



Relation between hydrocarbon selectivity and cobalt particle size for alumina supported cobalt Fischer–Tropsch catalysts

Shreyas Rane^{a,c}, Øyvind Borg^b, Erling Rytter^{a,b}, Anders Holmen^{a,*}

^a Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

^b Statoil R&D, Research Centre, Posttuttak, NO-7005 Trondheim, Norway

^c Trøndelag Forskning og Utvikling (TFOU), Box 2501, NO-7229 Steinkjer, Norway

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ABSTRACT

The relation between hydrocarbon selectivity and cobalt particle size was studied using different alumina supports. Alumina phases, i.e. δ -, θ - and α -Al₂O₃ were produced from a small and a medium pore γ -Al₂O₃ by heat treatment. All catalysts were prepared by incipient wetness impregnation resulting in a cobalt loading of 12, 20 and 30 wt.% cobalt. The catalysts were tested in a fixed bed reactor at 20 bar, 483 K and H₂/CO = 2.1. The relation between methane, olefin and C₅₊ selectivities was studied for 2–14 nm cobalt particles supported on δ - and θ -Al₂O₃ supports prepared from the two different γ -Al₂O₃. The C₅₊ selectivity increases with increasing Co particle size for particles less than 8–9 nm where the selectivity goes through a maximum. The C₅₊ selectivity decreases for larger Co particles and then seems to approach a constant value independent of the alumina phase and pore size. The lowest CH₄ selectivity and the highest olefin to paraffin ratio were obtained at maximum C₅₊ selectivity.

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1. Introduction

Fischer–Tropsch synthesis is a key reaction for converting natural gas, coal or biomass to liquid fuels. Supported cobalt catalysts are preferred when the synthesis gas is derived from natural gas due to their high activity and selectivity to linear paraffins, low water–gas shift activity and relatively high resistance towards deactivation. In order to maximize the exposure of cobalt to reactants, the metal is normally dispersed on a high surface area support. The impact of the support material and the cobalt dispersion on the catalytic performance is still not well understood and is a matter of debate.

Previous studies have shown that for alumina supported Co catalysts the selectivity of higher hydrocarbons (C₅₊) depends on the alumina and on the Co particle size [1,2]. For a constant Co metal particle size of 8–10 nm, it has been shown that for different alumina phases the C₅₊ selectivity follows the order: Co/ α -Al₂O₃ > Co/ δ -Al₂O₃ > Co/ θ -Al₂O₃ > Co/ γ -Al₂O₃ [1]. Medium pore catalysts gave higher C₅₊ selectivity as compared to small pore catalysts. Previous results have also indicated that for increasing Co particle size the C₅₊ selectivity seems to go through a maximum at about 7–9 nm for Co supported on γ -Al₂O₃ [2]. No correlation was, however, observed in this case between the Co particle size and the cobalt site–time yield [2].

Alumina is known to interact strongly with cobalt and more so for γ -Al₂O₃ than for α -Al₂O₃ [1]. For model systems, i.e. Co supported on carbon nanofibers (CNFs), it has been shown that the turnover frequency increases for increasing Co particle size to about 6–8 nm and then remains constant [3,4]. The same relationship was also observed for the C₅₊ selectivity, it increased with increasing Co particle size for particle sizes less than about 10 nm and then leveled out [5]. The above results for Co/CNF catalysts were discussed in terms of variations in surface coverage and residence time of surface intermediates leading to products [4].

The pore size is also an important parameter and studies have shown that medium pore γ -Al₂O₃ (pore size 12.6–44.5 nm) gave higher C₅₊ selectivity than small pore γ -Al₂O₃ (pore size 9.7–12.6 nm) provided that the Co particle size was constant. Other alumina phases (i.e., δ -, θ - and α -Al₂O₃) prepared from a medium (MP) and a small (SP) pore γ -Al₂O₃, showed the same behavior for Co particles of about 8–9 nm [1].

The objective of the present work was to study the relation between the C₅₊ selectivity and the Co metal particle size for the alumina phases δ -, θ - and α -Al₂O₃. An important part of the work has been to prepare catalysts with defined particle sizes supported on the different aluminas.

2. Experimental

2.1. Catalyst preparation

Two Sasol Puralox SSCa γ -Al₂O₃ samples, as received, were calcined at 1023 K. The samples were heated from ambient to 1023 K

* Corresponding author. Tel.: +47 73594151; fax: +47 73595047.

E-mail address: anders.holmen@chemeng.ntnu.no (A. Holmen).