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High-throughput experimentation in syngas based research

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ABSTRACT

The potential of high-throughput technology in studying catalysts and processes in syngas R&D was demonstrated through a series of Fischer–Tropsch studies. The results show that the exothermal nature of the processes is an important consideration in catalyst evaluations. In order to discriminate on the intrinsic catalytic properties, small reactor diameters are preferred. A three-month life-time study, performed on a 64-reactor high-throughput nanoflow unit, showed a reactor-to-reactor reproducibility within 95% for catalyst activity. The ageing behavior as function of catalyst composition, GHSV and temperature variation could be studied simultaneously, saving over 98% in experimental time compared to conventional 1-reactor systems. The consistent correlation between gas and liquid phase selectivity allows for measuring just the gas phase, simplifying reactor set up and reducing operational efforts, at least when no carbon chain-length dependent selectivity is expected. A study into preparation variables for Ru catalysts showed that silica supports promote the formation of ethanol. This is possibly formed by hydration of ethylene catalyzed by the acidic silica support.

1. Introduction

Continuing high oil prices in combination with the need to develop more sustainable green products has boosted the interest in fuels and chemical products made from natural gas, coal and biomass. Most of the routes involve the production of syngas and subsequent catalytic conversion to fuels or chemicals. The renewed interest in syngas-based products has resulted in extensive R&D activities in this field. In such a competitive area, it is important to be more effective and innovate faster than the competition. High-throughput experimentation [1–4] can help in this race. Its potential in the field of syngas R&D will be demonstrated through a series of Fischer–Tropsch examples. The challenges associated with Fischer–Tropsch include: a large variety of products, the need for gas–liquid separation at elevated temperatures, the formation of waxes and the risk of plugging reactors.

Reducing the scale of experiments has a number of advantages mostly in terms of costs and space, as discussed by Sie [5]. Lower cost of construction of equipment, less consumption of materials, less waste to be disposed off and reduced demands on laboratory infrastructure all lead to significant cost savings. In addition, the intrinsic safety is enhanced as is illustrated by the maximum hazard that may occur in case of a reactor malfunction. In a typical FT experiment, performed on a 64-channel reactor, the low flow rate would only sustain a flame the size of a candle and an emission of CO would be less than the amount of CO given up by a burning cigarette. In the event of an explosion the detonating power would be comparable with that of a small firecracker [5].

In addition, the absence of significant temperature gradients makes the small-diameter reactor an excellent tool for kinetic studies, even for highly exothermic reactions [5].

The most common application of high-throughput technology is catalyst screening (“catalyst discovery”) although as the technology has developed it has also proven suitable for more demanding studies such as process optimization, kinetic studies, mechanistic modeling and lifetime/poisoning studies. In this paper the potential and issues of high-throughput technology will be demonstrated through a series of Fischer–Tropsch experiments using both Co and Ru catalysts.

2. Materials and methods

High-throughput experiments for gas-to-liquid processes were performed in 64 fixed-bed tubular reactors operated in parallel and in co-current downstream mode (Fig. 1). The so-called 3rd generation Nanoflow consists of four independent temperature controlled reactor blocks of 16 reactors. The tubular reactors had internal diameters of 1.0, 1.5 or 2.0 mm and were typically used for testing catalyst masses of between 25 and 200 mg. The reactors can operate at a maximum temperature of 550 °C, a maximum pressure of 100 bar and GHSVs of up to 100,000 h^{-1}. To enable investigation and optimization of process conditions the pressure, temperature and flow rates were systematically varied during the run.

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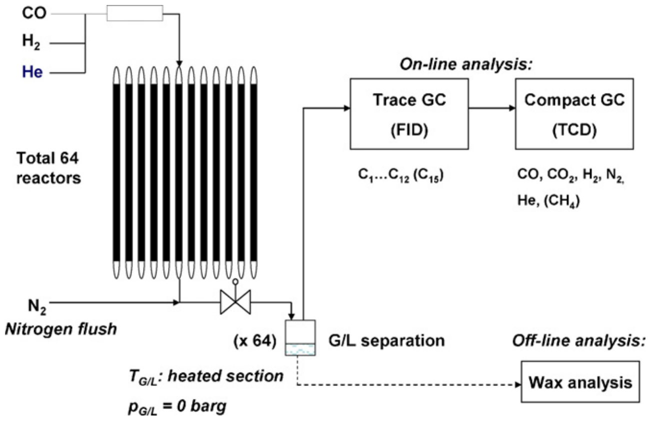

Fig. 1. Reactor set-up for high-throughput testing.

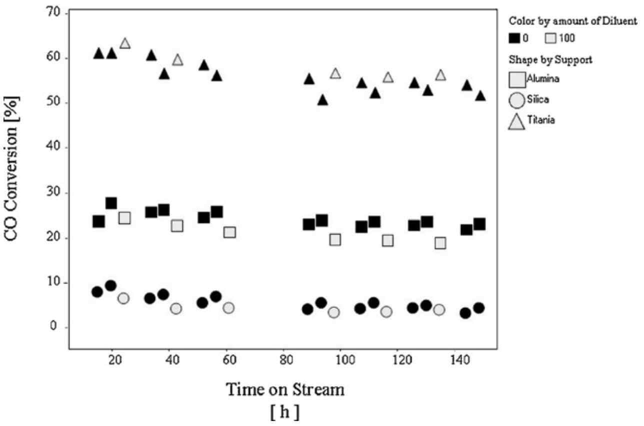

Fig. 2. Influence of catalyst bed (100 μl) dilution with or without α-alumina (100 μl) for 1 wt% Ru on silica, alumina and titania.

The reactor holder is of a special design allowing dilution of the reactor effluent with liquid or gas thus preventing condensation of products and/or downstream plugging [6].

After reaction the reactor effluent is depressurized to atmospheric pressure. In order to achieve this, a gas–liquid separator was employed for each reactor allowing evaporation of the light hydrocarbons from the main product stream. These lights could then be transported, in the gas phase, towards the GC. A continuous drain was installed to allow a low liquid level in the gas liquid separator thus minimizing carry over effect between reactor effluent streams. The separator was operated at 150 °C with a slight overpressure to aid gas transport to the GC. One of the 64 reactors is selected for on-line GC analysis by use of a selector valve. The on-line analysis performed used a two GC set-up able to measure both the permanent gasses and hydrocarbons up to C15. The heavy materials were analyzed off-line. To protect the GC from heavy waxes, each individual reactor was equipped with a downstream catch-pot.

Catalysts were prepared by incipient wetness impregnation of the appropriate support using the corresponding aqueous solutions of $RuNO(NO_3)_3$, $Ni(NO_3)_{2-x}$ H_2O or $Pd(NO_3)_2$ (Heraeus). Ruthenium loadings were 0.5, 1 or 2 wt%. Pd and Ni levels were 0.5 wt% always in combination with 0.5 wt% Ru. Extruded supports used were SiO_2 (Norpro, SA 166 m^2/g, PV 0.72 ml/g, 5000 mg/kg Na, 300 mg/kg Fe), Al_2O_3 (Norpro, SA 95 m^2/g, PV 0.52 ml/g) and TiO_2 (Norpro, SA 42 m^2/g, PV 0.37 ml/g). Impregnated materials were dried at 120 °C for 16 h after impregnation, and calcined for 3 h at 450 °C. Prior to catalytic testing, the Ru catalysts were reduced in situ using 5% H_2 in N_2 at 200 °C for 1 h at GHSV 6000 h^{-1}. The catalysts obtained were crushed and sieved to fractions of on average 75 (50–100) and 500 (400–600) μm particle size. The cobalt-on-alumina catalysts were proprietary catalysts differing in nature and level of promoter.

Ru catalysts were tested at a GHSV of 12,000 h^{-1} using $H_2/CO = 2$ with 2% He as internal standard. The conditions for the lifetime test for Co catalysts were chosen to target a constant CO conversion for the most active catalyst by adaptation of the feed flow, starting at a GHSV of 17,000 h^{-1} after which the GHSV was reduced over time to 13,000 h^{-1} using a H_2/CO ratio of 1.5, with 10% Argon as internal standard.

3. Temperature gradients and mass-transfer limitations

In testing and evaluation of catalysts it is important that all materials are tested under the same experimental conditions. Using parallel high-throughput catalyst evaluation methodologies allows operation of up to 64 reactors under constant feed, pressure and flow conditions, thus enabling proper evaluation of the intrinsic properties of various catalytic materials. In classical catalysis research, catalysts are often tested at identical conversion levels by adjusting process parameters. Due to the high degree of parallelization in high-throughput testing systems, adjustment of process parameters per reactor is not feasible and thus catalysts are tested under the same conditions hence a wide range of activities may occur. The impact of this is that a fair comparison can only be made if the catalytic results are not influenced by non-isothermal heat effects. Even for moderately exothermal reactions like hydrodesulphurization, significant temperature gradients may already exist under normal test conditions for conventional 1-reactor systems with a large diameter (>0.5–1 cm) [7,8]. Syngas conversions are typically highly exothermic (ΔH 170 kJ/mole CO) and, therefore, temperature gradients should be of a concern in the evaluation of the intrinsic properties of catalysts. In addition, for highly exothermic reactions with relatively low activation energies (like Fischer–Tropsch) with a typical E_{act} close to 100 kJ/mole, a small temperature rise due to non-isothermal reaction conditions, may lead to a significant increase in activity observed. Moulijn et al. [7] have recommended minimizing temperature gradients by using small reactor diameters, low conversion levels and dilution of the bed with inert particles with good heat conductivity (SiC).

To establish the presence or absence of non-isothermal behavior in the Nanoflow unit, three 1-wt% Ru catalysts (100 μl catalyst bed volume) were tested both diluted and undiluted with α-alumina (100 μl) (reactors 2 mm I.D.). The results are shown in Fig. 2. No significant difference between diluted and undiluted catalyst beds could be observed, this was true even at high CO conversion levels of 60% or more (GHSV of 12000 h^{-1}). From these data it could be concluded that micro reactors with an inner diameter of 2 mm are essentially isothermal.

Heat transfer effects were studied for Co catalysts at different conversion levels by measuring temperature with a thermocouple in the catalyst bed for reactors of 1.0, 1.5 and 2 mm internal diameter. At high productivity levels (150 mMol CO/gcat/h) a maximum temperature rise of 3 °C in the bed was observed, this corresponds to an increased conversion of about 15% for the 2 mm reactor. For the smaller diameter reactors no temperature and consequent conversion rise were found. In performing experimentation on small scale reactors one should thus be aware that temperature rise can be an issue and that, if needed, smaller reactor diameters should be applied to assess intrinsic catalyst properties.

A further concern is the presence of mass-transfer limitations. Particularly in the case of Fischer–Tropsch chemistry, the heavy waxes formed can cause severe internal mass diffusion limitations inside the catalyst. A generally accepted method for determining if internal mass transfer limitations exist is to determine catalytic activity for different particle sizes. As discussed above, in high-throughput catalysts testing the size of the reactors is often limited

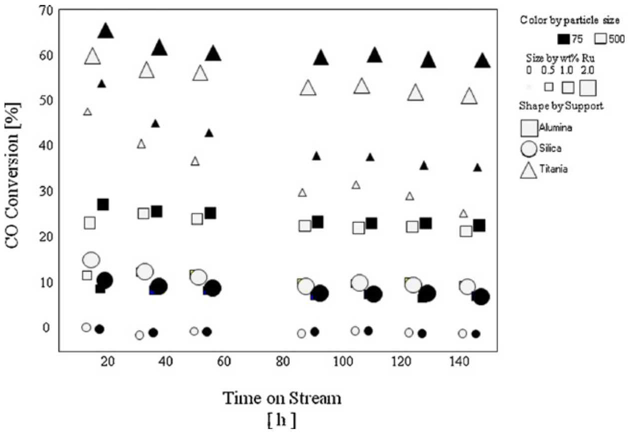

Fig. 3. Influence of catalyst particle size on CO conversion for single-metal Ru on three different supports.

and thus the particle size range that can be tested is often restricted. However, in our Nanoflow system particles up to 2000 μm, *i.e.* even extrudates, can be evaluated with high accuracy.

In this study the Ru catalysts were evaluated at two average particle sizes, 75 and 500 μm. The results are shown in Fig. 3 and indicate that there was a significant effect of particle size and thus internal mass transfer only in the case of the ruthenium-on-titania catalysts which were significantly more active than the other catalysts tested.

4. Cobalt catalysts

A series of Co-on-alumina catalysts were tested in lifetime studies with a continuous time-on-stream of over 2000 h. In this study the mass balance for 64 reactors showed a band width smaller than 10%. The relative standard deviation for the CO conversion was 4%.

Fig. 4 shows the CO-conversion over time while Fig. 5 shows the required CO feed flow to maintain a stable conversion. After 2000 h a regeneration step was performed resulting in an increased conversion. Overall using the Nanoflow parallel reactor technology allowed a 3-month lifetime study for 64 catalysts which would otherwise have taken 16 years on a single reactor thus saving over 98% in experimental time compared to conventional 1-reactor systems.

Moreover, in a similar study wax was collected in 64 catch pots, one for each reactor. The selectivity information from the liquid/wax phase for C20 to C52 showed the same trends and rankings as that from the gas phase (C4 to C12, Fig. 6). Hence, these observations seem to justify screening catalysts just by analyzing the gas phase, thus simplifying the set-up and limit operational efforts. However, Fischer–Tropsch catalysts may display a carbon-dependent alpha value (change of slope in the Anderson–Schulz–Flory plot), and for in depth selectivity studies the use of catch pots to collect wax still is advised.

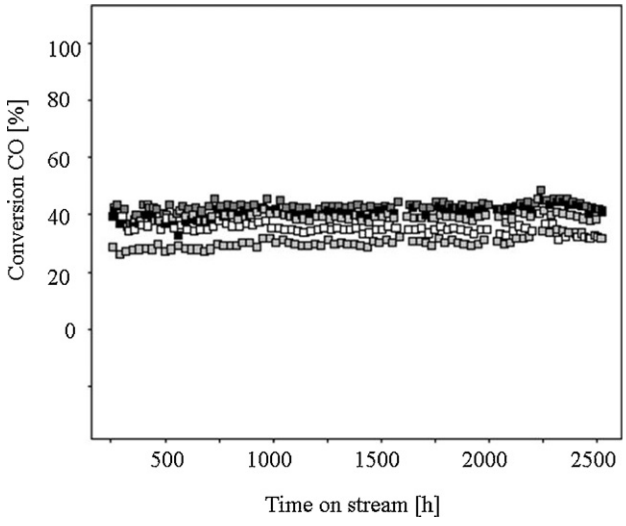

Fig. 4. CO conversion over time for Co-on-alumina catalysts.

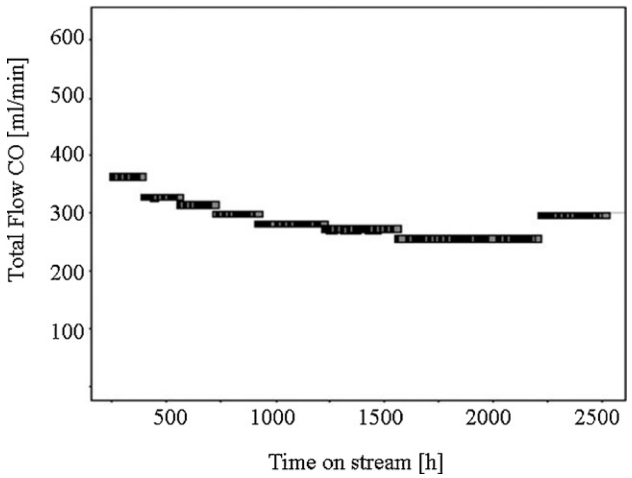

Fig. 5. CO flow adapted to maintain constant CO conversion for cobalt-on-alumina catalysts.

5. Ruthenium catalysts

In a case study with Ru catalysts the support (silica, alumina, titania), metal loading, catalyst particle size, reactor temperature and co-metals (Ni, Pd, none), were all varied within one experimental run. The entire testing programme was completed within one week.

Ni and Pd added to the Ru catalyst led to significantly lower activities than those observed for single-metal Ru catalysts, with Pd reducing activity to almost zero for all supports. In addition, at the low CO conversion levels, methane formation was high (Fig. 7). It was already clear from Figs. 2 and 3 that the nature of the support had a significant effect on catalyst activity. However, it was unclear if this effect was only on overall activity or whether it also influenced the catalytic behavior. In this respect the large number of conditions at which the catalysts were tested allowed the representation of the experimental results as shown in Fig. 8. The

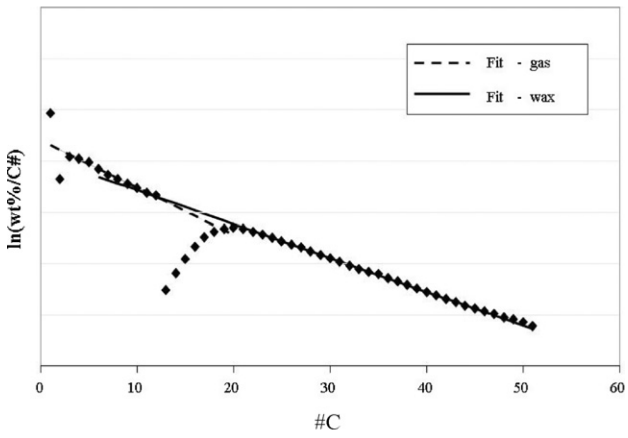

Fig. 6. Anderson–Schulz–Flory distribution for gas and liquid phase products for a 20% cobalt-on-alumina catalyst.

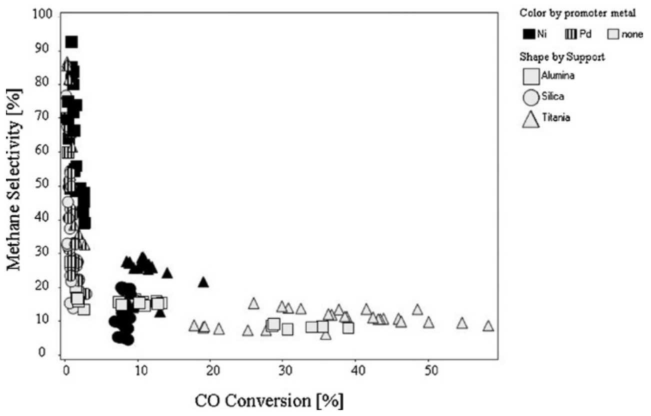

Fig. 7. Influence of Ni and Pd co-metals on the methane selectivity for Ru catalysts on three different supports.

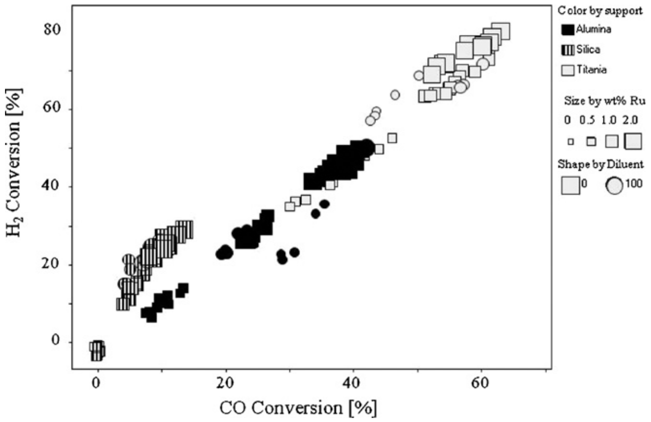

Fig. 8. Relation between H_2 and CO conversion for Ru catalysts on three supports.

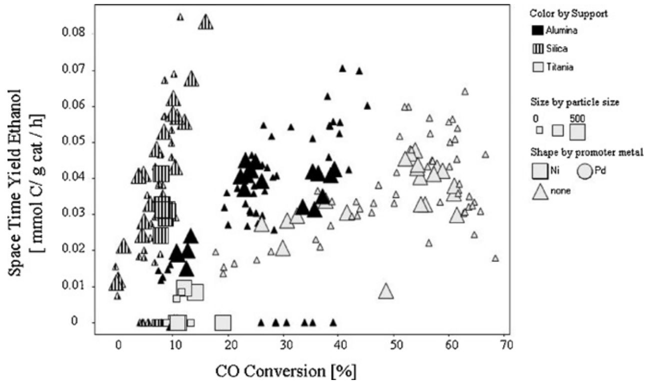

Fig. 9. Influence of support on the formation of ethanol for 1 wt% Ru catalysts.

Ru-on-Al_2O_3 and the Ru-on-TiO_2 both appear to have an identical slope and thus point to identical catalytic behavior. The Ru-on-SiO_2 catalyst clearly deviates from the other two by consuming relatively more H_2 at identical CO conversion. Indeed, the alkane/alkene ratio for this catalyst (0.5–0.6 molar ratio at 10% CO conversion) is higher than that observed for the alumina based catalysts (0.45–0.5 molar ratio at 10% CO conversion). It was also observed that, albeit at low levels, the Ru-on-silica catalyst produced significantly more ethanol than the catalysts based on alumina or titania (Fig. 9). Possibly the acidic groups in the silica support promote the hydration of ethylene. Alternatively, contaminants like Fe or Na (5000 mg/kg Na and 300 mg/kg Fe were present in the silica) may have catalyzed the reaction. From silica-based Rh catalysts it is known that low levels of support impurities like Na and Fe may promote the formation of alcohols from syngas [9].

6. Discussion

Overall it can be concluded that the high-throughput experimentation methods applied are suited to study syngas conversion processes. A life-time study of three months on a Fischer–Tropsch process has shown the reliability of the reactor systems with a reactor-to-reactor reproducibility within 95% for catalyst activity. In fact high-throughput experimentation is even more effective for mapping catalyst lifetime and process conditions than for more exploratory applications as a greater number of reactors are operating under “useful” conditions. Moreover, the feed, the operator and most other conditions remain identical for all reactors, while for consecutive studies using single reactors, feed, operator and/or process conditions may change between runs.

The consistent results for gas-phase and liquid-phase measured selectivity indicate that for those cases where no carbon chain length dependent selectivity is expected just measuring the gas phase suffices for measuring selectivity thus simplifying reactor set up. The results show that the exothermal nature of the processes is important to consider when selecting both reaction conditions and reactor configuration—ideally small reactor diameters should be used. After establishing the near-isothermal behavior of the reactors used, catalysts could be compared under identical conditions despite the highly exothermic nature of the reaction and high CO conversion levels applied. Therefore, intrinsic catalytic effects based on composition or variations in preparation method could be studied thus allowing for a true comparison of effects of catalyst compositions such as shown in the promoter and support study.

7. Conclusions

High-throughput experimentation now has fully matured into a powerful tool. Syngas conversion into a variety of products can be studied in great detail and with great precision. The most common application will be fast screening and optimization of catalyst and/or process conditions, but in addition high-throughput experimentation can be used in problems where traditional methods of testing are unthinkable because they would require too many experiments and time.

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