# Preferential CO oxidation over Cu/CeO$_{2-x}$ catalyst: Internal mass transport limitation

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## ARTICLE INFO

## ABSTRACT

The effect of internal mass transport limitation on the preferential CO oxidation in hydrogen-rich mixture over copper-cerium oxide catalyst in a form of pellets and washcoat in microchannel reactor is estimated. Internal effectiveness factor $\eta_{CO}$ >0.8 in the optimum interval of reaction temperature (170–230 °C) is reached if the pellet diameter and washcoat thickness do not exceed 100 and 20 μm, respectively. Compared to conventional packed-bed reactor with catalyst pellets, microchannel catalytic washcoated reactor is more appropriate for practical use.

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## 1. Introduction

Approaches to increase efficiency of CO removal from hydrogen rich gas mixtures have been attracting considerable attention for a long time. In recent years, the interest to this problem became even stronger in view of hydrogen-rich mixtures application for feeding proton-exchange membrane fuel cells (PEM FC). One of the promising methods of hydrogen production for PEM FC applications is the on-board multi-stage process including reforming of fuels such as hydrocarbons, alcohols or ethers, followed by the CO water–gas shift (WGS) reaction. Typically, the obtained hydrogen-rich gas contains 0.5–1.0 vol.% CO, in some applications (for example, after methanol or DME steam reforming) the low level of the outlet CO concentration (up to 2–3 vol.%) can be directly attained without WGS stage. Since carbon monoxide poisons PEM FC anode catalyst, its concentration in the hydrogen-rich gas mixture must be reduced to at least 100 ppm, or still better to 10 ppm [1–5].

Among the approaches investigated to remove the trace amount of CO in H$_2$-rich stream [1–5], the CO preferential oxidation (CO PrOx) has been considered to be suitable for sufficient CO removal. CO PrOx includes two reactions:

$$2CO + O_2 = 2CO_2 \tag{1}$$

$$2H_2 + O_2 = 2H_2O \tag{2}$$

Hydrogen oxidation via reaction (2) spends a part of PEM FC fuel and thus decreases the process efficiency; the contribution of this reaction must be minimized.

Supported Au, Pt, Ru, Rh, Co, and Cu catalysts demonstrated good performance for the CO PrOx reaction [1–31]. Among them, copper-cerium oxide systems appeared sufficiently active, most selective [12–29] and less expensive that the catalysts based on Au and Pt group metals and therefore seem to be quite promising for practical applications.

Although considerable progress has been made towards the development of active and selective catalysts, the removal of CO to a level below 10 ppm and the simultaneous minimization of hydrogen losses are achievable only in a narrow temperature interval. For example, the suitable temperature window on platinum, gold or copper-cerium oxide based catalysts is usually less than 40 °C.

Most CO PrOx studies have been based on packed-bed reactors (PBR) with diameters lager than 3 mm, which, because of the large heat generation from two oxidation reactions (see Eqs. (1) and (2)), are susceptible to mass and heat-transport limitations. Therefore, thermal and mass transport management is a key issue for practical PrOx reactor designs and efficient reactor operation in terms of highly selective CO reduction to levels acceptable for PEM FC application.

According to Kolb et al. [32], CO PrOx in microchannel reactors is the most appropriate technology for designing of compact fuel processors for portable PEM FC applications. Advantages of microchannel reactors for running highly exothermic CO PrOx reaction over conventional PBRs were demonstrated in a number of

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reports [28–31,33]. In a microreactor, the catalyst layer is deposited inside microchannel as a thin wall coating. Such a structure allows the achievement of high heat- and mass-transfer rates and nearly isothermal operation regime that helps to prevent side reactions (hydrogen oxidation, reverse water–gas shift, CO methanation) and provides the required level of CO concentration in a wide temperature interval [29–31].

Thin catalyst coatings help also to minimize internal diffusion resistance. According to [31], the effect of internal mass-transport limitation on preferential oxidation of CO in microchannel reactor with 2–5 $\mu$m thick, Pt/$\gamma$-Al$_2$O$_3$ catalyst coating is negligible. However, even for small Pt/$\gamma$-Al$_2$O$_3$ particles (360 $\mu$m diameter) the internal efficiency factor reduced to 0.5 at 250 °C [9]. Obviously, the use of ~5 $\mu$m catalyst particles in a packed-bed reactor is hardly possibly because of high pressure drop, while the use of "crusted" catalysts will lead to inevitable reactor enlargement.

In general, one can agree with the conclusions made in report [33], which presents comparative analysis of system designs of the PrOx device (with Pt-Ru/$\alpha$-Al$_2$O$_3$ catalyst) for conventional packed-bed reactor technology and microreactor technology on 0.1 and 5 kW$_e$ power output scales. It was proved that on both power output scales studied, the microreactor designs outperform the conventional designs, leading to lower reactor volumes and weights. However, the scaling factors of the reactor volume and weight were larger for the microreactor systems as for the conventional systems, indicating that at larger scales packed-bed reactors will ultimately outperform the microreactor designs.

Thus, to make valid choice between the conventional packed-bed reactor technology and microreactor technology, we should know their optimum operation parameters to provide the best process efficiency. In particular, it is necessary to determine the optimum catalyst pellet diameter and catalytic coating thickness that allow minimized mass-transfer limitations. The solving of this complex problem depends on a number of factors such as catalysts nature, morphology and texture, target and side reactions, etc. To the best of our knowledge, there are no reports in the literature on detailed studies of transport properties of microreactors and conventional packed-bed reactors with copper-cerium oxide catalyst for CO PrOx.

In our earlier work [29], the effect of internal mass-transfer limitations on CO PrOx over copper-cerium oxide catalysts was estimated using the Thiele–Zeldovich modulus. It was shown that the adverse effect of internal diffusion may appear at temperatures of ~200 °C for coating thickness (or pellet radius) of ~100 $\mu$m. More detail calculations require the knowledge on the catalyst texture and reaction kinetics.

In the present work, the data on the porous structure of copper-cerium oxide catalyst and reaction kinetics were used to study comparatively how internal mass transport limitations affect the performance of CO PrOx reaction both in thin catalytic coatings inside microchannel reactor, and in catalyst pellets. The study aims at the CO PrOx process optimization with respect to both conventional packed-bed reactor and microreactor technologies.

## 2. Materials and methods

### 2.1. Catalyst preparation

The 5 wt.% Cu/CeO$_{2-x}$ coatings were prepared as described elsewhere [28,29]. Stainless steel platelets were manufactured using a commercial photoetching technique based on wet chemical etching with an aqueous iron trichloride solution. The platelets each having 14 semicylindrical channels of 500 $\mu$m width, 250 $\mu$m depth, and 25 mm length were first cleaned with isopropanol for 10 min in an ultrasonic bath and after drying calcined at 800 °C for 2 h. This treatment presumably generated a thin oxide surface on the channel walls and provided good adhesion of oxide materials. A polymer film was used to cover the metal parts of the surface that were intended to remain uncoated.

The ceria support with a BET surface area of 80 m$^2$ g$^{-1}$ was prepared by calcination of Ce(NO$_3$)$_3$·6H$_2$O at 400 °C for 2 h in air. In a first step, 1.7 g polyvinyl alcohol (binder) was dissolved in 25 g deionized water by smoothly stirring with a magnetic stirrer at 65 °C for 2 h and left without stirring overnight. Then 7 g CeO$_2$ powder and 0.3 g acetic acid were added successively without stirring. The resulting suspension was stirred at 65 °C for 2 h, cooled to room temperature and stirred for 3 days.

The microchannels were completely filled with the prepared suspension and excess suspension was wiped off. After drying at 110 °C in air, the platelets were calcined at 400 °C for 2 h. To produce the 5 wt.% Cu/CeO$_{2-x}$ catalyst, the washcoated platelets were impregnated with the required quantity of an aqueous solution of Cu(NO$_3$)$_2$, then dried at 110 °C in air, and calcined at 400 °C for 2 h. The obtained coatings demonstrated good impact resistance and were still intact after contact with water [29].

Direct examination of the coating's porous structure by standard techniques is hardly feasible. Therefore we synthesized 5 wt.% Cu/CeO$_2$ catalyst powder by the procedure described above, excluding the step of catalyst washcoating into microchannels The obtained catalyst was pressed into pellets (hereinafter CuCe(I)). The 0.1–0.2 or 0.25–0.50 mm fractions were used in the experiments.

To check the effect of the reaction medium, the CuCe(I) catalyst was exposed to reaction mixture of composition, kPa: CO – 1, O$_2$ – 1.5, H$_2$O – 10, CO$_2$ – 20, H$_2$ – 65, He – balance, at 200 °C during 4 h. Gas mixture feeding rate (at standard temperature and pressure) with respect to catalysts weight (WHSV) was 14,400 cm$^3$ g$^{-1}$ h$^{-1}$. This catalyst is denoted as CuCe(R) hereinafter.

### 2.2. Catalyst characterization

The specific BET surface area ($S_{BET}$), pore volume and pore size distribution of the catalysts were determined from the complete nitrogen adsorption isotherms at −196 °C (ASAP 2400 instrument).

Pore volume and pore size distribution of the catalysts were also determined by mercury porosimetry (AutoPore IV 9500 instrument). The textural characteristics were calculated on the base of a non-crossing cylinder pore model.

HR TEM measurements were performed using a JEM-2010 electron microscope (lattice plane resolution 0.14 nm at accelerating voltage of 200 kV). Images of periodic structures were analyzed by Fourier method.

### 2.3. Catalytic activity study

The procedure of the catalytic activity experiments with CuCe(I) catalyst was the following. The reaction was performed in a fixed-bed U-shape quartz flow reactor (i.d.: 3 mm, catalyst bed length: 30 mm) at atmospheric pressure. A portion of 0.05 g of the catalyst (particle diameter: 0.1–0.2 or 0.25–0.50 mm) was mixed with 0.15 g of quartz (the same fraction as for the catalyst) and was placed in the reactor. The temperature was measured by a K-type thermocouple in the middle of the catalyst bed.

The experiments were performed with the following model gas feed compositions, kPa: CO – 1, O$_2$ – 1.6, H$_2$ – 84, with He as balance. Total feed flow rate was 2.6 cm$^3$ s$^{-1}$ (STP). No catalyst pretreatment was applied before the experiments.

The inlet and outlet concentrations were determined using a Chromos GC-1000 chromatograph equipped with molecular sieves NaX and Porapak Q columns and with thermal-conductivity (TCD) and flame-ionization (FID) detectors. The combination of a methanator (containing a reduced NKM-4 nickel catalyst) and the FID allowed highly sensitive analysis of CO, CO$_2$, and the gaseous