The activation of Mo based catalysts for methane aromatization

Kae S. Wong¹, Joris W. Thybaut¹,*, Elisabeth Tangsad², Michael W. Stocker² and Guy B. Marin¹

¹Laboratory for Chemical Technology, Ghent University, Krijgslaan 281-S5, B-9000, Ghent, Belgium
²SINTEF Mat & Chem, Dept Hydrocarbon Proc Chem, N-0314 Oslo, Norway
*Joris.Thybaut@UGent.be

The main energy supply is shifting from oil-based to more natural gas-based since the depletion of crude oil reserves. The non-oxidative direct methane aromatisation over zeolite supported molybdenum bifunctional catalysts produces benzene, toluene, and xylenes as desired products, and hydrogen as a valuable by-product [1]. It was suggested that the original Mo⁶⁺ ions in the zeolite are reduced and carbided to Mo₂C during the initial induction period [2]. The methane activation occurs on the Mo₂C sites forming ethene then, the oligomerisation of ethene takes place on acid sites producing benzene. The aim of the present work was to perform an in-depth investigation of the methane aromatisation kinetics and develop fundamental model to describe the dynamic reaction kinetics.

The mass balances of all species at the axial position in the reactor are obtained using a set of differential algebraic equations. The dynamic behaviour is governed by the generation of active Mo₂C species from methane, as shown below.

\[ 3\text{CH}_4 + 2\text{MoO}_2 \rightarrow \text{Mo}_2\text{C} + 2\text{CO} + \text{O}_2 + 6\text{H}_2 \quad r_1 = k_1\text{C}_{\text{MoO}_2}\text{P}_{\text{CH}_4} \tag{1} \]

Rival models have been developed and tested against an experimental data set consisting of 16 measurements. The methane aromatisation was carried out over 5.3 wt.%Mo/MCM-22 (Si/Al = 15.5), at atmospheric pressure, in the temperature range of 873 and 973 K, with a space time between 35 to 180 s.kg⁻¹mol⁻¹, in a quartz tube fixed-bed reactor.

The major experimentally observed trends are adequately captured by the model. Figure 1 shows how the dynamic model captures the decreasing amounts of produced CO which is directly related to the generation of active Mo₂C species (Eq. 1). The correspondingly increasing benzene yield is accurately predicted from the start of the reaction till 2 h on stream. The slight over-estimation in benzene yield at time higher than 2 h on stream is related to the absence of a deactivation mechanism in the employed model.

In conclusion, the activation of MoO₂ to Mo₂C is an essential reaction for methane aromatisation. Methane is dimerised into ethene on active Mo₂C then, oligomerisation of ethene takes place on acid sites forming benzene.

REFERENCES