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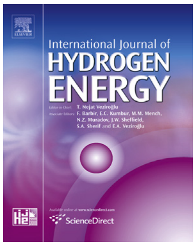

Hydrogen production by methane decomposition over MnO_x/YSZ catalysts

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ABSTRACT

CO_x-free hydrogen production via CH_4 decomposition has been studied for the first time using MnO_x-based catalysts, paying attention to the effect that the physicochemical properties of the catalysts have on the H_2 yield and on the type of carbon structures obtained as co-product of the reaction. Catalysts were synthesized via successive wet impregnation over yttria-stabilized zirconia (YSZ). Previously, YSZ supports were prepared through a modification of Pechini method. Different thermal treatments were performed to the YSZ in order to study its influence in their textural properties and, thus, in a possible influence on hydrogen production. Mn-based catalysts were characterized through XRD, N_2 adsorption-desorption, SEM, TEM and X-ray fluorescence. Methane decomposition reactions were carried out in a high temperature fixed-bed quartz-reactor connected to a mass spectrometer for analysis. Results showed activation at lower temperatures for pure Mn-oxide than for supported ones, which, in turn, seems to present a more stable hydrogen production for longer periods. Interestingly, it was also observed a high catalytic activity for the YSZ support. Additionally, depending on the specific preparation conditions of the catalysts, different carbon structures, ranging from nanofibers to disordered graphite layers were observed after methane decomposition. Besides, formation of Mn_7C_3 by interaction of Mn with methane at high temperature is detected by XRD. Finally, by selecting appropriate synthesis conditions it is possible to attain MnO_x/YSZ catalysts with moderate activity and high resistance to deactivation, opening up the possibility of developing promising catalysts for thermocatalytic methane decomposition based on Mn oxides, which are inexpensive, non-toxic abundant materials.

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Introduction

Fuel decarbonization emerged in the last decades as a promising approach to produce hydrogen from traditional fossil fuels while mitigating greenhouse gas emissions [1]. One of the most promising approaches to that end is the thermocatalytic methane decomposition (TCMD) [2]. Via this reaction, as described in Eq. (1), CO_x-free hydrogen is obtained with carbon as a co-product, which can be further used as a commodity or as carbon fixation route.

$$CH_4(g) \rightarrow C(s) + 2H_2(g)\ \Delta H_{298} = 75.6\ \text{kJ/mol} \qquad (1)$$

Life cycle assessment of this process has proved to be very effective for reducing greenhouse emissions [3]. However, due to the strength of C–H bond, it is necessary to operate above 1200 °C in order to achieve reasonable conversions in the absence of a catalyst [4]. Therefore, the use of a catalyst is essential as to obtain H_2 under less stringent conditions. A plethora of carbonaceous and transition metal based catalysts have been used for such purpose and have been recently reviewed by Ashik et al. [4]. In general, carbon-based ones showed limited deactivation and better stability but require larger reaction temperatures than metal-based ones. Additionally, using metal based catalysts produced attractive carbon structures such nanotubes [5], nanofibers [6,7], or even graphene layers [8], while in the case of carbonaceous materials amorphous carbon is formed [4]. Regarding metal catalysts, those based on Ni, Co or Fe have focused the interest on the scientific community in the last years due to their relatively high activity and lower cost in comparison with noble metals such as Pt or Pd. However, they also present some drawbacks. For instance, Ni based catalysts have a maximum operative temperature of 600 °C in order to avoid complete deactivation, and Fe based showed activity losses after repeated cycles [9]. In this respect, dispersion on oxide supports such as Al_2O_3, SiO_2 or MgO have been considered as a useful approach in order to enhance the catalytic activity, since they improve the textural properties and chemical stability of the metal catalyst.

In contrast, metal oxides have been scarcely used for TCMD. Among them, yttria-stabilized zirconia (YSZ) has shown a significant activity in this process [10,11]. However, to our knowledge there is not information available about the reactivity of redox oxides than can be stable at the relatively harsh conditions of methane decomposition. In this respect, the use of MnO_x materials seems to be potentially attractive considering that these oxides have shown good catalytic performance in different processes [12]. Furthermore, Mn oxides present the advantage of being inexpensive and less toxic than Ni or Co based materials. In addition, they have been used as additive to stabilize Ni/TiO_2 catalysts for methane decomposition [13], while $Ni/MnO–Al_2O_3$ has been applied to methane reforming [14].

Accordingly, in this work, we have explored the catalytic activity of Mn-based oxides supported over yttria-stabilized zirconia (YSZ) as an alternative to the metal-based catalysts previously studied. In addition, the influence of the support properties was studied by varying the synthesis parameters of the YSZ materials. This oxide can withstand high temperatures and, accordingly, it is a potentially interesting support for this application, as it has been previously reported [8,9].

Materials and methods

Synthesis of YSZ supports

Ytrria stabilized zirconia (YSZ) samples were prepared by a modification of Pechini method. First, citric acid (CA) was dissolved in distilled water at 70 °C and after homogenization of the solution, zirconium (IV) acetate hydroxide (Sigma Aldrich) and $Y(NO_3)_3{\bullet}6H_2O$ (Sigma Aldrich) were added to the solution. The amount of yttrium was selected so that the final molar ratio of Y_2O_3 to ZrO_2 was 8:92 (8 mol % YSZ). Two molar ratios of CA:Me were used, namely 5:1 and 10:1. After 3 h, ethylene glycol (EG) was added to the solution to promote esterification reaction. The molar ratio of CA:EG was 4:1. Then the temperature was increased to 90 °C with continuous stirring resulting in a viscous gel, which was dried at 200 °C for 3 h and then calcined at 400 °C for 4 h. After this step, the dried gel was ground to fine powders with an agate mortar. Finally, high-temperature calcination of the solids was performed in a furnace at either 950 °C or 1000 °C for 4 h, using a heating rate of 2 °C min^{-1}.

Synthesis of MnO_x-YSZ catalysts

Mn-based catalysts were prepared via wet impregnation of the YSZ supports using $Mn(NO_3)_3{\bullet}4H_2O$ (98%, Sigma Aldrich) as metal source. Impregnation was performed in two steps to enhance the dispersion, and the resulting catalysts presented a Mn total loading of 30% weight. After the first impregnation with appropriate amounts of the precursor solution in a rotary evaporator, the samples were dried at 120 °C for 15 h and, after the second impregnation using the same amount of precursor, the materials were dried at 120 °C for 3 h and then calcined at 700 °C for 4 h. In order to infer any improvement introduced by the support, MnO_x/YSZ samples were compared with an unsupported Mn_2O_3 catalyst prepared by the Pechini method, using a CA:Me ratio of 5:1. After drying at 200 °C for 3 h and 450 °C for 4 h, the dried solid was ground to fine powders and calcined at 700 °C for 4 h.

Catalyst characterization

Powder X-ray diffraction (XRD) analyses were carried out employing a Philips PW 3040/00 X'Pert MPD/MRD diffractometer using Cu K_α radiation ($\lambda = 1.54178$ Å) at a scanning rate of $0.2°s^{-1}$. The crystallite size was determined from the most intense reflection, according to the Scherrer formula. X-ray fluorescence (XRF) was performed with a X Philips MagiX equipment. The specific surface area (S_{BET}) was determined by nitrogen adsorption-desorption analyses at 77 K applying the multi-point BET method and using a Quantachrome QuadraSorb equipment. Degassing was carried out at 250 °C under vacuum. Scanning electron microscopy (SEM) images were taken with a Hitachi TM-100 microscope without any previous treatment of the samples. Transmission electron microscopy