Zeolite films as catalytic coating on micro-reactors for SELOX reaction

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Microstructured reactors (MSR) are devices containing open paths for fluids with dimensions in the submillimeter range. Mostly MSR have multiple parallel channels with diameters between 10 and several hundred micrometers where a chemical reaction occurs[1,2]. The main feature of microstructured reactors is their high surface to volume ratio in the range of 10,000–50,000 m^2/m^3 compared to more traditional chemical reactors (100 m^2/m^3). Due to the dimensions of the channels laminar flow conditions occurred in MSR. Accordingly, the heat transfer coefficient is inversely proportional to the channel diameter. The high heat transfer allows utilizing the full potential of catalysts during highly endothermic or exothermic reactions and avoiding hot-spots formation [3]. Higher reaction temperatures are attained leading to reduced reaction volumes and less amount of catalysts [2] improving the energy efficiency and reducing the operational costs. In addition, microstructures allow fast heating and cooling of reaction mixtures.

The small diameters of the reactor channels ensure a short radial diffusion time leading to a narrow residence time distribution (RTD). This is advantageous for consecutive processes since high selectivity to the desired intermediate is achieved. Isothermal conditions combined with short residence times and narrow RTD are the main characteristics of MSR. In addition, the typical dimension of MSR is just below the extinction length or quench distance of many fast reactions, which is about 1 mm. The main mechanisms are thermal quenching by wall heat conduction and radical quenching by kinetic effects [4].

The use of proton exchange membrane (PEM) fuel cell systems to obtain clean and efficient power for stationary as well as mobile applications has gained prominence over the last few years. PEM fuel cells operate at around 70– 80 ºC and combine hydrogen gas at the anode with oxygen at the cathode to generate useful electric power at a high efficiency [5].

One of the most promising production hydrogen methods is the reforming of hydrocarbon fuels, such as natural gas, gasoline, or methanol, followed by a CO shift reaction to form H_2-rich fuel gases. However, such reformates still contain at least 1% level CO. Owing to the fact that under the operating temperatures the anode Pt catalyst in PEFC is very sensitive to poisoning by CO, the concentration of CO must be reduced to < 10 ppm level. CO levels in the off-gas of a water-gas -shift reactor typically lie between 0.5 and 2 vol % and not significantly more than 1 vol % [6]. Selective CO oxidation (SELOX) is considered as the most promising and cheap method to reduce CO concentration.

Zeolitic materials, Mordenite and Zeolite Y, were selected as a suitable catalyst support for the present application due to its high specific surface area and uniform pore structure, which acts as a molecular sieve. Zeolite catalysts loaded with metals such as Pt, use the microporous structure as special reaction spaces. Furthermore, the physical fixation of metals within the micropores is expected to inhibit sintering, thereby preserving the high catalytic surface area required for effective operation conditions [7].

In this sense, the unique properties of MSR and the availability of a highly active-selective catalyst supported in a microporous layer should lead a notably improvement in SELOX reaction as a gas purification step.

Zeolitic materials have been prepared, both as powder and also as a film supported on stainless steel (304 SS) microreactors. The zeolite film supported on micro-channels were obtained by seeded liquid phase hydrothermal synthesis according to Sebastian and cols.[8],see figure b-e

The microreactors consist of two plates 50 mm long, 10 mm wide and with a thickness of 2 mm manufactured. In each plate 14 microchannels (length= 25 mm, diameter = 500μm) are connected to ther inlet and outlet sections as shown in figure a.

Pt was supported on Na-type zeolites (Mordenite and Zeolite Y) by a conventional ion-exchange method. After activation treatment, the activity of both, powder and microreactors were tested with a reformate gas containing 1,21% CO- 2,90 %H_2O- 25,25% CO_2 and H_2 balance. The WHSV is 120000 ml/h·g and the CO/O_2 ratio =1, the double amount than the stoichiometrically required

The activity test demonstrates the microchannel reactor advantages for this reaction as compared to a conventional fix-bed reactor. The SELOX activity in the microchannel reactor increases partly because the heat resistance is negligible, partly because the mass transfer is improved with a thin catalyst layer with a high aspect ratio crystals.

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Figure:a)MSR plates. b-c)Pt-Mordenite layer in a MSR. d-e)Pt-ZeoliteY layer in MSR