Inductively self-heating Fe(Co, Cu) catalysts for reverse water gas shift: evidence of temperature gradients at the nanoscale

Stylianos Spyroglou[1], Lorenz Lindenthal[2], Thomas Cotter[2], Christoph Rameshan[2], Maricruz Sanchez-Sanchez[1]*

1 Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9 1060 Vienna, Austria; 2 Chair of Physical Chemistry, Montanuniversität Leoben, Franz-Josef-Str. 18, A-8700 Leoben, Austria;

**Corresponding author: maricruz.sanchez@tuwien.ac.at*

Highlights

- Phase interconversions of Fe determine their stability as inductively heated catalysts.
- Temperature gradients at the nanoscale are detected under inductive heating.
- Cu doping improves activity without altering the magnetic properties of Fe catalysts.
- Co doping stabilizes Fe metal and leads to high temperatures under induction.

1. Introduction

Catalytic reactors for CO_2 utilization via reverse water gas shift (RWGS) can benefit from the localized heating to T > 500°C, precise temperature control and fast heat up and cool down rates of magnetic induction. Fe nanoparticles are ferromagnetic and can be inductively heated to RWGS reaction temperatures by an alternating magnetic field with intensities in the order of 10^{-2} T. The approach of using Fe nanoparticles both for catalysis and inductive heating is expected to bring advantages such as the elimination of heat transfer limitations, fast response and the possibility of directly using electricity from renewable sources [1]. This work studies the magnetic and catalytic properties of Fe and Fe-Co supported nanoparticles and their stability as catalysts and inductive heaters under RWGS reaction conditions. Combining operando and post-reaction characterization we determine the effects of inductive heating in the structure and properties of magnetic nanoparticles stabilized by non-magnetic supports.

2. Methods

Supported monometallic Fe and bimetallic Fe-Cu and Fe-Co inductively heatable catalysts were prepared by wet impregnation on different supports (γ-Al_2O_3, SiO_2, zeolites, CeO_2). Structure and redox properties of the catalysts were studied by in-situ XRD, temperature-programmed reduction and operando XAS. The catalysts were tested in a lab scale 9 mm ID fixed bed reactor equipped with a copper coil generating an alternating magnetic field (Bapp= 47 mT, f= 323 kHz) and online GC analysis. Preceding the tests, the catalysts were activated in a conventional oven. Temperature under induction was measured with an infra-red sensor focused on the upper layer of the bed. Heat balances are used to determine the heating capacity of nanoparticles in each material.

3. Results and discussion

Our materials containing supported Fe and Fe(Co, Cu) nanoparticles over mesoporous oxides inductively self-heat up to 500°C-600°C under Ar gas flow (100 mL min^{-1}). When switching to CO_2/H_2 mixtures (100 mL min^{-1} CO_2:H_2:Ar = 1:1:2) they catalyze the RWGS reaction with 100% selectivity towards CO at atmospheric pressure. Operando XAS combined with XRD revealed that about 50% of metal Fe is converted to Fe_3C under reaction conditions. This translates into a lower induction temperature due to its lower Curie temperature. Starting from Fe_3O_4 phase nanoparticles leads to high stability against coking and carburization [2], however its RWGS activity is limited at the Curie temperature of Fe_3O_4 (585°C). By adding Cu loadings in the range 2-4% the catalyst achieves high RWGS activity (0.256 mol CO g_{cat}^{-1} h^{-1} at WHSV=25 L_{CO2} g_{cat}^{-1} h^{-1}) while keeping the magnetic properties of Fe nanoparticles intact. Conversely, the addition of Co only achieves moderate increase in heating, on spite of the higher Curie temperature of FeCo alloys (ca. 950°C). The alloy with Co stabilises

Fe against carbide formation, ensuring stable induction heating at 600ºC for at least 2h. Interestingly, different Fe phases are formed under RWGS when the catalysts are inductively heated from inside the material in comparison to reaction at similar conditions in an externally heated oven (Figure 1). On-going characterization of the spent materials hints to nanoparticles with distinct size or aspect ratio – which largely impact their magnetic properties - as responsible for hotspots in the catalytic bed.

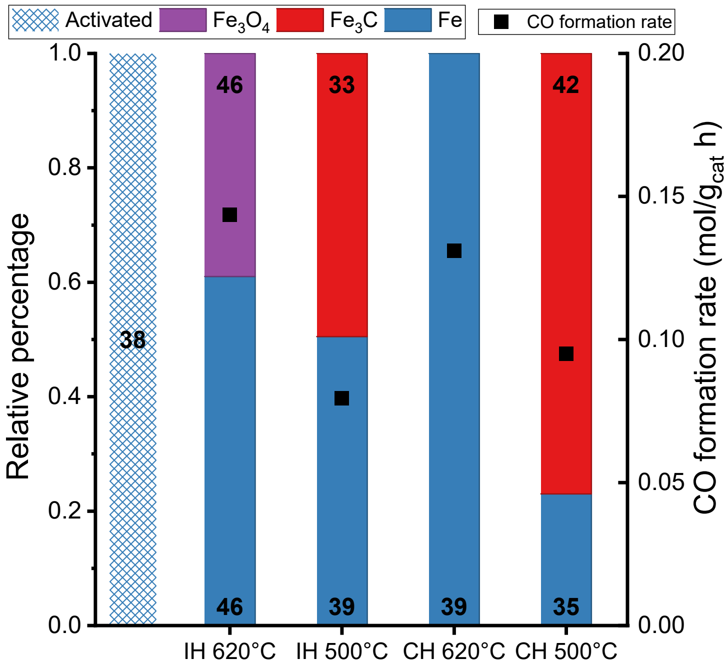

Figure 1. Crystalline phases and their average crystalline size (labelled, in nm) as obtained by XRD analysis of Fe/ZSM5 (Si:Al = 45:1) catalyst activated (550°C for 1h under 100 mol min^{-1} 10%H_2/Ar) and after RWGS tests performed with inducting heated (IH) and conventional heating (CH). Left Y: fraction of Fe phases from Rietveld refinement. Right Y: CO formation rate (mol g_{cat}^{-1} h^{-1}) on stream. Conditions: 100 ml min^{-1} CO_2:H_2:Ar = 1:1:2, WHSV = 11.5 L_{CO2} g_{cat}^{-1} h^{-1}, P = 101.3 kPa, TOS =1h. Applied field: 45-47 mT at 323 kHz.

4. Conclusions

Role of support and a second metal in redox properties of Fe nanoparticles is highly relevant for their stable performance as inductive heaters under RWGS catalytic conditions. In light of our studies using supports with different thermal conductivities (ranging from 0.1-15 W m^{-1} K^{-1}), the unexpected formation of Fe phases under induction is attributed to temperature gradients at the nanoscale. We are currently studying the effects of such gradients and controlled temperature oscillations on the activity and stability of these Fe-based inductively heated RWGS catalysts.

References

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Keywords

CO_2 utilization; Induction heating; supported nanoparticles; Reverse water-gas shift;