**Development of Multi-site Microkinetic Model for the Methanol Synthesis Catalysts**

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**Highlights**

* Tested Cu:M:Ti oxide catalysts (M=Sr, Ba, Ca) with various compositions.
* Investigated structural properties by CO2 TPD, N2O chemisorption and other techniques.
* Copper particle size and basicity important for the methanol synthesis.
* Observed trends incorporated into the multi-site microkinetic model.
1. **Introduction**

Methanol is important industrial chemical with the annual production of 110 Mton [1]. Development of new catalysts with enhanced properties is a key for an efficient methanol synthesis. Additionally, microkinetic models built on trends from experimental work, with reaction rate constants from quantum chemical calculation [2], can be used to obtain insights into catalytic reaction mechanisms and for further plant operation optimization.

The beneficial influence of the basicity of the copper catalyst on the methanol synthesis was previously reported [3,4]. In our work we prepared and tested different Cu:M:Ti oxide (M=Sr, Ba, Ca) catalysts. Catalysts were characterized by N2 physisorption, N2O pulse chemisorption, CO2 TPD and H2 TPR. We investigated structure-activity relationship for the preparation of the microkinetic model.

**2. Methods**

Catalysts were prepared by solution combustion synthesis with citric acid and calcined at 650 °C. We pelletized powders and reduced them at 300 °C for 12 h. For the catalytic tests, the temperature was varied at pressure 20 bar, GHSV = 6000, 12000 1/h and inlet gas composition H2:CO2= 3:1. Outlet gas composition was determinate using gas chromatography. N2 physisorption was performed using ASAP 2020, H2 TPR was executed in 50 mL/min flow of 10% H2/Ar gas with heating rate of 10 °C/min from 60 °C to 300 °C, N2O pulse chemisorption was performed after H2TPR, in the 20 mL/min flow of He at 90 °C. The consumption of N2O was determined using daily calibrated mass spectrometer. CO2 TPD were performed from -40 °C to 600 °C with heating rate of 20 °C/min in the 20 mL/min of He. Mass spectrometer was also used to analyze results. N2O pulse chemisorption, CO2 TPD and H2 TPR were performed on Autochem 2920.

**3. Results and discussion**

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| Methanol and carbon monoxide production at 220 °C and 20 bar were used and normalized to copper surface area obtained from N2O pulse chemisorption to calculate turnover frequency (TOF). We tested catalysts at various copper loadings (Figure 1), different Sr/Ti ratio (Figure 2) and different earth alkaline metals (Ca, Sr, Ti) (Figure 3). We observe, that at different Cu loadings, Cu particle size increase which increases TOF for MeOH, while TOF for CO remains constant. This suggests that larger copper particles expose surfaces, which are more selective for MeOH synthesis. Turnover frequency for MeOH increases with increasing Sr/Ti ratio, while CO TOF remains almost constant. This suggests that Sr promotes adsorption of CO2 and further reaction with adsorbed H\* species through Langmuir-Hinshelwood mechanism. Much larger benefits are obtained using Ca, which much strongly adsorbs CO2. Therefore for the development of the microkinetic model is important incorporation of multiple sites, such as basic sites with various copper metal sites. |
| **Figure 1.** Influence of copper loading on TOF for MeOH and CO at constant Sr/Ti. (GHSV=6000 1/h) | **Figure 2.** Influence of Sr/Ti ratio on TOF for MeOH and CO at constant copper loading 50 wt%.(GHSV=6000 1/h) |
| **4. Conclusions**Important catalyst properties were investigated to obtain structure-activity relationships. We found out that the basic sites importantly influence the catalyst activity and should be included into microkinetic model, beside copper sites. | **Figure 3.** Influence of different earth alkaline metals for Cu:M:Ti=5:3:2. (GHSV=12000 1/h) |

**References**

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