepared by LIE showed the typical chabazite (CHA) structure, revealing that copper loading does not affect the zeolite structure. Furthermore, the absence of CuO peaks (36° and 38°), suggests that copper species are mainly isolated Cu\(^+\)/Cu\(^{2+}\) ions or highly dispersed Cu\(_x\)O\(_y\) clusters, both beyond the XRD detection limit.

All the catalysts prepared by SSIE presented diffraction peaks attributed to CuO with increasing intensity with copper loading. Additionally, SiO\(_2\) formation (21°) was also observed above 3.7 wt.% Cu, what suggests that the presence of copper promotes the collapse of the zeolite framework. This fact can be further corroborated by the low intensity of the main diffraction peaks of CHA zeolite (located at 9°, 13°, 17° and 32°) with increasing copper content.
Figure S6. Arrhenius plot for the determination of the activation energy of samples prepared by LIE and SSIE with different copper loading. Note that y-axis is represented in logarithmic scale.

The NH$_3$-SCR reaction proceeds through the same reaction mechanism as revealed by the similar activation energies obtained for LIE and SSIE preparation methodologies. The apparent activation energy was around 40-47 kJ mol$^{-1}$ for LIE samples and 32-37 kJ mol$^{-1}$ for SSIE samples. The sample prepared by LIE with a copper loading of 1.1% presented a lower activation energy of 19 kJ mol$^{-1}$, which could be as consequence of such a low copper content. In addition, it can be observed that SSIE samples are more active than LIE samples due to a higher accessibility of copper ions.