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Co–SiO_2 aerogel-coated catalytic walls for the generation of hydrogen

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ABSTRACT

Cobalt–silica (Co–SiO_2) aerogel coatings were successfully grown on the walls of ceramic monolith channels, thus resulting in structured catalytic wall materials useful for gas–solid reactions. The preparation involved the synthesis *in situ* of SiO_2 gels by the sol–gel hydrolysis and condensation of tetraethylorthosilicate (TEOS), quenching at the gelation point, incorporation of Co by impregnation, and extraction of the solvent by supercritical drying. Characterization of the aerogel-coated monoliths revealed an excellent dispersion and homogeneity of the aerogel and good adherence properties. The catalytic performance of these materials in the ethanol steam reforming reaction addressed to obtain hydrogen was studied at atmospheric pressure by carrying out consecutive cycles at 473–773–473 K with a C_2H_5OH:$H_2O \sim 1$:3 (molar) mixture and stability tests, and the results were compared with those obtained over monoliths prepared by conventional washcoating methods from Co–SiO_2 xerogel. Co–SiO_2 aerogel catalytic walls were about four times more active for hydrogen generation at 623 K than conventional monoliths. An unusual rapid activation of aerogel-coated monoliths was attained at 580–590 K, even after several cycles and oxidation treatments at 563–613 K, which was attributed to highly dispersed cobalt particles and higher effective diffusivity of reaction species due to high porosity and larger average pore size. The reproducible low-temperature activation of Co–SiO_2 aerogels supported on ceramic monoliths may be useful for the practical application of fuel reformers to the on-site generation of hydrogen from ethanol.

1. Introduction

Aerogels are extremely light and porous materials obtained by removing the solvent from gels under supercritical conditions to avoid the capillary pressures, responsible for the porous collapse. The result is an open porous material with very high surface area and excellent mass transfer properties, becoming attractive in application as catalysts or catalytic supports [1–10]. High porosity and high surface area are interesting properties for catalytic chemisorption since they favor the accessibility to the active centers. However, given the low tensile strength of aerogels, the direct use of aerogel particles in a catalytic reactor may result in reactor blocking and pressure drop. In this work we have grown Co–SiO_2 aerogel coatings on the walls of ceramic monolith channels and studied their catalytic performance for the generation of hydrogen through the ethanol steam reforming reaction. The results are compared with conventional materials obtained by washcoating methods, i.e. xerogel coatings, synthesized by drying the gels at atmosphere pressure. Currently, the search for an active and selective catalyst for the generation of hydrogen through ethanol steam reforming at low temperature constitutes an active research area since ethanol is a renewable, liquid fuel with low toxicity and high energy density that is easy to handle and distribute [11,12].

Cobalt-based catalysts exhibit good performance for the generation of hydrogen from steam reforming of ethanol (1) at low temperature [13–25]:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad (1)$$

Other catalysts have been tested for ethanol steam reforming as well [26–28], but the requirement of higher temperatures to achieve reasonable activity values results in poor selectivity towards hydrogen and therefore, in accumulation of secondary products. In particular, as the reaction temperature increases, the reverse water gas shift reaction (2) is favored, thus hydrogen is consumed and the concentration of carbon monoxide in the product mixture increases. It is well known that carbon monoxide is a serious poison for polymeric fuel cells and its presence in the reactor effluent should be avoided in order to suppress costly

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additional purification processes in auxiliary units.

$$H_2 + CO_2 \leftrightarrow H_2O + CO \qquad (2)$$

Other undesired products of the reaction are mainly ethylene (originated from ethanol dehydration onto acidic sites of catalysts), methane (formed either by decomposition of ethanol or by methanation reactions) and condensation products such as dimethylketone [29]. Over cobalt-based catalysts, it has been demonstrated with *in situ* magnetic studies coupled to reaction tests and with diffuse reflectance infrared spectroscopy [30,31] that the simultaneous presence of metallic cobalt and cobalt oxide is required for the progress of the reaction. Two steps of the reaction have been identified. First, ethanol dehydrogenates into acetaldehyde and hydrogen (3) over cobalt oxide (Co_3O_4):

$$C_2H_5OH \xrightarrow{Co_3O_4} CH_3CHO + H_2 \qquad (3)$$

Hydrogen partly reduces the surface of cobalt particles into metallic cobalt and then, the second step, the reforming of acetaldehyde into the final products H_2 and CO_2, takes place (4).

$$CH_3CHO + 3H_2O \xrightarrow{Co} 5H_2 + 2CO_2 \qquad (4)$$

In powdered samples, cobalt oxide slowly reduces into metallic cobalt under ethanol steam reforming conditions and long induction times (typically of various hours) are necessary before enough metallic cobalt is present on the surface of the cobalt particles for the reaction to be completed [32]. In addition, as the temperature is lowered, metallic cobalt rapidly re-oxidizes into cobalt oxide under the ethanol:water reaction mixture and, again, the catalyst needs a slow reactivation before being catalytically active for reforming. In this work we demonstrate that cobalt particles in Co–SiO_2 aerogels supported on ceramic monoliths are activated very fast under ethanol steam reforming reaction conditions, even after warming up of the reformer in air, and furthermore, that high and stable yields of hydrogen can be obtained at temperatures as low as 598 K.

2. Experimental methods

2.1. Preparation of aerogels and catalytic walls

Silica gels were first synthesized by the sol–gel method, through hydrolysis and condensation of the silica precursor, tetraethylorthosilicate (TEOS), dissolved in ethanol and catalyzed with HNO_3–HF [33,34]. Cordierite ($Al_4Mg_2Si_5O_{18}$) monoliths of ca. 2 cm diameter and 2 cm long (Corning Inc., 400 cells per square inch) were immersed into the resulting sol and removed at the gelation point. Gelation was completed under continuous rotation (75 rpm) in liquid ethanol for ca. 30 min. Cobalt was then incorporated by impregnation of the gels with a $Co(NO_3)_2$ (0.57 M) ethanolic solution for 3 days. Finally, the gels were dried under supercritical conditions of ethanol (6.28×10^6 Pa, 516 K). On the other hand, conventional catalytic monoliths were obtained following the previously explained procedure, but allowing the solvent to evaporate at atmosphere pressure instead of under supercritical conditions. Afterwards, the Co–SiO_2 xerogel was calcined at 673 K for 2 h.

2.2. Characterization techniques

The morphology and composition of the interior of monolith channels were studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Images were taken at 15–20 kV with JEOL JSM 6400 and Hitachi S-2300 microscopes. Surface area measurements (BET) of powders were carried out with a Micromeritics ASAP 2000 apparatus. Samples were degassed at 443 K before surface measurements. Mechanical stability was evaluated by exposing monoliths directly to mechanical vibration. The vibration frequency was raised progressively from 20 to 50 Hz at a fixed acceleration value of 2 G, and at 50 Hz at acceleration values between 5 and 15 G. Weight loss was monitored after 30 min at each frequency, and after 3 h under the most severe vibration conditions (50 Hz, 15 G). G levels were controlled directly on the vibration test board with a Brüel & Kjaer 4370 accelerometer.

2.3. Catalytic studies

Catalytic tests were carried out at atmospheric pressure in a tubular, stainless-steel reactor. A $C_2H_5OH{:}H_2O \sim 1{:}3$ (molar) vapor mixture balanced with inert gas was passed through the reactor at 25 STP mL min^{-1} (0.26 mL min^{-1} C_2H_5OH). Prior to catalytic tests, the temperature of the reactor was raised up to 473 K in air and held at this temperature for 30 min. Thermal cycles at 473–773–473 K were performed at 2 K min^{-1} as well as stability tests at 598–673 K. In some experiments, the temperature of the reactor was raised up to 563 or 613 K in air before the catalytic test. The reactor effluent was monitored continuously on-line either by mass spectrometry (Cirrus MKS) taking 14 scans per minute (1–60 u), or by gas chromatography (Agilent 3000 A) using MS 5 Å, PlotU and Stabilwax columns.

3. Results and discussion

3.1. Coating monolith walls with catalytic aerogels

No previous attempts have been reported in the literature concerning the growth of catalytic aerogels on monolith walls. Here we have developed a method for coating cordierite monoliths with a Co–SiO_2 aerogel. The most critical point of the procedure described in Section 2.1 for avoiding the blocking of the monolith channels was the control of the gelation point during the condensation of the silica precursor inside them. Different mixtures of HF:HNO_3 (HF/NHO_3 from 1.1 to 4.2) were investigated in order to control the gelation point and to obtain reproducible results. Using a $H_2O{:}C_2H_5OH{:}TEOS{:}HF{:}HNO_3 = 16{:}6{:}1{:}0.11{:}0.03$ (molar) mixture and heating up to 313 K, an advantageous gelation point at 18 ± 1 min was obtained for sample manipulation. Fig. 1a corresponds to a low-magnification SEM image of the inner part of a monolith channel coated with Co–SiO_2 aerogel. The homogeneity and distribution of the aerogel layer were excellent and energy dispersive X-ray analysis performed at various locations yielded constant Co/Si atomic ratios of about 0.36. Fig. 1b–d shows SEM images at higher magnification corresponding to cordierite before coating (Fig. 1d) and after coating with Co–SiO_2 aerogel (Fig. 1b) or xerogel (Fig. 1c). The porous structure of the cordierite walls was not recognizable after coating due to the thickness of the aerogel and xerogel layers. The microstructure of the xerogel and aerogel coatings was strongly different. Aerogel-coated monoliths showed high porosity and a typical cluster-of-grape morphology [8], whereas xerogel-coated monoliths were constituted by agglomerated particles of varying size. According to their morphology at the microscale level, the surface area of aerogel samples was considerably higher than that of xerogel samples, 645 vs. 280 $m^2\,g^{-1}$. The average BJH pore sizes (Barret–Joyner–Halenda method) of aerogel and xerogel samples were 18.9 and 8.2 nm, respectively. Concerning mechanical stability, it was found that the adherence of aerogels onto the monolith walls was similar to that of washcoated xerogels. At increasing vibration

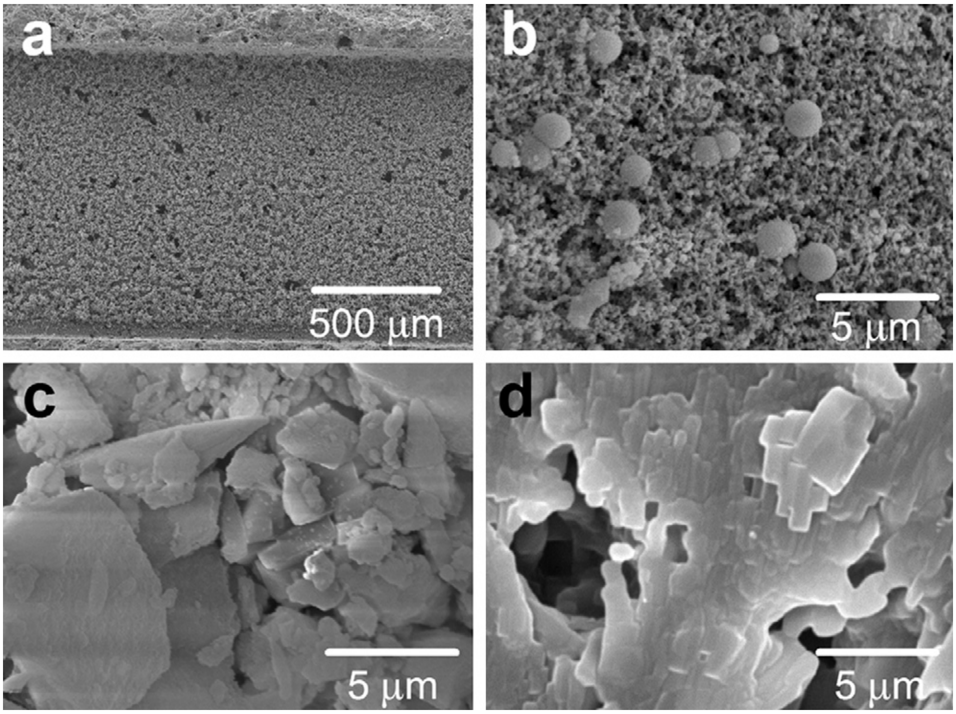

Fig. 1. Scanning electron microscopy images of Co–SiO_2 aerogel (a, b) and xerogel (c) coatings over cordierite monolith walls (d).

frequencies (20–50 Hz) and acceleration values (2–15 G) for 5.5 h the weight loss of both coatings was only ca. 20%. The amount of aerogel or xerogel deposited on the inner part of the monolith channels was 4–6% (w/w) and the amount of Co (measured by X-ray fluorescence) was ca. 20 wt.% with respect to SiO_2.

3.2. Ethanol steam reforming reaction

The catalytic behavior of catalysts was continuously monitored during several temperature cycles of 473–773–473 K. Fig. 2 shows some of such cycles for the monolith washcoated with xerogel and

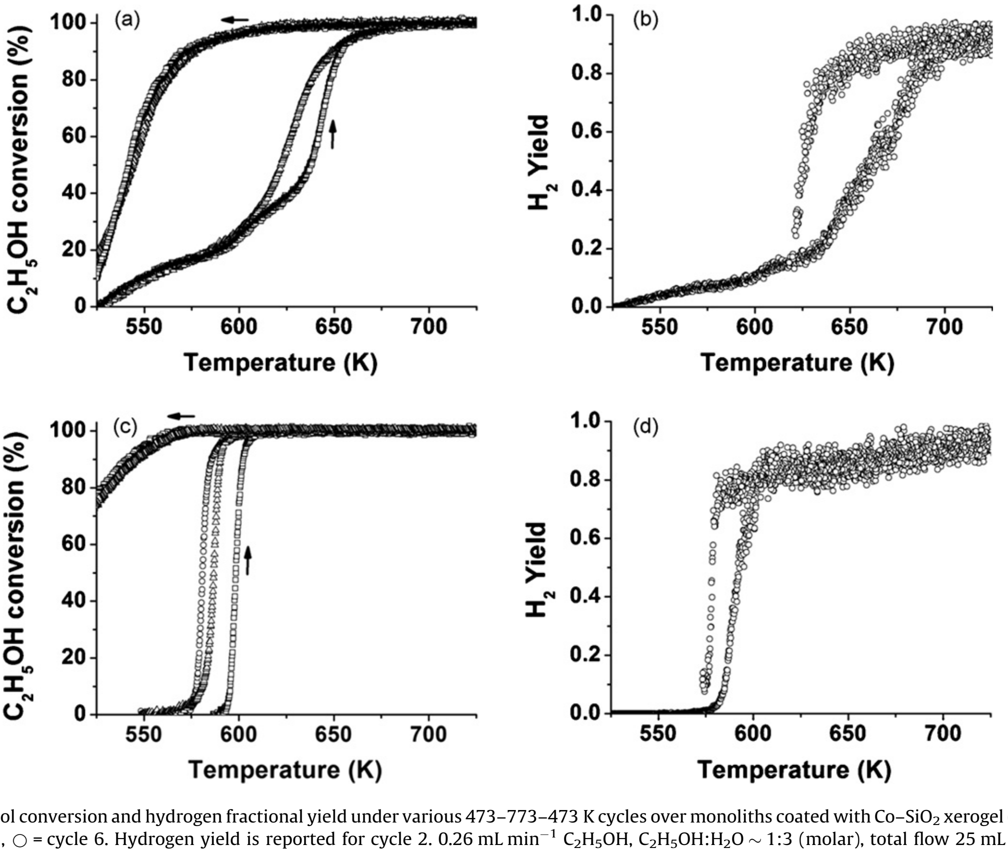

Fig. 2. Variation of ethanol conversion and hydrogen fractional yield under various 473–773–473 K cycles over monoliths coated with Co–SiO_2 xerogel (a, b) and aerogel (c, d). □ = cycle 2, △ = cycle 3, ○ = cycle 6. Hydrogen yield is reported for cycle 2. 0.26 mL min^{-1} C_2H_5OH, C_2H_5OH:H_2O ~ 1:3 (molar), total flow 25 mL min^{-1}.

for the monolith coated with aerogel in terms of ethanol conversion and hydrogen yield. Cycles corresponding to the monolith washcoated with xerogel (cycles 2 and 3) showed a slow increase of ethanol conversion (Fig. 2a) and hydrogen production (Fig. 2b) in a wide range of temperature as the temperature was raised. 40–50% of ethanol was converted at 623 K whereas a temperature of at least 698 K was required in order to obtain total conversion of ethanol and a good hydrogen yield. In contrast, as the temperature was lowered, ethanol conversion was maintained at temperatures higher than 623 K. This large hysteresis of ethanol conversion and hydrogen yield following temperature cycles is ascribed to the progressive reduction of cobalt oxide under ethanol steam reforming conditions at increasing temperature and the oxidation of metallic cobalt when the temperature is lowered, as has been discussed earlier [32]. On the contrary, the performance of aerogel-coated monoliths under exactly the same reaction conditions was strongly different (Fig. 2c and d). During the first part of cycle 2, there was a sudden increase of ethanol conversion from 10 to 100% in a temperature interval of only 13–14 K, accompanied by a rapid increase of hydrogen production. Ethanol conversion and hydrogen yield were maintained at higher temperatures, and in the second part of the cycle (as the temperature was lowered) the yield of hydrogen started to decrease only at 583 K. Exactly the same shape was observed for cycle 3, but now the temperature at which 50% of ethanol conversion was attained decreased from $T_{1/2}$ = 599 to 587 K (Fig. 2c), resulting even in a better performance at a lower temperature. The activation temperature progressively decreased during the following cycles until a constant value of ca. $T_{1/2}$ = 581 K was reached after cycle 5. 17.3 mol H_2/mol C_2H_5OH g^{-1} min^{-1} were produced over the aerogel-coated monolith at 623 K, being the composition at the reactor outlet 68.7% H_2, 23.2% CO_2, 1.0% CO and 7.1% CH_4. For comparison, 5.0 mol H_2/mol C_2H_5OH g^{-1} min^{-1} were produced over the xerogel-coated sample at this temperature.

The better catalytic performance and fast activation of Co–SiO_2 aerogels with respect to their homologue xerogels is attributed to highly dispersed cobalt particles and higher effective diffusivity of reaction species due to high porosity and larger average pore size of the aerogel. In order to further test this hypothesis, we carried out additional temperature cycles under ethanol steam reforming conditions after oxidizing the aerogel-coated monolith under air at 563 K (before the activation temperature) and 613 K (after activation). Fig. 3 shows the ethanol conversion corresponding to these cycles. In both cases the aerogel-coated monolith was activated almost immediately and hydrogen was obtained at the same time. In addition, the second part of the cycle, from 773 to 473 K, was indistinguishable from the previous cycles without the oxidation treatment (Fig. 2c). These results show that cobalt particles in the aerogel become easily activated under ethanol steam reforming conditions even after oxidation at high temperature or, in other words, cobalt particles in the aerogel undergo rapid redox equilibrium under reaction, irrespectively of their initial state.

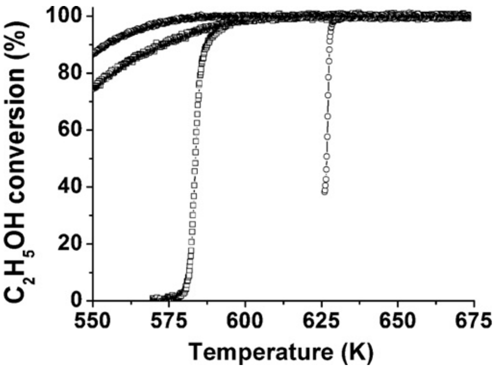

Fig. 3. Ethanol conversion and hydrogen fractional yield over Co–SiO_2 aerogel supported on cordierite monoliths after heating up the reactor in air at 563 K (□) and 613 K (○). 0.26 mL min^{-1} C_2H_5OH, C_2H_5OH:H_2O ~ 1:3 (molar), total flow 25 mL min^{-1}.

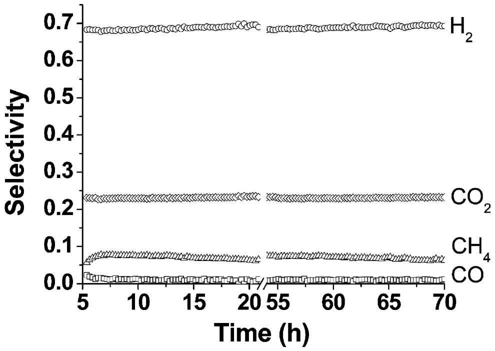

Fig. 4. Product selectivity obtained at 623 K during long term catalytic tests. The break between 21 and 54 h corresponds to an aging treatment at 673 K. 0.26 mL min^{-1} C_2H_5OH, C_2H_5OH:H_2O ~ 1:3 (molar), total flow 25 mL min^{-1}.

Long term catalytic runs were carried out over monoliths coated with aerogel in order to study their stability. The samples were subjected to continuous ethanol steam reforming at 623–673 K for several days and no deactivation was observed. Fig. 4 shows the selectivity results for a 3-day experiment. Successfully, the selectivity towards the reforming products, $H_2 + CO_2$, was maintained between 92 and 94%.

4. Conclusions

Ceramic monoliths have been coated with catalytic aerogel layers and used as structured materials for gas–solid reactions. Excellent homogeneity, dispersion and adherence were obtained with Co–SiO_2 aerogel coatings over the cordierite monoliths. The catalytic performance of Co–SiO_2 aerogel-coated monoliths for the generation of hydrogen from ethanol steam reforming was outstanding in terms of catalyst activation at low temperature (580–590 K), resistance to oxidation (563–613 K), stability and fast response to hydrogen production with respect to conventional catalytic monoliths washcoated with Co–SiO_2 xerogel. On-board reformers may benefit from monoliths coated with catalytic aerogels since they can be heated to the reaction temperature in air, they do not require long activation treatments prior to use and they are stable under start-up/shut down-cycles.

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