# Supported Metal Catalysts for Free Fatty Acid Rich Residues

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## Introduction

Hydrogenation of biomass rich in free fatty acids is a possible way to produce hydrocarbon compounds with characteristic similar to fossil fuels. Activity of heterogeneous catalysts in hydrogenation is strongly related to the metal dispersion and the preparation technique used often turns out to be a critical aspect in order to obtain stable and reliable systems. A series of heterogeneous catalysts has been prepared by using a traditional technique as the Incipient Wetness one (IW), and an unconventional method herein after mentioned as the Chemisorption-Hydrolysis method (CH), already shown to be succesful in obtaining highly dispersed catalysts [1].

## Experimental

Heterogeneous catalysts were prepared by using IW and CH methods. Silica and silica-alumina were the selected supports and $Cu(NO_3)_2{\cdot}3H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Pd(NH_3)_2(NO_2)_2$, $Pt(NH_3)_4(NO_3)_2$ and $PdCl_2$ the precursors. Samples characterization was carried out by using temperature-programmed reduction (TPR) and thermal gravimetric analysis (TGA) techniques. Metal content in the catalysts was checked by inductively coupled plasma spectroscopy (ICP).

**Table 1:** List of prepared supported catalysts.

| no. | Sample | Metal | Precursor | Method | Support |
|---|---|---|---|---|---|
| 1 | $Cu/SiO_2$Chrom IW | Copper | $Cu(NO_3)_2 \cdot 3H_2O$ | IW | Silica |
| 2 | $Cu/SiO_2–Al_2O_3$ 135 IW | Copper | $Cu(NO_3)_2 \cdot 3H_2O$ | IW | Silica-Alumina |
| 3 | $Cu/SiO_2$Chrom CH | Copper | $Cu(NO_3)_2 \cdot 3H_2O$ | CH | Silica |
| 4 | $Cu/SiO_2–Al_2O_3$ 135 CH | Copper | $Cu(NO_3)_2 \cdot 3H_2O$ | CH | Silica-Alumina |
| 5 | $Fe/SiO_2$Chrom IW | Iron | $Fe(NO_3)_3 \cdot 9H_2O$ | IW | Silica |
| 6 | $Fe/SiO_2–Al_2O_3$ 135 IW | Iron | $Fe(NO_3)_3 \cdot 9H_2O$ | IW | Silica-Alumina |
| 7 | $Fe/SiO_2$Chrom CH | Iron | $Fe(NO_3)_3 \cdot 9H_2O$ | CH | Silica |
| 8 | $Fe/SiO_2–Al_2O_3$ 135 CH | Iron | $Fe(NO_3)_3 \cdot 9H_2O$ | CH | Silica-Alumina |
| 9 | $Pd/SiO_2$Chrom CH | Palladium | $Pd(NH_3)_2(NO_2)_2$ | CH | Silica |
| 10 | $Pt/SiO_2$Chrom CH | Platinum | $Pt(NH_3)_4(NO_3)_2$ | CH | Silica |
| 11 | $Pd/SiO_2$Chrom IW | Palladium | $PdCl_2$ | IW | Silica |

## Results

TPR profile of copper catalysts prepared by CH technique showed a single, sharp peak, with a maximum centered at 245ºC, at lower temperature with respect to the corresponding IW catalysts. This witnesses better dispersion of the CuO phase and higher uniformity of the particles size. Iron catalysts made by IW showed a complex profile that can be caused by the presence of different iron oxide phases, by some differences in the oxide dispersion and by the interaction between the support and the oxide [2].

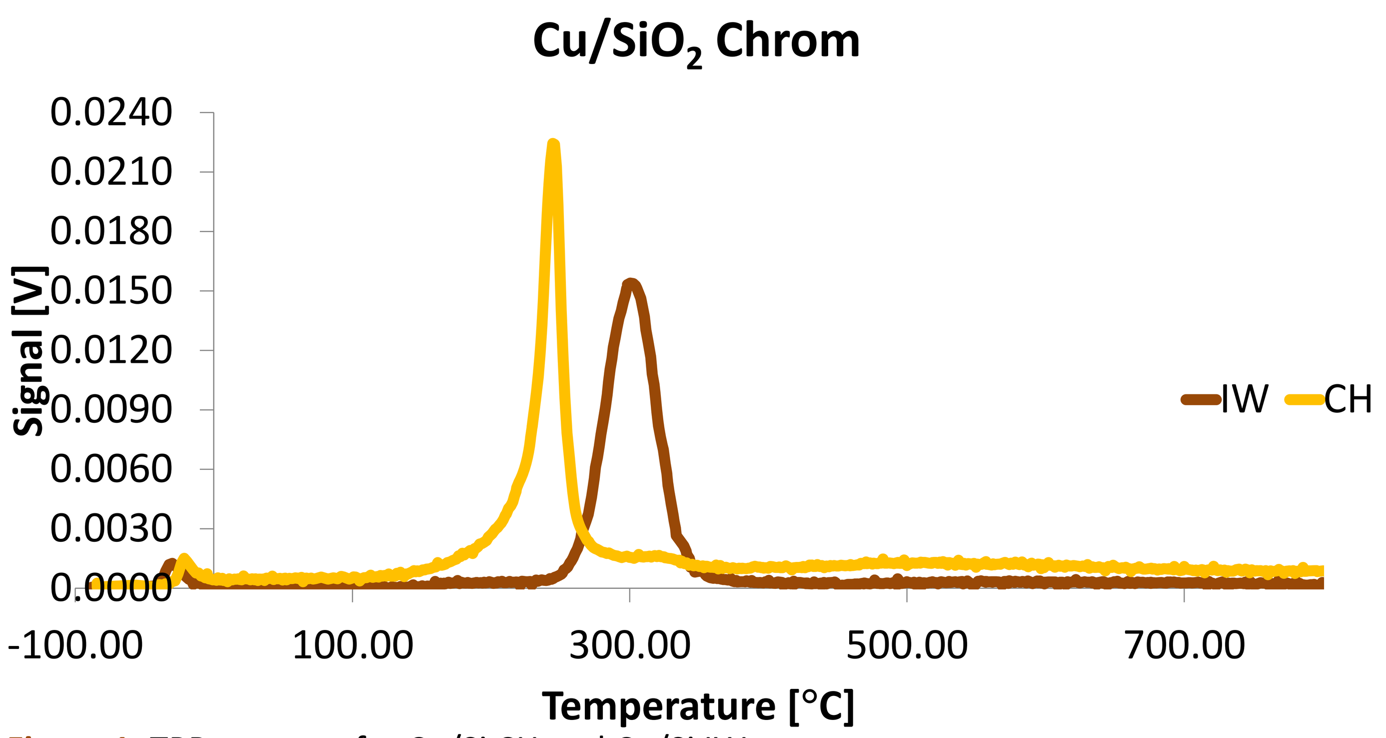


**Figure 1:** TPR patterns for Cu/Si CH and Cu/Si IW.

Reduction profile of iron CH catalysts displays only to two very distinct signals at 385-390°C and 803°C. Platinum and palladium catalysts were easily reduced at room temperature

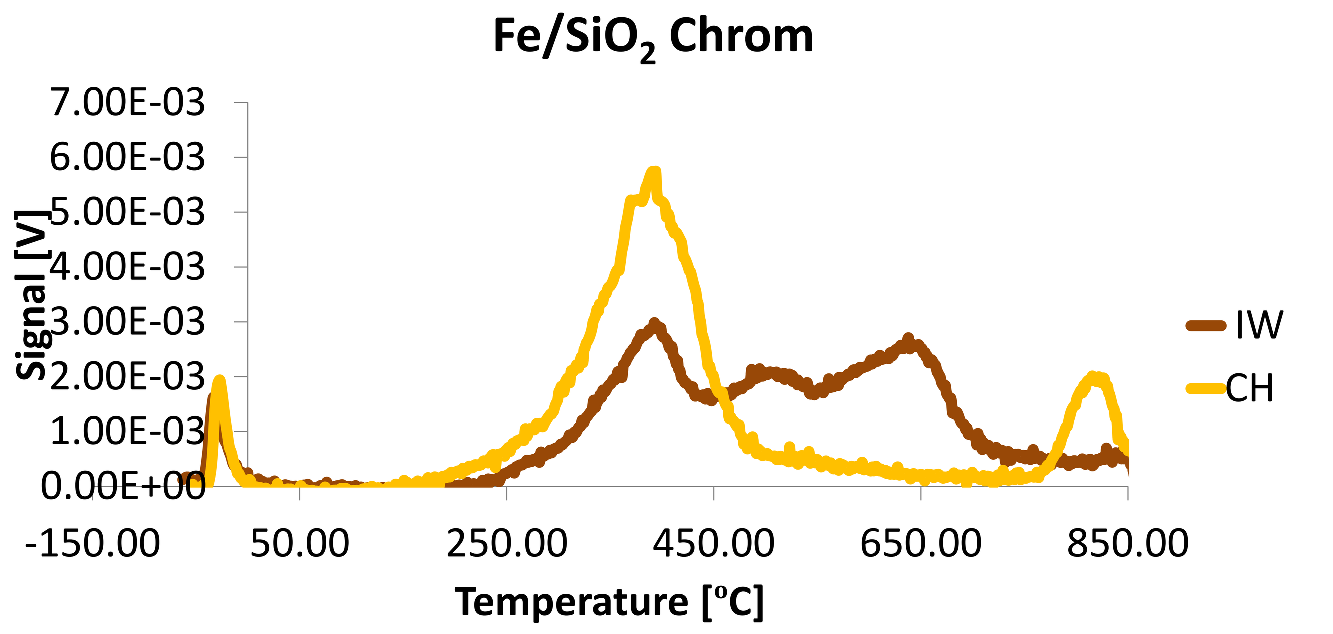


**Figure 2:** TPR patterns for Cu/Si CH and Cu/Si IW.

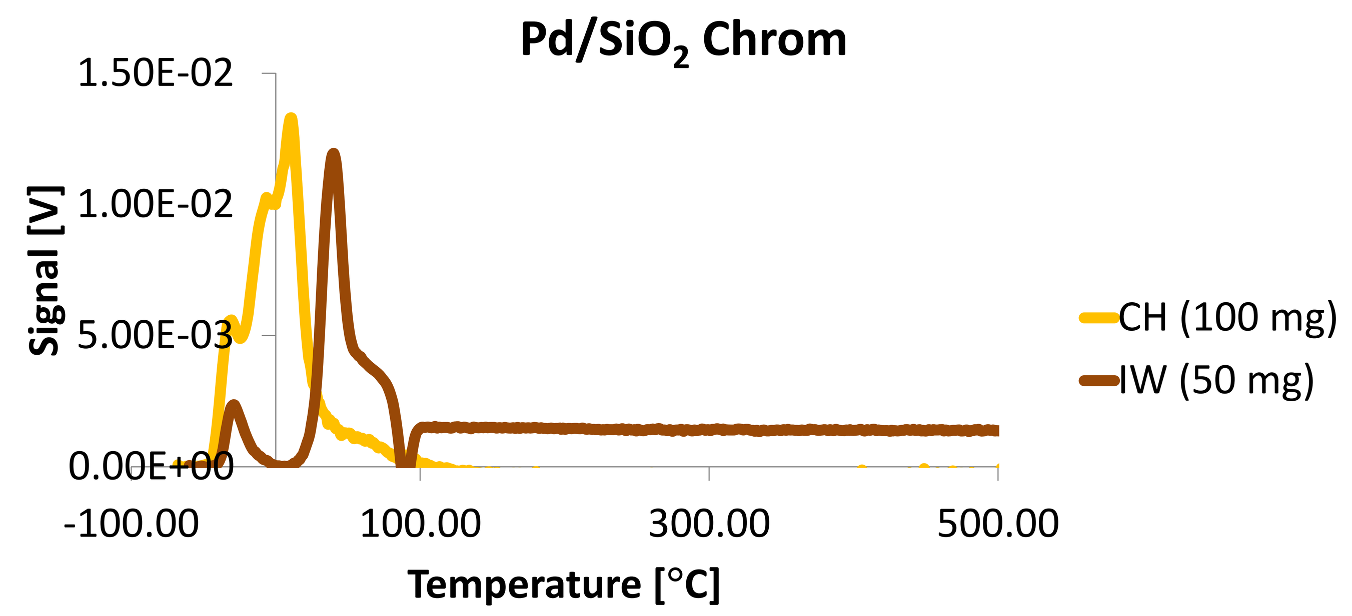


**Figure 3:** TPR patterns for Cu/Si CH and Cu/Si IW.

**Table 2:** ICP and TGA analysis results.

| no. | Sample | TGA weight loss | Theoretical metal loading | ICP metal loading |
|---|---|---|---|---|
| 1 | $Cu/SiO_2$Chrom IW | 3.83% | 8.00% | 7.87% |
| 2 | $Cu/SiO_2–Al_2O_3$ 135 IW | 5.48% | 8.00% | 8.42% |
| 3 | $Cu/SiO_2$Chrom CH | 4.41% | 8.00% | 8.85% |
| 4 | $Cu/SiO_2–Al_2O_3$ 135 CH | 4.58% | 8.00% | 9.83% |
| 5 | $Fe/SiO_2$Chrom IW | 2.62% | 7.00% | 6.72% |
| 6 | $Fe/SiO_2–Al_2O_3$ 135 IW | 3.62% | 7.00% | 7.55% |
| 7 | $Fe/SiO_2$Chrom CH | 2.79% | 15.00% | 5.50% |
| 8 | $Fe/SiO_2–Al_2O_3$ 135 CH | 4.82% | 15.00% | 2.03% |
| 9 | $Pd/SiO_2$Chrom CH | 3.05% | 2.00% | 1.68% |
| 10 | $Pt/SiO_2$Chrom CH | 3.15% | 2.00% | - |
| 11 | $Pd/SiO_2$Chrom IW | 3.73% | 2.00% | 1.68% |

## Conclusions

- Catalysts prepared by CH method benefit from a homogeneous and high dispersion of the metallic phase on the support.
- Improvements were obtained in the preparation of iron catalysts supported on silica.
- CH technique was successfully applied also to the preparation of noble metal supported catalysts.

## Acknowledgements

This work was supported by the COST Action CM0903 through the ECOST-STSM-CM0903-010513-029059. Support for this work was provided by FCT as part of the project "BIOFFA – Biodiesel production by (trans)esterification and hydrogenation of high fatty acid content residues" (FCOMP-01-0124-FEDER-013936; ex-PTDC/AAC-AMB/112957/2009).

## References

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