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Reverse Water-Gas Shift on Copper-based Catalyst Materials: Multi-Site Microkinetic Modelling

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Highlights

- Five copper catalysts (Cu / Al_2O_3, CeO_2, ZrO_2, SiO_2, TiO_2) were synthesized and analyzed
- The catalysts were tested for the reverse water-gas shift reaction
- A microkinetic model, considering different sites on the catalyst surface, was developed
- The model was fitted to experimental data using measured surface site concentrations

1. Introduction

Many alternatives to oil-based chemicals and liquid fuels have emerged over the past few decades. Reverse water-gas shift (RWGS) is one of them. As a reaction that converts a mixture of hydrogen and CO_2 to water and CO, it has the potential to offer a closed carbon cycle when greener energy like renewable electricity is used for hydrogen production. [1] In order to increase its industrial significance, many kinetic and modelling studies have been performed for this process, with the focus shifting toward microkinetic modelling lately.

Most of the models assume a single active phase on the catalyst surface. However, when it comes to supported catalysts, many different types of the active metal sites may be present. Whether the difference is in the oxidation state, the crystal planes exposed, or just different neighboring atoms, these different sites will behave differently during the reaction and a representative model should take this into account. In this study, we investigated the effects of five different supporting materials on the reaction on various types of deposited copper using experimental, analytical and modelling approaches.

2. Methods

Five copper catalysts on different supporting materials were synthesized using the deposition-precipitation method. They were tested for activity for the RWGS reaction under various conditions (3-7 bar, 280-360 °C, and various inlet flow rates with H_2/CO_2 ratios of 1.5, 1 and 0.67). The results were published in a previous paper. [2] The catalysts were examined by analytical techniques such as SEM, XRD, BET and EDX. Surface active sites were characterized and quantified using various temperature programmed reduction/oxidation techniques, namely CO and H_2 TPD and TPR as well as N_2O chemisorption. Site densities (mol/g_{cat}) for various different active sites were obtained in this manner and were further used in microkinetic modelling.

A microkinetic model was developed in order to describe the effects of the supporting material on the activity of the catalysts. It was assumed that each catalyst included multiple different active sites (ex. monolayer copper and bulk-like copper particles), each having their own set of kinetic constants. The kinetic parameters were then fitted to experimental data. The models were formulated for both CSTR and packed bed systems, the latter taking into account longitudinal convective and diffusive mass transfer.

3. Results and discussion

From the measured conversions at various operating conditions, it was observed that the catalysts showed variable activities, Al_2O_3 and CeO_2 supports being the most active, and SiO_2 and ZrO_2 the least. Different reduction and desorption temperature profiles were observed using the various TPD and TPR techniques, indicating different copper types present. For example, multiple peaks were observed in H_2 TPR for each catalyst, as shown in **Fig. 1 b)**. In this case, the copper present can be divided in roughly three different types (α, β, γ), while in other cases like CO TPD, two peaks can be observed.

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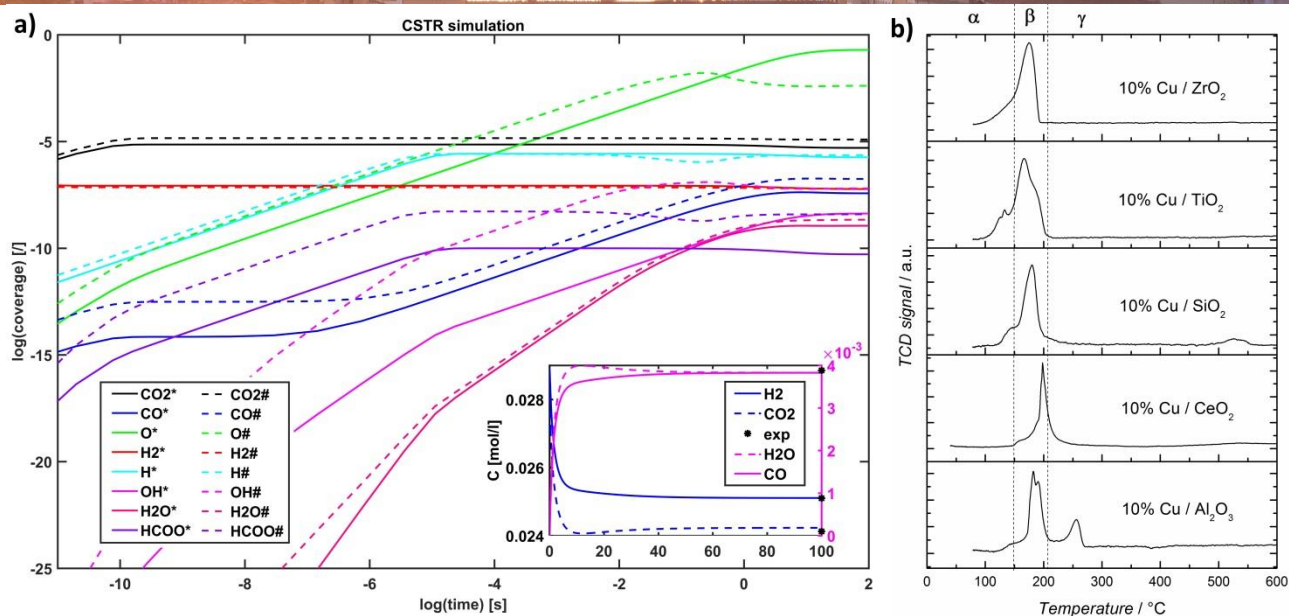www.aidic.it/iscre25

Figure 1. a) An example of a CSTR reactor simulation with fitted constants (10% Cu/Al$_2$O$_3$, 360 °C, 6.772 SCCM flow rate, 1.03:1 H$_2$/CO$_2$ ratio, 1 mL reactor volume). Main graph is showing the coverages of surface species on bulk (*) and well-dispersed (#) copper, and the smaller graph is depicting the time evolution of bulk concentrations. b) H$_2$ TPR of the five catalysts.

An example of a CSTR simulation is showed in **Fig 1. a)**. It was performed using CO TPD data to collect the information about the surface concentration of two different copper types. We have assumed that the low CO TPD temperature peak corresponds to bulk like copper (*), and the high temperature one to well dispersed, monolayer-like copper (#). The pathway scheme for the reaction on both of these copper types was taken from a DFT study paper, [3] and so were the initial kinetic constants for regression analysis. The kinetic constants were fitted to a large set of experimental data obtained from the different synthesized catalysts. The regression was first performed with the CSTR model for speed, and once reasonably good parameters were obtained, the packed bed reactor model was used for further regression to determine the final parameters. Two sets of kinetic constants, one for each copper type, were attained in this way and showed good agreement with the experimental data. Different coverages and reaction rates can be observed for the two catalytic sites under consideration.

4. Conclusions

The multi-site approach was used to describe the effects of the supporting material on the active phase reaction networks and kinetics. Providing the experimentally measured gas phase concentrations at various operating conditions as well as the active site concentrations, obtained by CO TPD, it was possible to calculate the model concentrations with our microkinetic scheme. After numerical regression of constants on various different sites, a good fit was obtained between the model and experimental data.

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