Development of a magnetometer for in-situ catalyst characterization

Michael Claeys[1]*, Simon Kelly[1], Eric van Steen[1], Jakobus Visagie[2], Jan van de Loosdrecht[2], Igor Krylov[3]
[1] *Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch, 7701, South Africa*
[2] *Sasol R&D, Sasolburg, 1947, South Africa*
[3] *Department of Physics, University of the Western Cape, Bellville, 7535, South Africa*
*michael.claeys@uct.ac.za

Introduction

High activity of supported metal catalysts is usually obtained by providing high metal surface area or small metal crystallites respectively. The stability of supported metal catalysts in Fischer-Tropsch synthesis can be negatively affected as deactivation can result, inter alia, from sintering and phase changes such as oxidation [1,2,3]. Characterization of such catalysts, in particular used ones, is notoriously difficult as exposure to air can cause dramatic changes of their physico-chemical properties. Moreover, they are often surrounded by a wax layer which can further complicate analysis by conventional techniques such as XRD and TEM characterization. Ultimately therefore in-situ characterization techniques of these catalysts are becoming crucially important in order to study the relation of catalyst changes and their performance.

This paper describes the development of an in-situ magnetometer which allows following effects of catalyst oxidation/reduction as well as sintering under fully realistic reaction conditions of temperature and pressure. Although originally developed for use in Fischer-Tropsch synthesis this novel instrument can be applied to investigate any ferro-magnetic matter in a controlled environment.

Materials and Methods

Ferromagnetic material such as metallic iron, cobalt and nickel becomes magnetized to a large extent when exposed to an external magnetic field. It usually shows the phenomenon of hysteresis with a limit of magnetization at high fields (saturation) and usually residual magnetization upon removal of an external field (remanence). The latter effect is restricted to crystallites of a certain critical size which depends on the particular material and temperature (e.g. for cobalt: ca. 12-15 nm at 300 K [4]). Crystallites smaller than this size show no remanence, i.e. superparamagnetic behavior, which can be described mathematically. These properties can be used to determine (a) the amount of metal present in a sample or degree of reduction respectively (from saturation magnetization), (b) the percentage of ferro-magnetic material (from remanence), which relates to large crystallites and may indicate effects of sintering, and (c) crystallite size distributions.

A Weiss extraction magnetometer has been designed and built in which catalysts can be tested in a fixed bed reactor at realistic conditions (T_{max}=500ºC, p_{max}=50 bar) while the magnetic properties can be monitored. A previously described in-situ magnetometer did not allow for testing at elevated pressures5. The signal is generated via low frequency movement of the sample/reactor within the homogenous magnetic field. Field strengths of up to 2 Tesla allow full magnetic saturation of typical catalyst samples. Details of our set-up including sample movement, its heating and the control of the instrument will be described in detail.

Results and Discussion

The set-up has been used to study temperature programmed reduction, temperature programmed oxidation as well as temporal changes of the degree of reduction (see figure 1) and the percentage of ferro-magnetic material of a cobalt catalyst while catalytic performance data were collected. Examples of this work will be discussed in the paper.

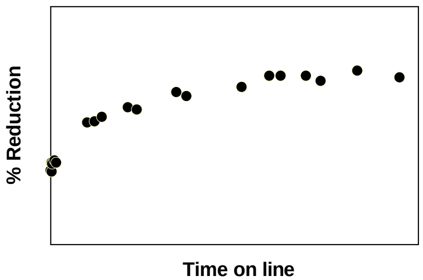

Figure 1. Temporal changes of degree of reduction of cobalt catalyst tested at commercial conditions.

Significance

The novel magnetometer provides a unique new tool for in-situ/operando characterization of ferromagnetic catalysts.

Acknowledgements

This project has been conducted in collaboration with Sasol Technology R&D and the financial support is greatly acknowledged.
s

References

1. Moulijn, J., van Diepen, A., Kapteijn, F., Appl. Catal. A: Gen. 212, 3 (2001).
2. van Steen, E., Claeys, M., Dry, M., van de Loosdrecht, J., Viljoen, E., Visagie, J.L., J. Phys. Chem. B 109,3575 (2005).
3. van de Loosdrecht, J., Balzhinimaev, B., Dalmon, J.A., Niemantsverdriet, J.W., Tsybulya, S.V., Saib, A.M., van Berge, P.J., Visagie, J.L., Catalysis Today 123, 293 (2007).
4. Dalmon, J.A., “Magnetic measurements and catalysis”, in “Catalysis characterization: Physical techniques for solid materials” (B. Imelik, J.C. Vedrine, Eds.) 1994, p. 585. Plenum Press, New York,
5. Chernavskii, P.A., Khodakov, A.Y., Pankina, G.V., Girardon, J.-S. , Quintet, E., Appl. Catal. A: Gen. 306, 108 (2006).