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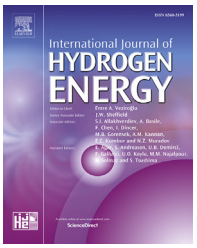

Hydrogen production by methane decomposition: A comparative study of supported and bulk *ex*-hydrotalcite mixed oxide catalysts with Ni, Mg and Al

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ABSTRACT

A catalytic comparative study of CO_x-free hydrogen production by methane decomposition was carried out. Catalytic performances of bulk Ni-mixed oxides derived from Ni/Mg/Al-hydrotalcites (*ex*-HTs-Ni) were compared with those obtained with Ni supported on mixed oxides derived from Mg/Al-hydrotalcites (Ni/*ex*-HTs), or on commercial supports (γ-Al_2O_3, MgO and MgO-modified γ-Al_2O_3). Catalyst characterization and their catalytic performance showed both *ex*-HTs-Ni and Ni/*ex*-HTs appear to be a similar regardless of their method of preparation. Ni/γ-Al_2O_3 was the best supported catalyst, although the catalytic performances of the *ex*-HTs catalysts were better. Higher Ni–Mg interaction in *ex*-HTs provides higher resistance to deactivation. Characterization by TG, Raman spectroscopy and TEM of spent catalysts in the reaction suggest the degree of ordering of the graphitic layers of the carbon deposit onto the catalyst surface is the key factor in the catalyst deactivation. The higher degree of ordering or graphitization of the carbon produced with the higher concentration of sp2 carbons on the surface of the Ni/γ-Al_2O_3 favours its faster deactivation by Ni-coverage than the bulk catalyst (*ex*-HT-Ni), in which the MWNT type carbon is mainly obtained.

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Introduction

Hydrogen is considered to be a promising energy vector that could replace a significant amount of fossil fuels [1,2]. However, hydrogen is not a primary energy source and other resources are required for its production [3]. Steam reforming and the partial oxidation of hydrocarbons, mainly natural gas, are the most economical and popular technology for producing hydrogen [4,5]. Nevertheless, these processes generate considerable amounts of CO_2 (approximately 13.7 kg CO_2/kg H_2 produced). Moreover, these hydrogen streams contain traces of CO which need hydrogen purification steps before its use in fuel cells [3]. Consequently, the current desire to reduce

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greenhouse gas emissions [4,6] has prompted research into other methods of hydrogen production.

Recently, catalytic methane decomposition has attracted the interest of researchers because this method produces free-CO_x hydrogen that is optimal for its direct use in fuel cells [1,7]. Methane is thermocatalytically decomposed into hydrogen and carbon, which are easily separated, and being a moderately endothermic process the energy requirement per mole of hydrogen produced is less than that corresponding to the steam reforming process (37.8 and 63.3 kJ/mol H_2 respectively) [8,9]. Moreover, the exploitation of carbon as a by-product is a key factor in the economy of this process [8], because it can be used either as feedstock, in the production of plastics, in the metallurgical industry, and as a support or adsorbent. The nature of the carbon formed during the methane decomposition being the determining factor in its application [10].

However, due to the strength of C–H bonds the non-catalytic methane decomposition requires temperatures higher than 1200 °C to attain considerable yields. In order to decrease this temperature, catalysts are required in the process. Several types of catalysts have been employed to decrease the temperature, but metal based catalysts [11–17] and carbon materials [18–24] are the most common. It has been reported that higher activation energies and consequently higher temperatures are needed to catalyze this process on carbon materials than on metal catalysts [1,18]. Different metal catalysts have been tested for methane decomposition, including Ni, Fe, Co and others [15,25–29]. Ni-catalysts have been widely researched and have shown the highest values for activity and yield. However, the carbon by-product inevitably leads to deactivation by covering or blocking the active Ni sites. Both the composition of the catalyst and the method of synthesis influence the activity, the production, and nature of the carbon formed. These factors consequently affect the catalytic deactivation and the regeneration cycles needed to expand the life of the catalysts. Therefore, the active sites must be stable enough to tolerate different cycles of reaction-regeneration, which can be considerably improved when the metal phase is stabilized into a mixed oxide matrix [1,30,31]. In this context, the mixed oxides derived from hydrotalcites have proved to be appropriate substrates for the stabilization of the Ni centers [30,32]. Hydrotalcites (HTs) are layered double hydroxides of M^{2+} and M^{3+} cations with compensating anions as pillars of the layered structure. These HTs form amorphous mixed oxides (*ex*-HT) by thermal treatment, which are characterized by a high specific surface area and a strong interaction between di- and trivalent cations [32]. Li et al. have reported that nickel-alumina catalysts synthesized from hydrotalcites doped with copper are active in methane decomposition to produce CO_x-free hydrogen [33–36]. A previous study carried out by our group [37] compared three different types of mixed oxides: the perovskite $LaNiO_3$ oxide, the mixed oxides derived from Ni–Al hydrotalcite structure and the $NiAl_2O_4$ spinel. This study demonstrated that the catalysts derived from the hydrotalcite precursor provided the highest activity in methane decomposition and the lowest threshold temperature in the programmed temperature decomposition experiments. Conversely, Liu et al. [38] studied Co/Mg–Mn *ex*-HT for methane combustion and concluded that MgO improved the dispersion of metals and decreased the surface area loss after calcination, i.e. increased the thermal stability of the active centers in the mixed oxides. Therefore, Ni–Mg–Al mixed oxides prepared from layered double hydroxides are promising catalysts for methane decomposition exhibiting high thermal stability [30,32,39]. They were even more active than the carbon catalysts under the same reaction conditions; although the metal catalysts were less resistant to deactivation than their carbon counterparts, they have advantage of being able to be regenerated [40]. However, the mixed oxides derived from hydrotalcite present a peculiarity in which traces of CO and CO_2 appear just before the hydrogen starts to be produced. However, once the production of hydrogen proceeds these traces of COx disappear [32].

In this work, the catalytic performance of different nickel-based catalysts has been evaluated for methane decomposition. Thus, bulk Ni–Mg–Al mixed oxides derived from hydrotalcites (*ex*-HTs) with different compositions have been compared with Ni-supported oxides. The supports used were (1) a conventional-basic MgO, (2) conventional acid γ-Al_2O_3 support, (3) γ-Al_2O_3 modified with magnesium, and (4) Mg–Al mixed oxides from hydrotalcite, where the Ni content was maintained in all catalysts.

Methods

Materials

The hydrotalcite-like precursors (HT) were synthesized using the urea co-precipitation method [41] with 0.5 M aqueous solutions of $NiCl_2 \cdot 6H_2O$ (Sigma-Aldrich), $MgCl_2 \cdot 6H_2O$ (Sigma–Aldrich), and $AlCl_3 \cdot 6H_2O$ (Sigma-Aldrich) in presence of urea (atomic ratio urea/Σ metals = 3). The mixture was heated to 90 °C and the temperature controlled to attain the precipitation pH value, this was maintained under vigorous stirring for 48 h. The precipitate was filtered and then washed repeatedly until the pH of the filtered water reached the pH 6. The precipitate was then dried overnight at 80 °C. Suitable amounts of Ni^{2+}, Mg^{2+} and Al^{3+} cations were added in order to obtain two different precursors: HT_1 (7.5 %Ni, 57.5% Mg and 35 %Al (mol %)) and HT_2 (18 %Ni, 46% Mg and 36 %Al (mol%)). The loadings of the NiO in HT_1 and HT_2 precursors were 12 and 27 wt %, respectively. The same method was used to prepare the Mg–Al *ex*-HT (Mg/Al ratio = 3.0, 75% Mg and 25 %Al) which was denoted as HT_3. Finally, the HT precursors were calcined at 850 °C (1.5 °C min^{-1}) for 10 h to obtain the corresponding mixed oxides. The calcined oxides were labelled as *ex*-Z, where Z indicates the pertinent precursor (*ex*-HT_1-12Ni, *ex*-HT_2-27Ni and *ex*-HT_3).

Four different supports were used to prepare the Ni-supported catalysts: (i) the aforementioned *ex*-HT_3, (ii) a commercial γ-Al_2O_3 (iii) the commercial γ-Al_2O_3 modified with MgO, and, (iv) a commercial MgO. Commercial alumina (γ-Al_2O_3, Alfa-Aesar, 235 m^2 g^{-1}) was stabilized by calcination at 800 °C for 10 h, to generate the *Al* support. After stabilization part of the Al support was suspended in a solution (10 mL H_2O $g^{-1}_{support}$) with the required amount of $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) to achieve 15 wt % MgO in the final catalyst (10 mL H_2O $g^{-1}_{support}$). The mixture was stirred for

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