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L-IV Comparison of the Steady-state Kinetics of the CO Hydrogenation to Higher Alcohols **Using Different Industrial Co-Cu Catalysts**

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A series of industrial Co-Cu-based catalysts provided by Evonik Resource Efficiency GmbH was investigated regarding the steady-state kinetics of CO hydrogenation to higher alcohols. Two different generations of Co-Cu catalysts were studied, which were all doped with Mn and embedded in a carefully created carbon matrix. Additionally, the catalyst of the 2nd generation was not reduced prior to the HAS and compared to the reduced catalyst. Especially the partial pressure variation of CO and H₂ showed that the pretreatment is strongly influencing the catalyst.

1ST GENERATION OF CO-CU-BASED CATALYSTS

Prior to the measurement with synthesis gas, the catalyst was reduced with 20 % H_2/N_2 at 250 °C and afterwards cooled to 180 °C. After reaching the pressure of 60 bar, the catalyst was heated slowly to 280 °C. During this heating phase, structural transformations of the catalyst occurred which were also observed during the isothermal induction period. As a result of these transformations, CO conversion decreased constantly during the first 70 h TOS, before in-

2ND GENERATION OF CO-CU-BASED CATALYSTS

A 2nd generation catalyst was investigated similarly to the 1st generation catalyst. This catalyst was investigated at 260 °C instead of 280 °C with the goal to avoid the formation of long-chain hydrocarbons and therefore favoring the oxygenate formation.

Similar to the other system, structural transformations were observed to take place during the induction period. But more

creasing slightly and reaching a stable value after 115 h TOS.

During the investigation of the steady-state kinetics performed after the induction period, the residence time, the partial pressures of CO and H_2 , and temperature were varied. These variations gave significant insight into the reaction mechanisms taking place during CO hydrogenation. In addition to the known interplay between MeOH synthesis and Fischer-Tropsch synthesis, acetic acid and propionaldehyde were observed in the chromatograms. Therefore, it must be concluded that the hydroformylation of olefins and the carbonylation of primary alcohols are taking place.

interestingly, the global reaction orders of H₂ and CO derived from the partial pressure variation were different compared with the 1st generation catalyst. Previously, the surface of the catalyst had neither been saturated with CO_{ads} nor with H_{ade} (Figure 1). However, for the 2nd generation (Figure 2) a positive reaction order was derived for H₂, while the global reaction order of CO was -1.24. Therefore, it is reasonable to assume that the surface of the catalyst was oversaturated with CO_{ads} , resulting in an inhibition of the formation of products. The analogously conducted study without reduction showed that also the pretreatment of the catalyst significantly influences the steady-state kinetics.





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Fig. 1: Partial pressure variation of a 1st generation catalyst.

Fig. 2: Partial pressure variation of a 2nd generation catalyst.

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