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In situ neutron diffraction under high pressure—Providing an insight into working catalysts

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ABSTRACT

In the present work the construction and application of a continuous flow cell is presented, from which neutron diffraction data could be obtained during catalytic reactions at high pressure. By coupling an online gas detection system, parallel structure and activity investigations of working catalysts under industrial relevant conditions are possible. The flow cell can be operated with different feed gases in a wide range from room temperature to 603 K. Pressures from ambient up to 6 MPa are applicable. An exchangeable sample positioning system makes the flow cell suitable for several different goniomter types on a variety of instrument beam lines. Complementary operational test measurements were carried out monitoring reduction of and methanol synthesis over a $Cu/ZnO/Al_2O_3$ catalyst at the high-flux powder diffraction beamline D1B at ILL and high-resolution diffraction beamline Echidna at ANSTO.

1. Introduction

Nowadays catalysts are considered as dynamic materials whose active centers can be formed or transformed due to the chemical potential of reactants or products under reaction conditions. If such changes are reversible, application of in situ methods is needed to study catalysts in their working state to gain a general understanding of structure–activity relationships. It is especially attractive to bridge the so-called 'pressure gap' and to go to pressure ranges beyond Ultra-High-Vacuum to ambient pressure regimes. Unfortunately, not many in situ techniques can be operated at high pressures above ca. 5 MPa and allow a direct observation of the working catalyst under realistic chemical potentials as are present in industrial reactors. It often remains questionable, if the properties of model catalysts studied at low pressure can be extrapolated to real catalysts under industrial reaction conditions. Due to their high penetration depth, neutrons allow application of complex sample environment as is needed to study commercial catalysts under industrial reaction conditions, e.g. elevated temperatures and high pressures (up to 6 MPa) under strongly reducing gaseous atmospheres like hydrogen/deuterium-rich synthesis gas. Furthermore neutron diffraction is a powerful tool to study structural and microstructural properties of a catalyst (phase identification, strain, particle size, alloy formation, phase transformations) in operation. A lot of technical effort was made by Turner et al. [1] and Walton et al. [2] to study catalysts or related materials under demanding reaction conditions; but still far away from typical industrial conditions. In this present contribution a reaction setup will be presented, which allows carrying out in situ neutron diffraction studies on various catalyst systems under industrial relevant synthesis conditions.

2. Apparatus design

Aim of the apparatus design was to build a safe reactor, which allows to collect structural data of a working catalyst under industrially relevant conditions with neutron diffraction and a parallel monitoring of the product gas stream by mass spectrometry to correlate structural and catalytic properties.

The apparatus consists of three basic components: The flow cell including the heated reactor body, the gas supply and the effluent gas analytics.

2.1. Flow cell and reactor body

The operation of a flow cell under high pressure is devoted to strict safety regulations. According to these regulations, a bursting

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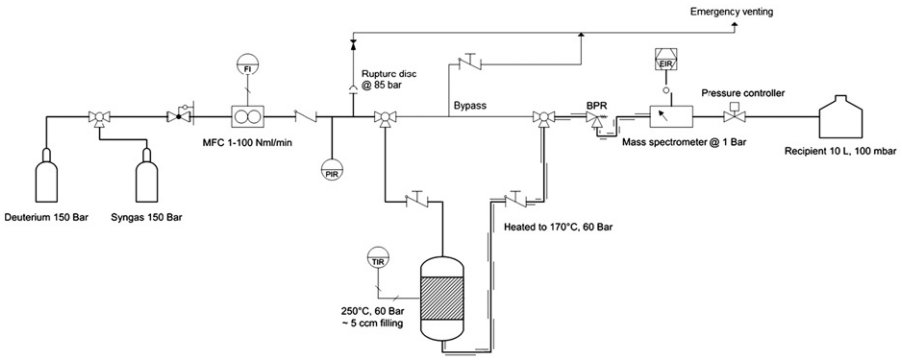

Fig. 1. Process flow chart of operating reactor including gas supply and effluent analytics. The system is kept under high pressure until the back pressure regulator (BPR). Gas analytics is carried out under ambient pressure.

of the cell walls must be excluded at any time of the operation. The most critical point is the balance in between finding a material, which shows neutron transparency and a moderate coherent scattering behavior on the one hand and is resistant to high pressures of reactive gases like hydrogen, deuterium or carbon monoxide at elevated temperatures on the other hand. Most common materials used in the nuclear branch like vanadium and zirconium alloys show hydrogen embrittlement or intragranular corrosion [3], if they are operated under high pressures on a long-term scale. Especially under alternating high pressure cycles, which occur under in situ conditions a high tensile yield strength of the material must be guaranteed. We have decided to fabricate the cell from thick-walled aluminum–magnesium alloy EN AW-5754 (AlMg3) offering sufficient pressure and chemical resistance, low absorption and activation and still acceptable coherent scattering. The tubular flow cell was manufactured from a AlMg3 rod with a nominal outside diameter of 20 mm and a tensile yield strength of 283 N mm^{-2} at room temperature. Using a lathe, the outer diameter was reduced to 19.05 mm and a hole with a diameter of 10 mm was set through, which led to a effective wall thickness of 4.52 mm. Strain calculations by assuming a tensile yield strength of 98 N mm^{-2} at 573 K [4] and a increased safety factor of 3.6 [5] have shown, that the tube is resistant up to the conditions of 140 MPa at 573 K. Static load tests of the setup have been successfully conducted at 9 MPa and 373 K for 2 h and the limits for flow operation have be set to 6 MPa at 603 K. The total length of the tubular reactor was 150 mm and the catalyst bed bathing in the neutron beam can have a length of up to 70 mm resulting in a volume of up to 5.5 cm^3. To achieve high intensity of the neutron diffraction patterns at short counting times, large sample sizes are required. The cell can be loaded with variable sample amounts from approximately 5 g to 20 g. The loaded catalyst bed is fixed by quartz wool plugs, which are inserted from both ends. A thermocouple which is inserted from the top allows to measure the bed temperature in the core of the catalyst bed during the reaction. Reactant feed is injected from the top, the product stream flows out at the bottom. Both ends of the tube are supported by crimped stainless steel adapting sleeves to assure a self-tightening seal. By inserting the end of the flow cell into Swagelok™ stainless steel (SS 316) 3/4 to 1/4 in. reducing unions the cell material forms a tight seal in between the adapting sleeves and the inner mating tape of the reducing unions by its larger thermal expansion coefficient at 523 K.

The body of the reactor is also made of AlMg3, due to its good heat capacity and corrosion resistance. If the incident neutron beam is poorly collimated, the reactor body shows low activation behavior as well as a good radiation damage resistance [6]. Given that the body is made out of the same material as the flow cell itself, it is practically seamless in the diffraction pattern. Pedestras and sampling base plate are made out of SS316 and fixed with screws via threading. Six heating cartridges are inserted into holes in the reactor body with a total heating power of 600 W (2×150 W, 4×75 W), enabling heating rates of up to 5 K min^{-1}. Each heating element is equipped with a thermocouple to check its heating behavior for linearity and over-heating. Loading of the filled flow cell is performed by removing the frontal heating covers and inserting the cell into the notch. The installed system with a total weight of 7.5 kg shows high temperature stability. An insulating cover and a convection-reducing thin Al-shield before the opening of the reactor body allows more efficient heating and more isothermal temperature profiles across the reactor. In case of potential power interruption the initial temperature loss is limited to 0.4 K min^{-1}. Safety precautions against over-heating are implemented by a bimetallic thermostat into the current circuit of the heating elements, which cuts of the power at a pre-defined temperature limit. The flow cell is equipped with a bypass to allow a proper purging of the lines at atmospheric pressure, which is important to avoid oxidation of the catalyst or local explosive atmospheres from residual air in the lines. The schematic process flow chart of the cell system is shown in Fig. 1, the detailed assembly of the reactor is shown in Fig. 2.

2.2. Gas supply

The lines of the feed gas supply are set under high pressure by a back pressure regulator (Tescom 44-1100) at the end of the product line. The pressurized gas lines are made of 1/8 and 1/4 in. stainless steel (SS316) tubing and connected with Swagelok couplings, fittings and reducing unions. The flow of the premixed syngas mixture (which had to be supplied at a pressure of ca. 7 MPa to achieve a stable outlet pressure of 6 MPa) was dosed using a mass flow controller (Brooks 5866) which was able to set a flow between 0 and 100 Nml min^{-1} in an operating pressure range from 0 to 10 MPa. The system pressure was electronically measured with an Endress+Hauser PMP 131 pressure transducer which was connected to a Schwille SPE 670 digital display and linked with a serial cable to a Labview application which allowed automated read-out and data-recording. For additional safety reasons a rupture disk with a specified relief pressure of 8.5 MPa and a check valve was installed between the outlet after the pressure transducer and the reactor inlet, which was able to shut down the gas supply in the case, the flow exceeded 500 Nml min^{-1} (e.g. in a case of a rupture). The pressurized product lines can be heated to 423 K–443 K to avoid condensation of products like steam.

2.3. Effluent gas analytics

Gas analytics is performed online at the heated product line beyond the back pressure regulator at atmospheric pressure. By