A Disruptive Innovation for Upgrading Methane to C3 Commodity Chemicals:
SUPPLEMENTARY INFORMATION

Technical challenges faced by the C123 European consortium

Alvaro Amieiro Fonseca*, Johnson Matthey, Blounts Court, Sonning Common, Reading, RG4 9NH, UK
Richard H. Heyn, Morten Frøseth, SINTEF Industry, PO Box 124 Blindern, 0314, Oslo, Norway
Joris W. Thybaut, Jeroen Poissonnier, Ghent University, Laboratory for Chemical Technology, Technologiepark-Zwijnaarde 125, B-9052, Gent, Belgium
Andreas Meiswinkel, Hans-Jörg Zander, Linde GmbH, Dr.-Carl-von-Linde-Str. 6–14, 82049 Pullach, Germany
Jérôme Canivet, The University of Lyon, Université Claude Bernard Lyon 1, National Centre for Scientific Research (CNRS), Institute for Researches on Catalysis and Environment of Lyon (IRCELYON)- UMR 5256, 2 Avenue Albert Einstein, 69626 Villeurbanne cedex, France

*Email: Alvaro.Amieiro@matthey.com

1 Hydroformylation catalyst screening

Three different experimental systems were used for HF catalyst testing

1. A Baskerville 10 parallel reactor autoclave. Each micro vessel has a 25 ml volume and operates under isothermal isobaric conditions. Experiments were performed using a 1:1:1 H₂:CO:C₂H₄ feed, 20 bar dynamic pressure and 100 °C for a period around 1 h as standard test. The magnetic stirrer was set at 1000 rpm to guarantee vigorous mixing. Typical loadings were 5 mg catalyst in 5 ml toluene with 1-20 molar equivalent phosphine added.

2. A 50 mL high-pressure reactor from Asynt. The reactor is equipped with gas in- and outlets, and a manometer to monitor the pressure during the reaction. A glass liner was used that reduced the volume of the autoclave to 47 mL. All reactants and solvents were mixed in a glove box and added to the autoclave, prior to connecting the autoclave to the gas lines. As standard protocol, the autoclave was pressurized with the diluent gas, either argon (Ar) or CO₂, heated to the reaction temperature and then the CO:C₂H₄:H₂ gas feed was added.

3. High throughput experiments. These were conducted in an in-house constructed HT reactor featuring four rows of six reactor wells; each row of reactors has a common gas feed. All wells were closed during the reaction to avoid well-to-well contamination. In a glove box, stock solutions of catalysts and phosphines were added by autopipette to each well according to the experimental design. Three steel balls (5 mm diameter) were added to each well to ensure proper mixing. The set of 24 reactor wells was then attached to the gas inlet portion of the reactor under a flow of argon and pressured with Ar to 5 bar. Feed gas was then added sequentially to each reactor, either at room temperature or at the reaction temperature of 100 °C. Reactions were run for 2 hours from addition of reactant gas. Mixing was accomplished with the help of a variable speed vortex (shaker). At the end of the reaction, the reactor was cooled by placing it in an ice bath. Approximately 15 min were required to cool the reactor sufficiently before the pressure could be released. The pressure was carefully released overnight to a holding container.
Each HT experimental combination was duplicated within each HT experiment, i.e., the maximum number of unique combinations within any single HT experiment was 12. Analytical and reproducibility variations within and between HT experiments were on the order of 5-10%. Much more variation was observed at high static pressures (high C$_2$H$_4$/Rh ratios), due to the high reactivity of the investigated systems.

2 Product analyses

Product analyses were performed either by GC or $^1$H NMR spectroscopy. The GC analyses were conducted on a Teledyne Tekmar HT3 HeadSpace analyzer coupled to an Agilent 6890 gas chromatograph, using a HP-PLOT U GC Column (30 m x 0.320 mm x 10 µm) and flame ionization detector. Samples were subjected to a 100 °C, 5-minute temperature profile. For the HT experiments, analyses were conducted on two 10 µl samples withdrawn from the reactor wells at the end of reaction. For the batch reactions, analyses were conducted on three 10 µl samples.

$^1$H NMR spectra were recorded on a Bruker UltraShield 400 spectrometer at a resonance frequency of 400 MHz.