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Mn promoted Co catalysts for Fischer-Tropsch production of light olefins – An experimental and theoretical study

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ABSTRACT

Three different CoMn/γ-Al_2O_3 catalysts were prepared by the incipient wetness impregnation route and compared to a Co/γ-Al_2O_3 catalyst. The effect of co-impregnation vs. sequential impregnation as well as the order of component addition was investigated. All catalysts were characterised by TPR, H_2-chemisorption, XRD and XPS and their activity and selectivity in the Fischer-Tropsch reaction was investigated. Complementary, self-consistent DFT calculations were performed to further address the observed promotion effects. All Mn promoted catalysts displayed heightened intrinsic activity, heightened selectivity to light olefins and C_{5+} species and lowered selectivity to CH_4 compared to Co. The promotion effects on selectivity and intrinsic activity were found to be independent on catalyst preparation method. The catalysts undergo a restructuring during operation, in which an excess of Mn saturates the catalytically relevant sites causing the similar behaviour. The Co-specific activity differed between the Mn promoted catalysts. This was attributed to varying degrees of Mn incorporation in the Co_3O_4 particles, causing different degrees of reduction limiting the available metallic Co surface area. The DFT calculations suggested that the binding energy for all investigated species increases on Co in the presence of Mn, facilitating CO dissociation which can explain the higher intrinsic activity. The affected selectivities for olefins, C_{5+} and CH_4 can all be attributed to an inhibited hydrogenation activity demonstrated by the increased barriers for CH_3 and CH_4 formation.

1. Introduction

Light olefins are among the most important chemical intermediates in the production of plastics, fibres and other organic chemicals. In 2011, the production of ethylene and propylene was 127 and 70 MT respectively, and the demand for both is projected to grow by 3.3 and 4.4%/year, respectively [1]. Ethylene is produced mainly by steam cracking of natural gas and naphtha which carries a high capital investment cost. Propylene is primarily a by-product in ethylene plants and in fluid catalytic crackers used for gasoline production. Due to the increasing demand of propylene and a shifted focus towards higher ethylene selectivity in steam crackers, the gap between conventional propylene supply and demand is expected to grow. Consequently, there has been a growing interest towards alternative, on-purpose production of light olefins in both industry and academia [2].

Among the proposed alternative routes, the Fischer-Tropsch synthesis (FTS) process presents a potential option. As a synthesis gas process, it is highly flexible with respect to its source of carbon (coal, biomass, natural gas) in comparison to e.g. propane dehydrogenation. Compared to the other proposed syngas processes, (methanol to olefins, lower alcohol dehydration, cracking of FTS liquids) it presents a potential advantage as it is the only process that can convert syngas to olefins in one reaction step.

The FTS process produces hydrocarbons from synthesis gas ($CO + H_2$) by a chain-growth polymerisation process. Depending on the synthesis gas precursor, impurities and H_2/CO ratio the preferred catalysts are either Fe or Co based. Conventionally, the hydrocarbons produced can be used as chemical intermediates or high purity fuels. More recently, it has been shown that high selectivity to light olefins is obtainable through tailored catalysts and specialised operation conditions. Fe based catalysts are the most frequently employed for this purpose, with high selectivity towards light olefins reported coupled with a low selectivity towards methane [2,3]. Cobalt catalysts are known for their high activity, may also provide high olefin selectivities, and is the preferred choice for synthesis gas with high H_2:CO ratio [4–7].

FTS products are to a large extent produced in accordance with the Anderson–Schulz–Flory (ASF) distribution. To increase the

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yield of light products, a higher temperature and lower pressure than conventional is applied. This has the drawback of also increasing the selectivity towards methane, which is the least desirable product in the FTS product range. Manganese is in both Co and Fe based FTS a frequently reported promoter for increasing olefin selectivity [2]. The experimental investigations into the promotion effect of Mn have been significant. As a general trend, in addition to increasing the olefin selectivity, Mn is in Co based FTS catalysts reported as to increase catalyst activity, Co dispersion, C_{5+} selectivity and to decrease CH_4 selectivity [8]. However, with different support materials, pre-treatments, Mn:Co ratios and preparation methods, reported results are also ranging from Mn having no discernible effects [9] to activity effects only [10] and to negative effects [4,11]. From the experimental data available, it is clear that the promotion effect of Mn is not fully understood, and strongly depends on the state and location of Mn with respect to Co, which again depends on preparation method, support etc.

While the experimental efforts to investigate the Co-Mn catalyst system have been substantial, the efforts from a theoretical point of view are limited. While there have been a significant number of theoretical investigations into FTS [12–14], the majority of the works focus on the much debated reaction mechanism [15–17], geometric effects [18–20] and the complicated selectivity scheme [21–24]. A few works exist on promotion with noble metals [25,26] and boron [27]. Cheng et al. [28] investigated transition metal promotion, Mn included, and found only late transition metals to be likely olefin promoters, disagreeing with the experimental work. The need for an investigation on the promotion effect of Mn combining experimental and theoretical methods seems evident.

In the present work, the effects of Mn on Co based FTO are investigated by a combination of experimental and theoretical methods in order to further elucidate the nature of Mn promotion. In the experimental part, Mn promoted Co/Al_2O_3 catalysts are prepared, characterised and tested at industrially relevant FTS conditions favouring light olefin formation. The effect of preparation procedure, i.e. co-impregnation vs. sequential impregnation, is investigated as well as the order of component addition.

DFT calculations are performed where adsorption energies of relevant species as well as elementary reaction barriers are evaluated on clean and Mn modified Co(1 1 1) model surfaces. While *in situ* studies have found the operating state of Mn to be MnO [29], this work employs a simplified model where $Mn^{(0)}$ is considered in a surface alloy with Co.

2. Methods

2.1. Experimental

2.1.1. Catalyst synthesis

All catalysts investigated were prepared by the incipient wetness impregnation (IWI) method using $Co(NO_3)_2{\cdot}6H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$ as precursors and γ-Al_2O_3 ($S_{BET} = 175\ m^2/g$) as the support material. The catalysts were dried overnight under reduced pressure and calcined in flowing air at 300 °C (2 °C/min) for 16 h. Prior to further characterisation and testing, all catalysts were sieved to a particle size of 53–90 μm.

Three $CoMn/Al_2O_3$ catalysts were prepared in addition to Co/Al_2O_3 to serve as the Co reference. Of the three CoMn catalysts, one was prepared in one step, hereafter referred to as Co + Mn, and two were prepared in two steps, one with Co followed by Mn (Co → Mn) and one with Mn followed by Co (Mn → Co). For all catalysts the Co loading was kept constant at 15% with respect to $Co + Al_2O_3$ and the Mn:Co ratio was kept at 1:4 w/w. For the sequentially impregnated catalysts, it was assumed that Co and Mn were present as Co_3O_4 and MnO_2 respectively after the first step [30]. For characterisation purposes, a fifth 3.75% Mn/Al_2O_3 sample without Co was also prepared.

2.1.2. Temperature programmed reduction

Temperature Programmed Reduction (TPR) was performed using an Altamira Instruments BenchCAT^{TM} Hybrid instrument. The sample (0.15 g) was inserted into a 4 mm i.d. quartz U-tube reactor between two plugs of quartz wool. Pre-treatment consisted of heating in Ar flow (50 mL/min) to 300 °C (10 °C/min) for 30 min. Reduction took place in 50 mL/min 10% H_2/Ar flow, heating from ambient temperature to 800 °C (10 °C/min). The effluent gas was passed through a Drierite^{TM} filled trap, to extract moisture before being passed over a thermal conductivity detector (TCD). To estimate the degree of reduction (DoR), the catalysts were reduced *in situ* by heating to 350 °C (1 °C/min) for 16 h in 25/25 mL/min H_2/Ar flow. The reduced catalysts were then cooled to 50 °C before being subjected to the same TPR procedure described above. The TPR profiles for the pre-reduced and calcined catalysts were integrated and compared. It was assumed that full $Co_3O_4 \rightarrow Co^{(0)}$ and $MnO_2 \rightarrow MnO$ reduction took place in the calcined samples and that only $CoO \rightarrow Co^{(0)}$ reduction took place in the pre-reduced samples.

2.1.3. H_2-chemisorption

Volumetric H_2-chemisorption was performed using a Micromeritics ASAP 2020C instrument. The sample (0.3 g) was placed into a 9 mm i.d. quartz u-tube reactor between two plugs of quartz wool. The sample was reduced *in situ* in H_2 flow for 16 h at 350 °C (1 °C/min) before being cooled under vacuum. Chemisorption data was gathered at 40 °C at 15–507 mmHg H_2. The data between 100 and 507 mmHg were used to extrapolate and estimate the monolayer. For estimation of the dispersion, it was assumed that H_2 chemisorbs dissociatively and one H atom occupies one Co surface atom.

2.1.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD instrument using a monochromated Al Kα X-ray source. The samples were mounted by pressing onto carbon tape. The equipment base pressure was in the range of $2\text{–}5{\cdot}10^{-9}$ Torr during acquisition. Measurements were done with take-off angle normal to the surface and individual core level spectra were recorded at a pass energy of 40 eV. Low energy electrons were used for charge compensation. Reported binding energies are referenced to the C 1s peak of adventitious carbon at 284.8 eV, resulting in an Al 2p contribution of Al_2O_3 at around 74.3 eV.

2.1.5. X-ray diffraction

X-ray diffraction experiments (XRD) were performed at ambient temperature on a Bruker D8 Advance DaVinci X-ray diffractometer using a Cu Kα X-ray source. Co_3O_4 lattice constants and average particle sizes were obtained using the Pawley method [31] of full pattern fitting in the Topas 5.0 software [32]. A separate scan and fit of the γ-Al_2O_3 pattern was obtained and used in the refinement of the supported catalysts. Refinements were obtained with R_{wp} values of approx. 4.2%. Mn species were excluded from the refinement due to a very weak signal. The Co particle size was corrected for contraction during reduction by $d_{Co}^{(0)} = 0.75{\cdot}d_{Co3O4}$ [33] and Co dispersion was then estimated by assuming spherical, uniform Co particles with site density of 14.6 atoms/nm^2 and using the formula $D = 96/d$, where D is Co dispersion (%) and d (nm) is average particle diameter [33].

2.1.6. Fischer-Tropsch synthesis

Fischer-Tropsch Synthesis was performed in a 10 mm i.d. tubular stainless steel fixed bed reactor at 240–270 °C, 5 bara and