Influence of Alumina Precursor Properties on Cu–Fe Alumina Supported Catalysts for Total Toluene Oxidation as a Model Volatile Organic Air Pollutant

Tadej Žumbar [1,2], Alenka Ristić [1], Goran Dražić [1], Hristina Lazarova [3], Janez Volavšek [1], Albin Pintar [1], Nataša Zabukovec Logar [1,4] and Nataša Novak Tušar [1,4,*]

[1] National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia; Tadej.Zumbar@ki.si（T.Ž.); alenka.ristic@ki.si (A.R.); goran.drazic@ki.si (G.D.); janez.volavsek@ki.si (J.V.); albin.pintar@ki.si (A.P.); natasa.zabukovec@ki.si (N.Z.L.)

[2] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

[3] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 9, BG-1113 Sofia, Bulgaria; hristina.lazarova@orgchm.bas.bg

[4] University of Nova Gorica, Vipavska 13, SI-5000, Nova Gorica, Slovenia

* Correspondence: natasa.novak.tusar@ki.si

SI.1 Synthesis procedures

In all cases, the prepared iron containing alumina precursors were dried at 105°C for 24 h and then calcined at 500°C for 2 h, with a heating ramp of 100°C/h. After they cooled down to room temperature, they were impregnated by means of the incipient wetness impregnation method [44] with a copper (II) nitrate trihydrate solution that corresponds to the theoretical amount of 6 wt.% of CuO in the activated sample. After the impregnation, the samples were dried at 105°C for 2 h and then activated at 500°C for 1 h (heating ramp 100°C/h). All materials that contained iron or copper were marked as *"Fe"* or *"Cu"* or *"FeCu"*, when both metals were present.

Synthesis of bayerite precursors

Two bayerite, α-Al(OH)$_3$, precursors were prepared and studied, first, *"N"* was prepared with combining the sodium aluminate solution and nitric acid with iron (III) nitrate hexahydrate, which were combined instantaneously in the amounts that the ending pH value of the mixture was around 7. The slightly pink material immediately precipitated as the pH value of the aluminate solution dropped. The mixture was then vigorously stirred for 3,5 h. After that it was filtered and washed with deionized water to remove any impurities. The filter cake with addition of deionized water was then transferred to a 200 ml Teflon coated stainless steel autoclaves for heating to 150°C for 48 h. The material was cooled and filtrated and the normal procedure of drying, calcining and activating was performed as described above.

The second aluminum hydroxide material, named *"b-O"* was prepared with combining sodium aluminate and ammonium acetate with iron (III) chloride hexahydrate. A glass beaker contained deionized water, which was vigorously stirred. The sodium aluminate solution and the acetate with chloride solutions were added slowly, so the total amount of sodium aluminate was used at a constant pH value between 7 and 8. The initial water content serves as a medium that the vigorous stirring can be performed and has a beneficial effect on the formation of the bayerite phase. Its amount corresponds to the volume of added sodium aluminate solution. The mixture that contained a slightly pink precipitate was aged for two hours and then filtrated and washed with deionized water. Then the normal procedure of drying, calcining and impregnating was performed.

Synthesis of pseudoboehmite precursors

As in the case of bayerite precursors, two materials were chosen for the study. First was named *"p-N"* and was prepared with controlled addition of 32% nitric acid with iron (III) chloride hexahydrate and sodium aluminate solution to a vigorously stirred starting content of deionized water that corresponds to the volume of added sodium aluminate. The pH value of the reaction mixture was controlled continuously and held at around 7. After all the reagents were mixed, the mixture was heated at 95°C for 3 h. After that, the material was filtrated and washed with deionized water. The drying, calcining and impregnating procedure followed as in all cases.

The second material, named *"p-AS"* was prepared with combining aluminum chloride solution, which contained iron (III) chloride hexahydrate in a corresponding amount and sodium aluminate solution. They were mixed during vigorous stirring of starting deionized water as in case of sample p-N, with constant pH control, which was held stable at around 7. The solution was aged for 4 h under stirring. Then the product was filtrated, washed and transferred to a 200 ml Teflon coated SS autoclave with addition of deionized water for 48 h at 150°C. The product was filtrated, dried, calcined and impregnated with procedure.

Synthesis of dawsonite precursors

The dawsonite material named *"d"* was prepared in a 1 liter pressure vessel, which contained 0,5 l of sodium aluminate solution which was previously polished [45]. The

temperature of the solution was raised to 110°C; at that point simultaneous addition of iron (III) chloride hexahydrate solution and carbon dioxide gas was performed. The pressure of the gas was slightly above the pressure of the vessel, so dissolution of the formed carbonic acid was enabled and equilibrium was reached. Afterwards the small amount of iron chloride solution was added quickly. The carbon dioxide was left to pass the solution for another 2 h. After that, the vessel was cooled down to room temperature. A thick orange precipitate was formed. The material was washed with deionized water and filtrated to remove the formed sodium carbonate. After calcination, the material was washed again to remove impurities formed during calcination.

Synthesis of an amorphous precursor

An amorphous material named *"a"* was prepared with a similar procedure to that of the sample *p-AS*, with the difference that no hydrothermal treatment was performed and the washed filter cake was immediately dried and treated as described above.

SI.2 Nitrogen physisorption isotherms of prepared Cu Fe alumina supported catalysts.
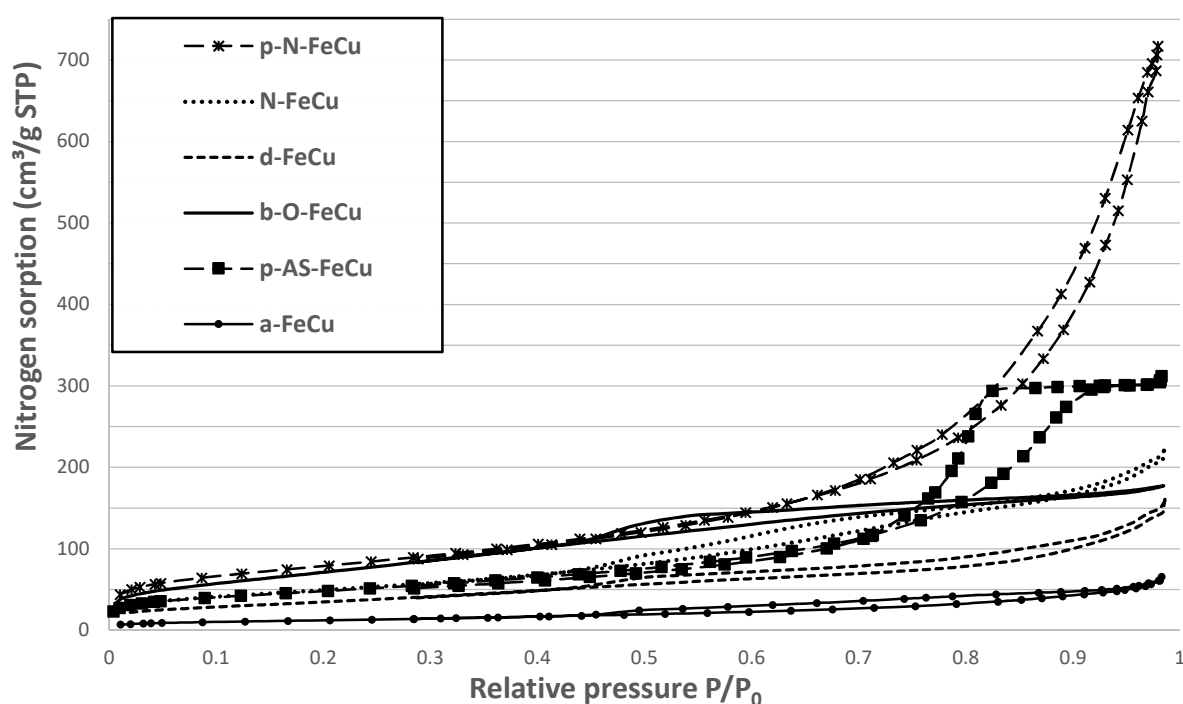

Figure S2. presents N_2 adsorption-desorption isotherms of copper and iron containing alumina supported catalysts. The differences in the synthesis procedures and the fact that the supports originate from different types of alumina precursors, lead to very different textural characteristics presented by N_2 physisorption analysis.

SI.3 Concentration of acid sites and desorption temperature of pyridine.

As shown in Figure SI.3, pyridine desorption occurs at different temperatures. Samples "a-FeCu" and "p-N-FeCu" display only one desorption peak at around 240°C, whereas samples "N-FeCu" and "p-AS-FeCu" display three desorption peaks at around 240, 440 and 415°C, respectively. This suggests the presence of two types of acid sites in samples "N-FeCu" and "p-AS-FeCu", as the stronger acid sites need more energy that the probe pyridine molecule can be desorbed, which occurs at higher temperatures than in case of weaker acid sites. Sample "b-O-FeCu" has the first desorption peak at 240°C and afterwards an increase that could suggest the presence of additional type of adsorption sites, expressed at higher temperatures. Sample "d-FeCu" is weakly acidic with only 47 µmol per gram and a slight desorption peak at 230°C.
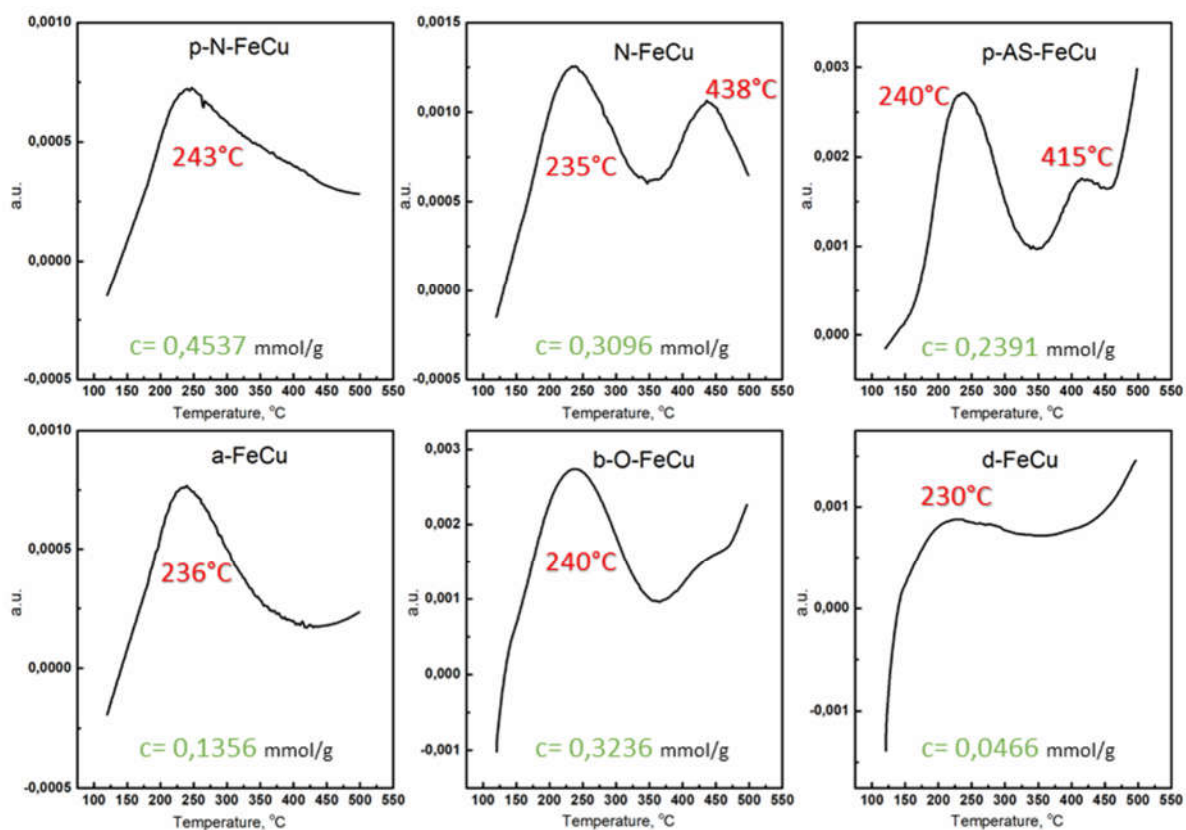
Figure S3.1 Pyridine desorption peaks for samples "p-N-FeCu", "N-FeCu", "p-AS-FeCu", "a-FeCu", "b-O-FeCu" and "d-FeCu" with presented acid site concentration per gram of sample.
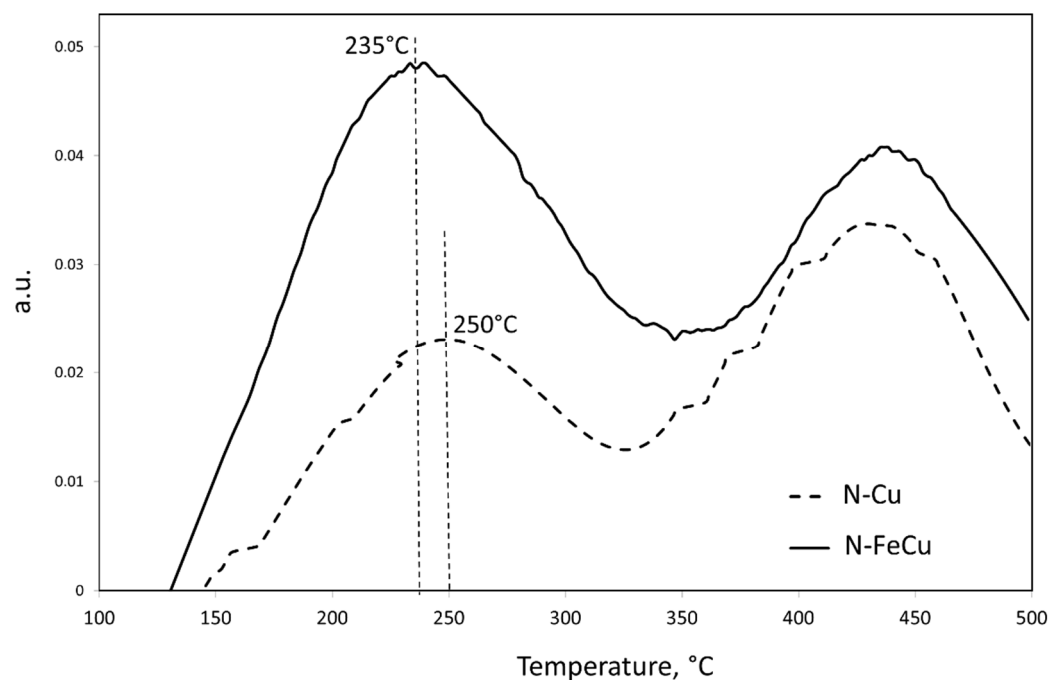

Figure 3.2 Pyridine desorption peaks for samples "N-Cu" and "N-FeCu" with indicated desorption peak temperature in low temperature side. Sample »N-Cu« has stronger acid sites in low temperatures (<300°C).

SI.4 Al NMR spectroscopy
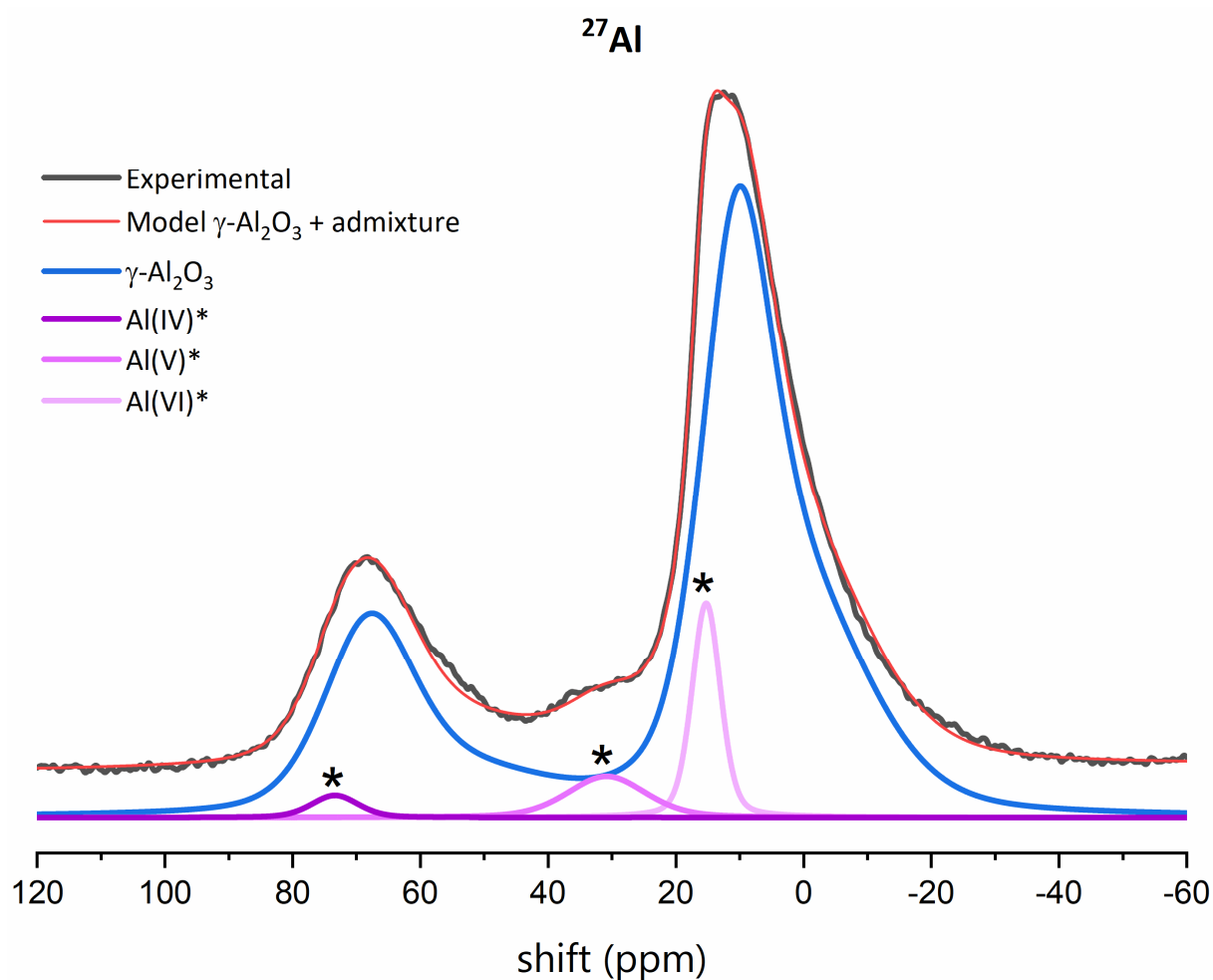
Figure S4. Figure shows that ^{27}Al MAS NMR spectrum of p-N-FeCu can be decomposed into strong contributions of γ-Al$_2$O$_3$ and into weak contributions of admixture(s). The signals of AlO$_4$, AlO$_5$ and AlO$_6$ species of admixture(s) together represent 10 % of the total Al signal. The model γ-Al$_2$O$_3$ signal was 'extracted' from the ^{27}Al MAS NMR spectrum of b-O-FeCu.

SI.5 H$_2$-TPR of samples from precursor N
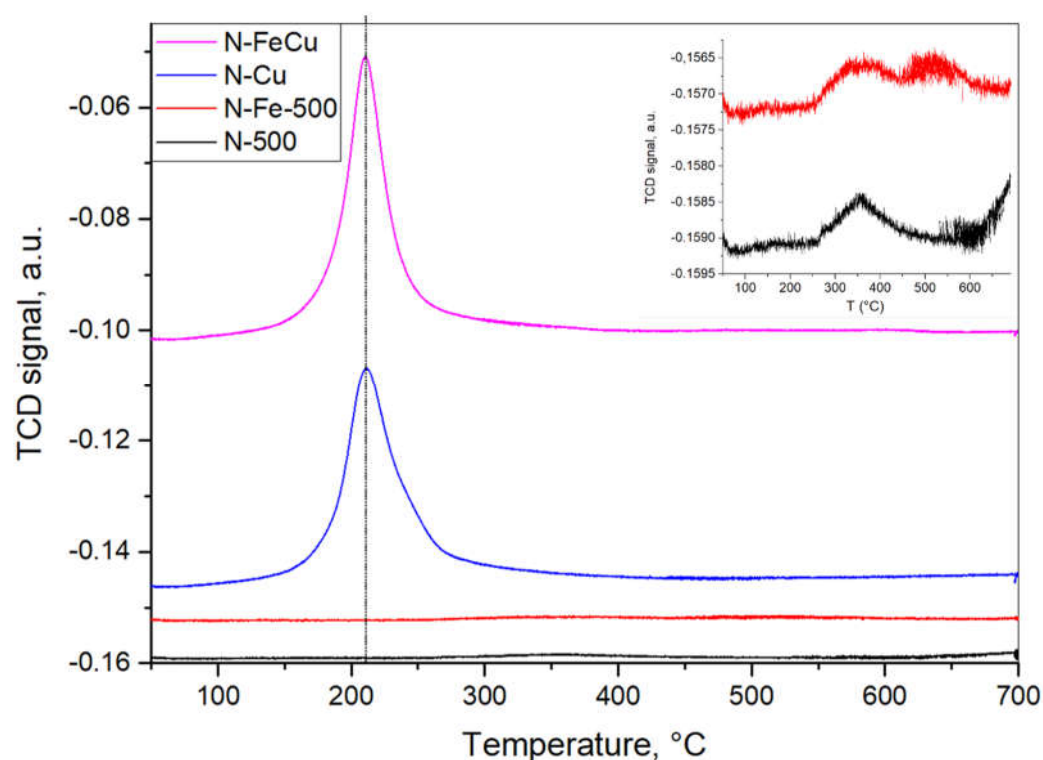
Figure S5. shows H_2-TPR profiles of samples "N-FeCu", "N-Cu", "N-Fe-500" and "N-500" with inserted close-ups of the two copper absent samples. Reducibility of the copper containing catalysts is similar, with a reduction peak at 210°C, where the sample "N-Cu" possesses a slightly broader peak with an extend on the high temperature side, indicating the possibility that the copper oxide particles have a broader size distribution and larger average particle size compared to the sample "N-FeCu". The samples prepared without presence of copper have poor reducibility and therefore only a small peak is observed between 340 and 360°C. The sample "N-Fe-500" also exhibits a small peak between 500 and 600°C that could be ascribed to the contribution of iron-containing species to the recorded TPR profiles.

SI.6 High temperature (HT) XRD
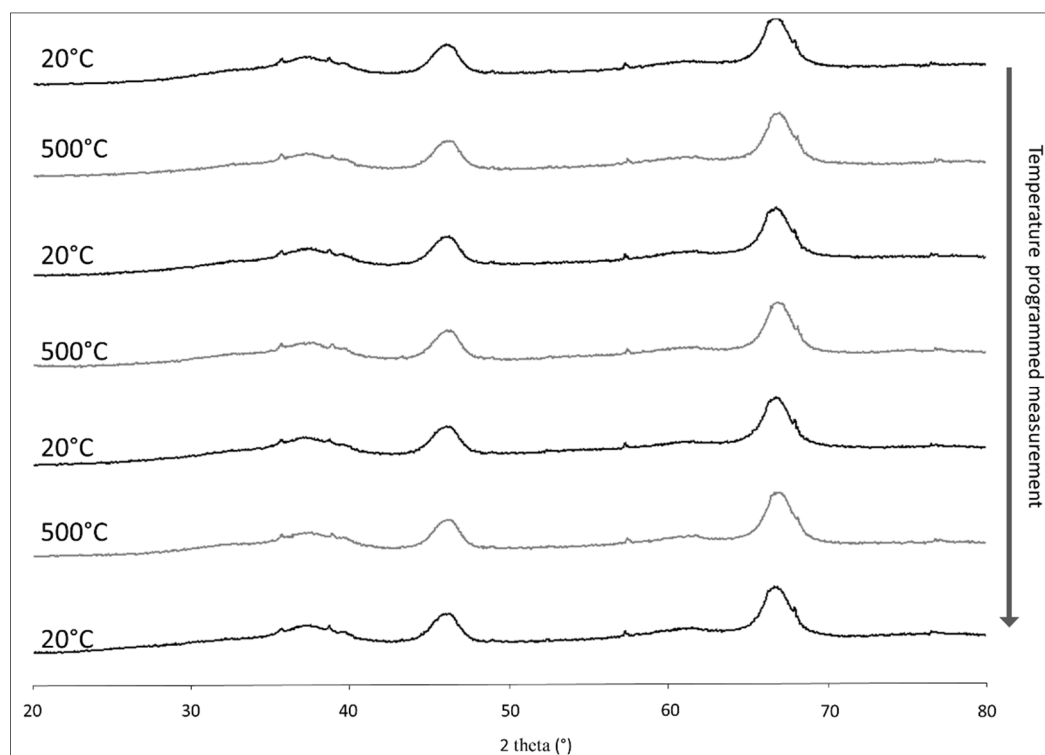
Figure S6. XRD patterns of sample "N-FeCu".The sample was exposed to room temperature and then heated in air (10°/min) to 500 °C for three repeated cycles. According to XRD, the structure was completely preserved and no changes in peak intensity or position was observed, indicating that no sintering of the CuO nanoparticles occurred and that the alumina support structure remained stable and that therefore the catalyst itself is stable under reaction conditions.