

Copper catalysts for H₂ production via CH₄ decomposition

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Abstract

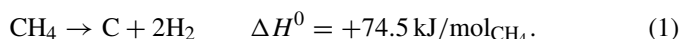
Cu/ γ -Al₂O₃ catalysts with different copper content prepared by wet impregnation have been studied for the thermo-catalytic decomposition (TCD) of methane in the temperature range 800–1000 °C. The materials have been characterized using ICP-MS, X-ray diffraction (XRD) and BET analysis. Their redox and catalytic behaviour has been investigated using H₂ and CH₄ temperature programmed reduction (TPR), FT-IR, TGA under reaction mixture and isothermal tests in a fixed bed reactor. The nature of the active phase and the best catalyst composition have been determined by comparison with reference compounds containing copper oxide and copper aluminate, respectively. Finally, the applicability of catalysts in a fluidized bed has been analyzed.

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1. Introduction

Hydrogen can be considered as environment friendly energy source since no CO₂, the main greenhouse gas, is produced by its combustion. It is generally accepted that hydrogen production will be based in the near-to-medium term on fossil fuels, primarily natural gas. Nevertheless, the traditional hydrogen production techniques, such as methane steam reforming and partial oxidation, both produce CO₂. In this framework the direct thermal decomposition of methane is an attractive process to produce CO_x free hydrogen and carbon. In fact, as a result of the absence of oxidants, no carbon oxides are expected to be formed in this process:



The endothermic reaction (1) is thermodynamically favoured at high temperatures: at atmospheric pressure methane conversions higher than 60% could be achieved, whatever the inlet methane concentration, provided that temperature is higher than 600 °C.

Moreover, due to the large energy of the C–H bond (440 kJ/mol) of methane molecule, even high temperatures are required (above 1200 °C) to activate this hydrocarbon [1]. Therefore, the use of a suitable catalyst is required in order to limit the operating temperatures at $T \leq 1000$ °C.

Thermo-catalytic decomposition (TCD) of methane has been studied [1]. Carbon itself has intrinsic catalytic properties towards this reaction although providing relatively low methane conversions, lower than 50%, in spite of the high reaction temperatures (up to 950 °C) [2–5].

The metal based catalysts proposed for TCD, mainly constituted by elements of the iron group (Fe, Co, Ni) supported or not on oxides (TiO₂, SiO₂, Al₂O₃, etc.), are more active [6]. Supported Ni catalysts have been indicated as the most effective ones [6–12]. Nevertheless, their maximum operative temperature is 600 °C due to catalyst deactivation. As a consequence, being methane conversion thermodynamically limited at this temperature, concentrated hydrogen streams (H₂ > 60%) cannot be obtained using nickel based catalysts [13]. Fe based catalysts are more stable at higher temperatures (700–1000 °C), however, deactivation occurs upon repeated cycles resulting in a short lifetime [13–15].

As regards the nature of the deposited carbon, for Ni based catalysts it has generally a filamentous form (nanofibres or nanotubes), while for Fe based catalysts no filamentous carbon deposition has been observed up to 680 °C [14–17]. The metal

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particle is located on the tip of the nanofibres. These are fragile carbon structures and a permanent deactivation of the catalyst can occur as a result of the loss of active phase [1].

Noble metals (Pt, Rh, Pd) have been used as promoters to improve the thermal stability of transition metal catalysts and their capability to accumulate carbon [7]. Very recently, Oghara et al. [13] proposed Pd-based alloys containing Ni, Co, Rh or Fe which show high activity and long lifetime for methane decomposition in the range 700–850 °C.

For Ni based catalysts also copper has been proposed as promoter [6–9]. Although not increasing the activity [7,8], copper enhances the ability to accumulate carbon and allows operation at temperatures higher than 600 °C. Furthermore, it has been also reported that the presence of Cu promotes the formation of carbon grains rather than nanofibres [8,9]. Cu has been also used as active phase dispersed on silica [18] but with quite poor results.

On the basis of the above considerations, studies are active to develop new catalytic systems able to operate at elevated temperatures to improve methane conversion into hydrogen streams. In addition, actual interest for TDC reactor configurations different from traditional fixed beds [10,11] like bubbling or spouted fluidized beds [10,19] requires additional features in the design of the optimum catalytic system. Mechanical and fluid-dynamic constrains of catalyst particles could be taken into account. In this framework, the formation of carbon nanofibres should be avoided due to attrition phenomena occurring in fluidized bed reactors which could remove the active metal particles from the support.

In this work copper has been used as active phase for methane decomposition. γ -Al₂O₃ has been chosen as support instead of SiO₂ in order to promote support-active phase interactions which can result in the formation of surface compounds more active for TCD reaction.

The effectiveness of the catalyst in CH₄ decomposition as concerns both activity and thermal stability (800–1000 °C) has been studied. The nature of the active phase and the best catalyst composition have been determined. Also its applicability in fluidized bed reactors has been characterized and data obtained in few exploratory runs carried out by means of a laboratory scale fluidized bed apparatus have been reported.

2. Experimental

2.1. Catalysts preparation

Catalysts with different Cu contents were prepared by wet impregnation by dissolving different amounts of Cu(CH₃COO)₂·H₂O (Aldrich) in aqueous solution and adding a suitable amount of γ -Al₂O₃ as reported in [20]. They were calcined for 3 h in air flow at 800 °C. Only the sample with the highest copper load has been also calcined at 900 and 1000 °C. A SiO₂ supported CuO sample with a high copper load and a bulk copper aluminium mixed oxide were also prepared in order to promote the formation of CuO and CuAl₂O₄ XRD detectable particles, respectively. The CuO/SiO₂ sample was prepared by wet impregnation as described for Cu/Al₂O₃ cata-

lysts and then calcined at 800 °C. The copper aluminium mixed oxide was prepared by co-precipitation from an aqueous solution of Cu(NO₃)₂·2.5H₂O (Aldrich) and Al(NO₃)₃·9H₂O (Fluka) alkalized with NH₄OH. The filtered powder was dried and calcined at 800 °C for 3 h. A fraction of this material was finally ground and calcined at 950 °C to further favour the formation of CuAl₂O₄.

Alumina supported catalysts will be indicated with the code x Cu/Al- y , where x stays for copper amount and y for temperature of calcination, and the alumina support calcined at 800 °C with the code Al-800. In the same way the sample dispersed on SiO₂ will be denoted as x Cu/Si; while the bulk samples calcined at 800 and 950 °C will be indicated as CuO-CuAl₂O₄ and CuAl₂O₄, respectively.

2.2. Catalysts physico-chemical characterization

The copper content (wt.%) of the catalysts was determined by ICP-MS using a Agilent 7500CE instrument after dissolving the alumina containing samples in HCl/HNO₃ solution at 80 °C while CuO/SiO₂ was dissolved in a HNO₃/HF solution.

The possible presence of different copper crystalline species has been detected by X-ray diffraction (XRD) analysis using a PW 1100 Philips diffractometer.

BET surface areas were measured by N₂ adsorption at 77 K with a Carlo Erba 1900 Sorpomatic instrument.

The redox behaviour of catalysts has been analyzed performing H₂ temperature programmed reduction (TPR) experiments and FT-IR analysis.

An experimental apparatus equipped with a fixed bed quartz micro-reactor operating under atmospheric pressure has been used for H₂ TPR tests. The H₂ inlet and outlet streams were analyzed by an on line continuous analyzer Hartmann & Braun CALDOS 17. In the experiments the sample (particles size: 180–400 μ m) was reduced by a 2% H₂/N₂ mixture with a contact time (W/F) of 0.12 g s Ncm⁻³ heating at 10 °C min⁻¹ up to 800 °C.

FT-IR analysis before and after a H₂ reducing treatment at 800 °C was performed on catalysts pressed into self supported disk in a IR cell equipped with a ZnSe windows operating under gas flow up to 800 °C using a Perkin-Elmer Spectrum GX FT-IR spectrometer. CO was used as probe molecule on both fresh and H₂ reduced catalysts. CO was adsorbed at room temperature on both fresh and H₂ pre-reduced at 800 °C catalyst, after purging with Ar.

2.3. Catalytic activity measurements

The catalytic behaviour of the different systems has been analyzed performing CH₄ TPR experiments, isothermal decomposition tests and thermogravimetric analysis.

The same experimental apparatus used for H₂ TPR experiments has been employed for both CH₄ TPR and isothermal decomposition tests. The inlet and outlet streams were analyzed by an on line continuous analyzer Hartmann & Braun URAS 14 for the analysis of CO, CO₂ and CH₄. For CH₄ TPR tests a 5% CH₄/N₂ mixture and a heating rate of 10 °C min⁻¹ up to

800, 900 and 1000 °C, respectively, were used. The contact time (W/F) was 0.25 g s Ncm⁻³. For isothermal methane decomposition tests a 5% CH₄/N₂ mixture at 800 °C has been fed. Before these tests the samples were heated at 800 °C in N₂ flow. The contact time (W/F) was always 2.8 g s Ncm⁻³, except for the silica copper system ($W/F = 1.4$ g s Ncm⁻³). Carbon balance was closed within 4% error in all experiments.

Thermogravimetric analysis was performed with a Perkin-Elmer TGA-7 thermobalance coupled with a Perkin-Elmer spectrum GX FT-IR for the analysis of the released gases. The sample was heated 10 °C min⁻¹ up to 800 °C in Ar flow and, after the stabilization of the weight, 5 vol.% CH₄ was introduced. The final temperature was maintained for 3 h.

The amount of carbon deposited on the catalyst after methane decomposition tests was determined using elemental analyzer CHN2000 LECO while its morphology was investigated using a scanning electron microscopy (SEM) with a Philips XL30 apparatus equipped with an EDAX instrument.

2.4. Catalysts properties for fluidized bed applications

A first assessment of the catalyst applicability in a fluidized bed (fluidization quality, determination of minimum fluidization velocity and mechanical resistance to attrition phenomena) has been also characterized.

A preliminary granulometric analysis of the catalyst has been carried out in order to determine the sizes of particles and their group of Geldart powders classification [21].

The laboratory scale fluidized bed experimental apparatus consists of a 2.6 cm i.d. stainless steel reactor equipped with a gauze type gas distributor, an electrical oven surrounding the reactor employed to heat up the reactor to the reaction temperature, a ceramic filter for collecting fine particles larger than 300 nm escaping from the reactor in the exit gases. Temperature and pressure were measured by means of thermocouples horizontally inserted in the reactor and pressure transducers, respectively.

Table 1

Catalysts code, copper amount from ICP, calcination temperature and BET surface area

Catalyst	% Cu (wt.%)	$T_{\text{calcination}}$ (°C)	Surface area (m ² g ⁻¹)
Al-800	0	800	168
CuAl ₂ O ₄	35 ^a	950	6
CuO-CuAl ₂ O ₄	35 ^a	800	26
12.5Cu/Si	12.5	800	172
8.4Cu/Al-800	8.4	800	156
8.4Cu/Al-900	8.4	900	136
8.4Cu/Al-1000	8.4	1000	122
2.0Cu/Al-800	2.0	800	165
0.4Cu/Al-800	0.4	800	169

^a Nominal content.

Experiments have been carried out in order to characterize the fluid-dynamic regimes occurring during the fluidization of a bed of catalyst (50 g) at 800 °C in nitrogen flow. Pressure drops curve as a function of the superficial gas velocity was obtained in order to determine the experimental value of minimum fluidization velocity (u_{mf}) at bed temperature.

Propensity of the catalyst to generate fines during fluidized bed operation has been characterized by operating a bed of the catalyst (50 g) at 800 °C in nitrogen flow under conditions of purely mechanical attrition for 15 h at a superficial gas velocity $u_0 = 4u_{mf}$ and calculating the elutriation rate by weighting the solids collected.

3. Results and discussion

3.1. Catalysts physico-chemical characterization

The amount of copper, the calcination temperature and the surface area of the catalysts are reported in Table 1.

For the γ -Al₂O₃ supported catalysts calcined at 800 °C the presence of copper does not significantly affect the value of surface area of support up to 2% Cu whereas a small (about 10%)

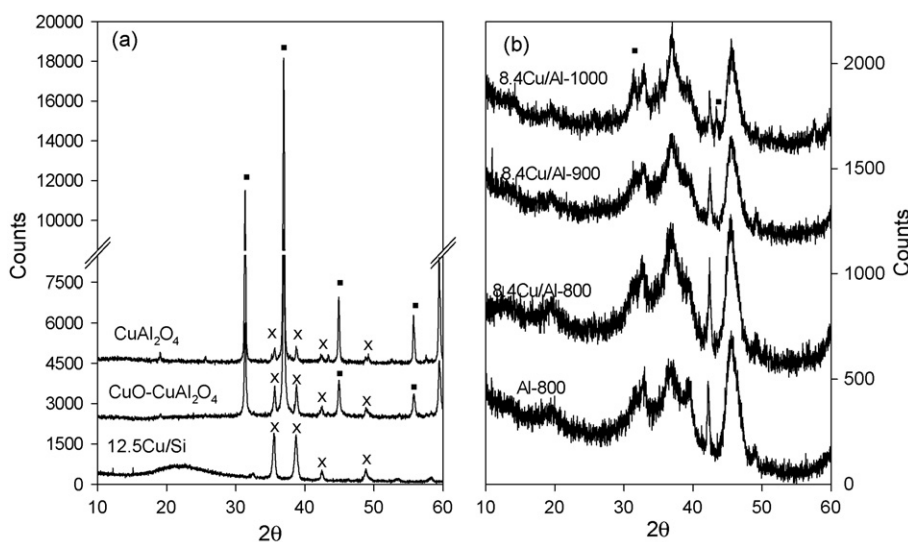


Fig. 1. XRD patterns of 12.5Cu/Si, CuO-CuAl₂O₄ and CuAl₂O₄ (a), Al-800, 8.4Cu/Al-800, 8.4Cu/Al-900 and 8.4Cu/Al-1000 (b). (x) CuO signals and (•) CuAl₂O₄ signals.

reduction is observed for the catalyst with the highest copper load. Higher temperatures of calcination give rise to a more significant reduction of the surface area, as shown by the values of BET area of catalysts treated at 900 and 1000 °C, respectively, likely related to the incipient transition of γ -alumina to other phases. A reduction of the original surface area of the SiO_2 support ($200 \text{ m}^2/\text{g}$) is also observed for the Cu/SiO_2 catalyst due to the quite large copper content.

In Fig. 1 the XRD patterns of the reference compounds 12.5Cu/Si and copper-aluminium oxides (Fig. 1a) and of Al-800, 8.4Cu/Al-800, 8.4Cu/Al-900 and 8.4Cu/Al-1000 (Fig. 1b) have been reported.

In the XRD pattern of 12.5Cu/Si the presence of copper oxide is well evident, as expected due to the scarce dispersion ability of silica [22]. The presence of both copper oxide and copper aluminate can be detected in the spectra of both mixed oxides. Nevertheless, the thermal treatment at 950 °C reduces the amount of copper oxide with respect to CuAl_2O_4 .

The spectrum of γ -alumina calcined at 800 °C shows that no phase transition occurs at this temperature, in agreement with that reported by [23]. As concerns the alumina supported catalysts, only the signals of γ -alumina phase are present in the XRD pattern of 8.4Cu/Al-800 suggesting a good dispersion of the active phase in agreement with a copper content lower than that corresponding to the theoretical monolayer coverage, estimated about 10 wt.% Cu for an alumina support powder with similar surface area [24]. The thermal treatments at 900 °C and, in a greater extent, at 1000 °C, promote the formation of a bulk CuAl_2O_4 spinel, in agreement with what reported in [24] but no detectable phase transition of the support (from γ to α) takes place.

In Fig. 2 the H_2 TPR curves of 12.5Cu/Si (Fig. 2a), bulk Cu-Al oxides (Fig. 2b) and 8.4Cu/Al-800 system (Fig. 2c) have been shown. The H_2 uptake (mmol/min) has been normalized to the amount of copper present in the different samples. In Fig. 3 the values of H_2/Cu ratio, obtained by integration of the curves, have been reported.

The H_2 TPR profile of 12.5Cu/Si shows a single peak with a maximum at about 320 °C. The value of H_2/Cu ratio is 0.99, very close to the theoretical ratio corresponding to the complete reduction of CuO to Cu^0 in a single step.

The H_2 TPR curves of bulk mixed copper oxides appear more complex and the presence of six peaks has been evidenced. The first two partially overlapped contributions are probably related to the CuO phase and the other peaks to the CuAl_2O_4 , since the intensity of the first two signals decreases in the TPR profile of the sample treated at 950 °C, containing a lower fraction of CuO , in correspondence of an enhancement of higher temperatures peaks. This is also supported by the results of Severino et al. [25], who showed that copper oxide is more reducible by H_2 than copper aluminate. Moreover, the temperatures of reduction reported by these authors for the different phases are in agreement with those obtained for our samples. Nevertheless, it should be noticed that the two peak temperatures (about 200 and 240–250 °C), attributed to CuO for the bulk copper-aluminium oxides, are lower than that associated to CuO in 12.5Cu/Si sample suggesting a better dispersion of CuO in bulk

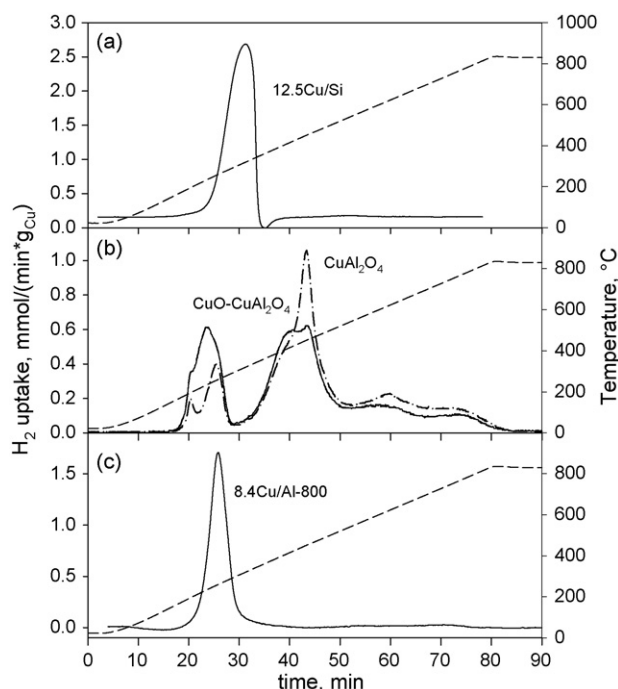


Fig. 2. H_2 TPR curves of 12.5Cu/Si (a), $\text{CuO-CuAl}_2\text{O}_4$ and CuAl_2O_4 (b) and 8.4Cu/Al-800 (c). Feed composition: H_2 2 vol.% in N_2 ; heating rate = 10 °C/min; $W/F = 0.12 \text{ g s Ncm}^{-3}$.

mixed oxide. For both mixed oxides the total H_2/Cu ratio is about 0.95 suggesting that also for these materials the initial state of the copper is Cu^{2+} even if different oxide phases are present in the samples.

All the γ -alumina supported catalysts show the same redox behaviour. In Fig. 2c the TPR curve of 8.4Cu/Al-800 sample is reported. A single peak with a maximum at about 270 °C is present. This signal has been related by Iamarino et al. [20] and Strohmeier et al. [24] to a surface CuAl_2O_4 spinel. The lower temperature of reduction with respect to bulk oxides is in agreement with a higher reducibility observed for the surface species with respect to the bulk ones. For these samples the H_2/Cu ratio is always very close to 0.5. This value can suggest that either the copper present in the fresh catalyst is not in the +2 oxidation state either that reduction is not completed and formation of Cu^+ occurs, being the +1 oxidation state quite stable in spinel type structure.

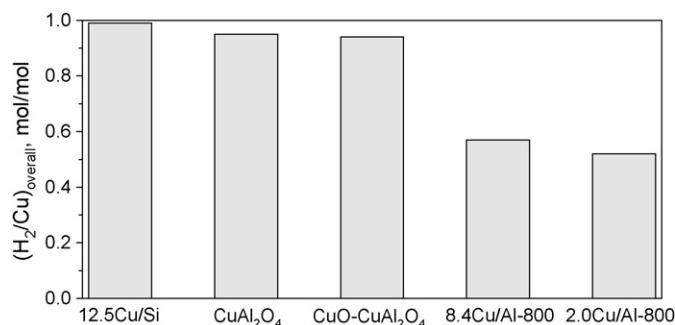


Fig. 3. H_2/Cu ratios from H_2 TPR experiments.

As described in Section 2, CO was adsorbed at room temperature on both fresh and pre-reduced with H₂ at 800 °C 8.4Cu/Al-800 catalyst.

Lokhov et al. [26] and Padley et al. [27] report that CO interact both with Cu⁺ and Cu⁰ giving bands at 2130, 2122 and 2110 cm⁻¹ for Cu⁺-carbonil complex, and at 2087–2099 cm⁻¹, for Cu⁰ complex. The presence of Cu⁺² species cannot be evidenced by this experiment.

In the FT-IR spectrum of H₂ pre-reduced 8.4Cu/Al-800 sample the signal attributed to the presence of Cu⁺ (2110 cm⁻¹) in addition to that of metallic copper (2090 cm⁻¹) appears. On the contrary no signal due to the presence of metallic copper and a very weak band associated to Cu⁺ have been observed on the fresh sample. Consequently, the H₂/Cu ratio quite lower than one found in the H₂ TPR experiment can be associated to a not complete reduction of copper rather than to the presence of copper in the +1 oxidation state in the starting material.

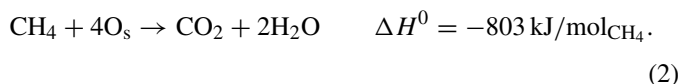
3.2. Catalytic activity measurements

Blanc tests using inert material (quartz with the same size of catalyst) have been carried out in order to verify that no homogeneous methane conversion occurs up to 900 °C under the same reaction conditions (*W/F*, inlet methane concentration) of catalytic tests. The activity of pure alumina has been also tested. A negligible methane conversion has been obtained up to 900 °C.

3.2.1. CH₄ TPR tests

In Fig. 4 the curves of CH₄ consumption and of H₂, CO and CO₂ production obtained for the 8.4Cu/Al-800 catalyst during the CH₄ TPR experiment are reported as a function of both time and temperature.

The methane consumption starts at very low temperature (about 300 °C) being initially converted to CO₂ and water by reaction with the surface oxygen (O_s) of the oxidized catalyst according to the following total oxidation reaction:



At about 500 °C, when the production of CO₂ and water is almost completely finished, the production of CO and H₂ starts related to the occurrence of the partial oxidation reaction, promoted by the reduced availability of O_s amount and the temperature increase:



The amount of H₂ produced is higher than that expected by stoichiometry of the reaction (3), suggesting that methane decomposition reaction (1) also occurs at the same time.

The rates of methane decomposition and of hydrogen production strongly increase at about 600 °C and the maximum value of methane conversion (>40%) is reached at about 800 °C. Subsequently, a rapid activity decay due to carbon deposition is observed.

The H₂ production is associated to the presence of reduced copper obtained by reduction of the catalyst with methane and

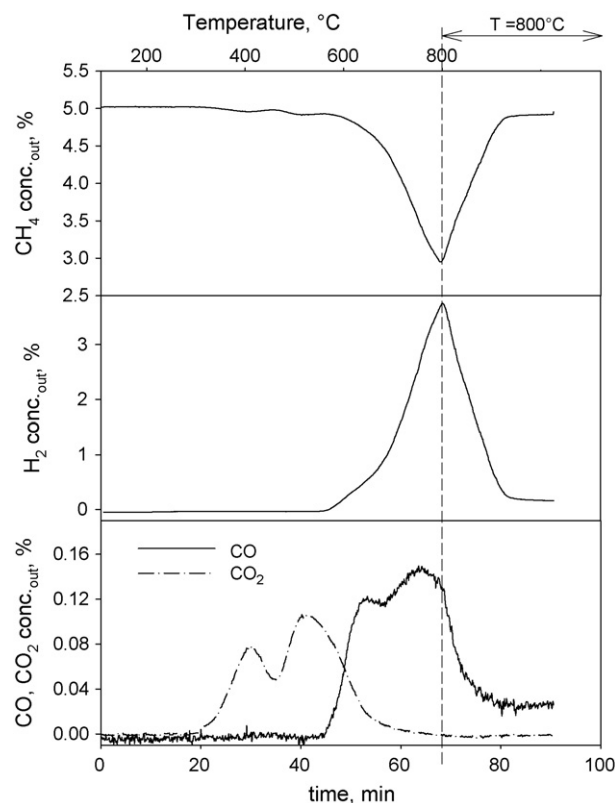


Fig. 4. CH₄ TPR curves of 8.4Cu/Al-800 sample. Feed composition: CH₄ 5 vol.% in N₂; heating rate = 10 °C/min; *W/F* = 0.25 g s Ncm⁻³.

consequent CO₂, H₂O and CO productions. In fact, the amounts of CO₂, H₂O and CO produced (1.32 mmol/g_{cat}) are in agreement with those expected on the basis of the amount of surface oxygen of active phase (O_s) present in the oxidized catalyst (1.32 mmol/g_{cat}). This result also shows that methane can reduce copper more deeply than hydrogen.

A residual activity is evident since base line for all gaseous species is not restored.

The same tests have been performed on the catalysts treated at higher temperatures (8.4Cu/Al-900 and 8.4Cu/Al-1000). The concentration profiles of all gaseous species obtained are superimposable to those reported in Fig. 4 for the sample 8.4Cu/Al-800, suggesting that this catalytic system is stable up to 1000 °C.

The temperature of the maximum methane conversion apparently corresponds to the end of the heating ramp, however, the same temperature of deactivation (820 °C) has been found in further experiments performed on 8.4Cu/Al-900 and 8.4Cu/Al-1000 heating up to 900 and 1000 °C, respectively (Fig. 5). This behaviour suggests that the maximum is probably related to the amount of carbon accumulated on the catalyst reaching a threshold value (34 mg/g_{cat}) that, when exceeded, results in the catalyst deactivation. In Fig. 5 it is also possible to observe that at temperatures higher than 900 °C the homogeneous reaction of methane decomposition starts and the conversion of methane increases rapidly again even if the catalyst is deactivated.

The heating rate affects the amount of carbon deposited on the catalyst. 34 mg_C/g_{cat} are deposited heating the sample 10 °C/min

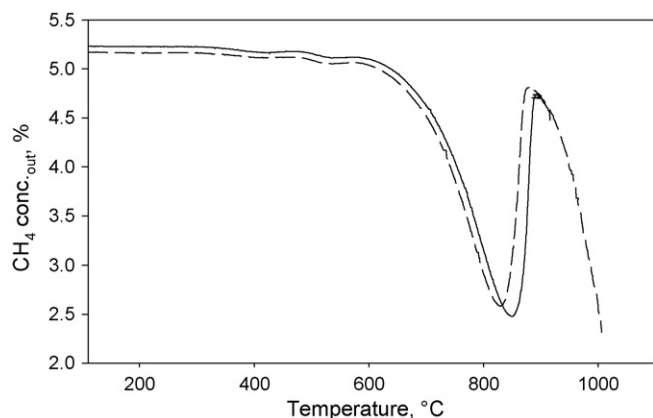


Fig. 5. CH₄ TPR curves of 8.4Cu/Al-900 (—) up to 900 °C and 8.4Cu/Al/1000 (---) up to 1000 °C. Feed composition: CH₄ 5 vol.% in N₂; heating rate = 10 °C/min; W/F = 0.25 g s Ncm⁻³.

while 60 mgC/g_{cat} are deposited with a 2 °C/min heating rate. This is likely due to higher carbon deposition rate in the former case which can inhibit its further deposition due to diffusion limitations.

The results of CH₄ TPR suggest that the range of applicability of these catalysts for purely catalytic methane decomposition is 600–900 °C. The catalyst is stable also at higher temperatures when the homogeneous reaction occurs in addition to the catalytic one. This range is the same found for Pd-based catalysts [13] but with the advantage to use a less expensive active phase.

3.2.2. Isothermal methane decomposition tests

Curves of CH₄ consumption, H₂ and CO_x production obtained during a methane TCD test carried out on the 8.4Cu/Al-800 sample at 800 °C in the fixed bed reactor are reported in Fig. 6 as a function of time. A 5% CH₄/N₂ mixture is fed to the reactor.

As already observed for the TPR tests, at the beginning methane is converted to CO₂ and water reacting with a fraction (about 60%) of the oxygen O_s of the oxidized catalyst according to the total oxidation reaction (2). This reaction is faster than those of decomposition (1) and partial oxidation (3) and, consuming completely CH₄, inhibits the occurrence of the latter reactions.

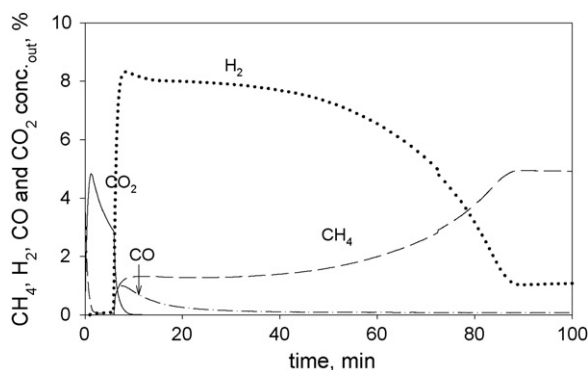


Fig. 6. Methane decomposition activity test in fixed bed reactor on 8.4Cu/Al-800 catalyst. Feed composition: CH₄ 5 vol.% in N₂; T = 800 °C; W/F = 2.8 g s Ncm⁻³.

After this initial step the reaction (2) is suppressed and CO is produced according to the reaction (3), suggesting that a lower surface oxygen availability inhibits the reaction (2). At the same time the decomposition reaction starts and H₂ is produced according to both reaction (1) and reaction (3). The simultaneous occurrence of both reactions probably generates the initial sharp H₂ peak.

For longer times, when CO concentration is close to zero, H₂ is mainly produced according to the reaction (1) and the partial oxidation reaction (3) is quite suppressed due to the poorer O_s availability. During this step the rate of both CH₄ consumption and H₂ production decreases as a result of the decrease of catalyst activity due to carbon deposition.

After this transient period, CH₄ conversion does not drop to zero but keeps a not negligible value (about 10%). This behaviour agrees with that observed during the CH₄ TPR experiments. This residual activity could be attributed to deposited carbon as reported by many authors [2,3,28,29].

The value of maximum methane conversion to hydrogen (78%) is far from that estimated by thermodynamic equilibrium ($X_{\text{methane}} = 99.1\%$ at 800 °C for methane concentration of 5 vol.%) but, as suggested by the observed trend of methane conversion as function of W/F ($X_{\text{methane}} = 23.1, 29.5, 44.2\%$ for W/F = 0.25, 0.34, 0.69 (g s Ncm⁻³), respectively), higher conversions can be obtained increasing W/F. As expected, the copper based catalyst is more active than carbon which provides a methane conversion of 75% at 850 °C with W/F = 4 g s Ncm⁻³ [3]. Instead it is less active than the best noble metals system (Pd-Co) which provides a methane conversion of 55% at 800 °C but with a very low contact time (0.02 g s Ncm⁻³) [13].

For both 0.4Cu/Al-800 and 2.0Cu/Al-800 catalysts a similar qualitative behaviour has been found.

In Fig. 7 the concentration profiles for bulk CuAl₂O₄ (Fig. 7a) and 12.5Cu/Si (Fig. 7b) systems, under the same conditions used for alumina supported catalysts, are reported. They both show a trend similar to that found for the 8.4Cu/Al-800 catalyst,

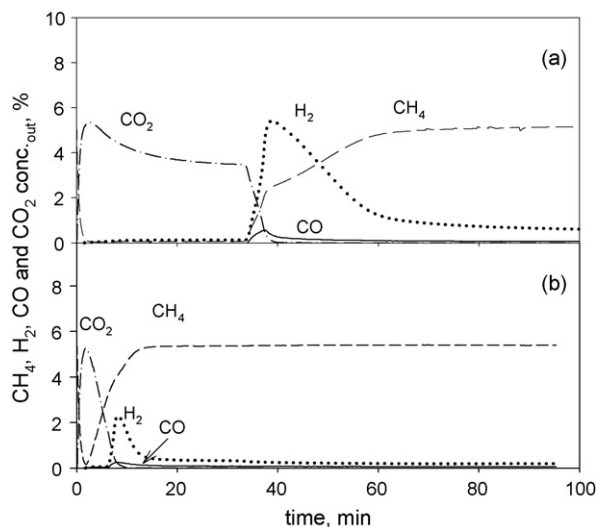


Fig. 7. Methane decomposition activity test in fixed bed reactor on CuAl₂O₄, W/F = 2.8 g s Ncm⁻³ (a), and on 12.5Cu/Si, W/F = 1.4 g s Ncm⁻³ (b). Feed composition: CH₄ 5 vol.% in N₂; T = 800 °C.

Table 2

Time between starting of H₂ production and catalyst deactivation, contact time and amounts of methane converted and gaseous products per mass of catalyst in the TCD isothermal tests evaluated up to the catalyst deactivation

Catalyst	Δt (min)	Contact time (g s Ncm ⁻³)	CH ₄ /m _{cat} (mmol/g)	CO/m _{cat} (mmol/g)	CO ₂ /m _{cat} (mmol/g)	H ₂ /m _{cat} (mmol/g)
CuAl ₂ O ₄	30	2.8	2.26	0.09	1.27	1.10
12.5Cu/Si	10	1.4	0.68	0.16	0.44	0.55
8.4Cu/Al-800	80	2.8	2.84	0.16	0.21	4.88
2.0Cu/Al-800	40	2.8	1.07	0.13	0.07	1.94
0.4Cu/Al-800	20	2.8	0.28	0.14	0.02	0.60

Δt = time between starting of H₂ production and catalyst deactivation.

H₂ production starting when CO₂ formation, related to copper reduction, is completed. Nevertheless, the relative amount of products is very different. In Table 2 a comparison of the efficiency of all catalysts in terms of time between starting of H₂ production and catalyst deactivation and amounts of CH₄ converted and gaseous products per mass of catalyst, evaluated up to the catalyst deactivation, is reported. The 8.4Cu/Al-800 catalyst produces the highest H₂ amount and deactivates after the longest time.

In order to make a direct comparison among the different systems, independently on the amount of copper present in the catalyst and on the different contact times, the moles of methane converted and those of CO₂, CO and H₂ produced in the isothermal decomposition tests, integrated for the whole lengths of the experiments and normalized to the amount of copper present in the catalyst, are reported in Table 3.

The H₂/Cu and CH₄/Cu ratios clearly show that the activity towards methane TCD reaction of CuAl₂O₄ and 12.5Cu/Si is about 10 times lower than that obtained for the alumina dispersed copper systems. The different activity cannot be attributed to the different surface area of the catalyst, since the silica supported sample shows a high BET area, but should be probably associated to a different activity of the copper oxide phases. Furthermore, Cu-Al mixed oxides, mainly constituted of CuAl₂O₄, have almost the same activity of the 12.5Cu/Si sample, although a very low surface area. These results suggest that the copper oxide, even if dispersed, is not active for methane decomposition as the aluminate phase.

The low activity measured for 12.5Cu/Si is in agreement with the results reported by Matsukata et al. [18] even if these authors do not relate the poor activity of this system to the presence of copper oxide.

Among the alumina dispersed systems the activity per mole of copper increases with decreasing of copper amount in the catalyst, i.e. with increasing of dispersion.

A quite good correlation between the H₂/CO ratio and the amount of copper present in the catalyst has been observed from data reported in Table 3. The production of hydrogen enhances with the increasing copper load more than the production of CO. This suggests that highly dispersed copper activates reaction (3) more than reaction (1).

The CO₂/Cu ratio is not constant for all catalysts and the extent of the reduction by methane, evaluated on the basis of CO₂ production, corresponds to the same reduction level obtained by H₂ TPR experiments. According to this result, a reducing treatment with hydrogen completely suppressed the formation of CO₂ during the methane decomposition. On the contrary, CO/Cu ratio follows about the same trend found for CH₄/Cu and H₂/Cu suggesting that catalysts active in the methane decomposition are also active in the partial oxidation.

Finally, it is worth noting that a smaller amount of carbon (17 mg_C/g_{cat}, calculated from a balance on carbon species for the 8.4Cu/Al-800 catalyst) has been deposited during the isothermal test with respect to that deposited during methane TPR test (34 mg_C/g_{cat}), confirming that the rate of methane decomposition affects the amount of produced carbon. On the contrary, the value of CO₂/Cu ratio obtained during the isothermal test (0.16) is the same of that obtained in the TPR test (0.17) in agreement with a CO₂ formation associated to the reduction of active phase.

3.2.3. TG analysis

A quantitative analysis of carbon deposition has been obtained by carrying out TGA experiments under conditions similar to those of catalytic tests. In Fig. 8 the results of the experiment performed on 8.4Cu/Al-800 catalyst is reported. The sample is initially heated in Ar and only when the temperature reaches 800 °C and the weight of the sample is stable, methane is introduced into the feed. The weight loss observed under Ar flow is due both to the desorption of adsorbed species, as CO₂ and H₂O, and to the condensation of OH groups on the

Table 3

Amounts of methane converted and gaseous products per Cu amount in the catalyst in the TCD isothermal tests evaluated up to the catalyst deactivation

Catalyst	CH ₄ /Cu (mol/mol)	CO/Cu (mol/mol)	CO ₂ /Cu (mol/mol)	H ₂ /Cu (mol/mol)	H ₂ /CO (mol/mol)
CuAl ₂ O ₄	0.41	0.02	0.23	0.20	12.1
12.5Cu/Si	0.35	0.08	0.22	0.28	3.50
8.4Cu/Al-800	2.15	0.12	0.16	3.70	30.9
2.0Cu/Al-800	3.40	0.41	0.22	6.16	15.1
0.4Cu/Al-800	4.50	2.20	0.24	9.50	4.30

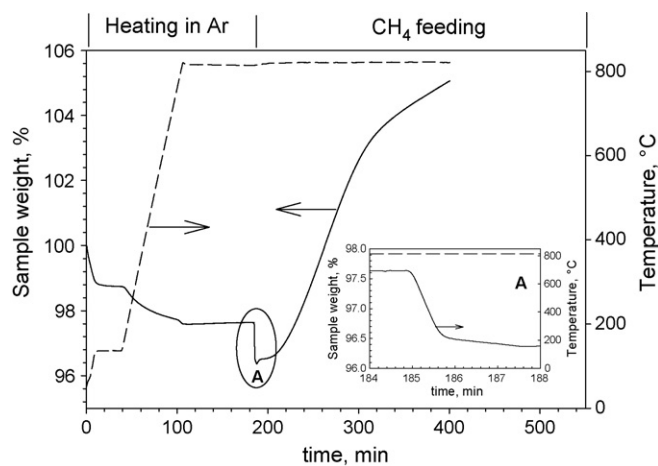


Fig. 8. TGA experiment for 8.4Cu/Al-800 catalyst. Sample weight (—) and temperature (---) curves.

catalyst surface; the weight loss associated to this second step (1.17 wt.%) is in good agreement with the OH surface density typical of γ -alumina (3.6×10^{-6} mol/m² corresponding for our alumina to 1.02 wt.% weight loss) [30]. When methane is introduced, a rapid decrease of sample weight, due to the reduction of catalyst, has been observed, as also observed in the isothermal experiments previously described. Formation of CO₂ and H₂O was detected at the same time. This reduction is very fast at 800 °C, as shown by the apparently vertical weight loss evidencing a slope of -1.14% min, corresponding to an initial methane conversion rate of 6.7 μ mol/min, determined only by expanding the scale. Afterwards, the sample weight increases due to the accumulation of the carbon produced on the catalyst surface confirming that the catalyst is active in the methane decomposition. The change of the weight curve slope, observed at about 300 min, is probably due to the catalyst deactivation and to the residual activity of the deposited carbon.

3.2.4. Characterization of deposited carbon

SEM analysis carried out on the samples after methane decomposition tests shows that no carbon fibres with the metal particles on their tips grew on the catalyst surface up to 800 °C, in contrast with that observed for nickel and iron based catalysts. The carbon grains produced during the decomposition are uniformly dispersed on the surface of the catalyst.

The amount of carbon deposited on the samples after methane decomposition tests, determined by carbon elementary analysis of samples, is in agreement with the stoichiometric amount calculated by the carbon balance on species consumed and produced during the CH₄ decomposition tests. This analysis also shows that the deposited carbon is very poorly hydrogenate.

3.3. Properties for fluidized bed applications

The most efficient catalytic system, 8.4Cu/Al-800, has been tested as regards its behaviour in fluidized bed reactors in preliminary tests carried out by means of a laboratory scale apparatus. The bed consisted of 50 g of catalyst particles in the granulometric size range 300–400 μ m. According to the size and density

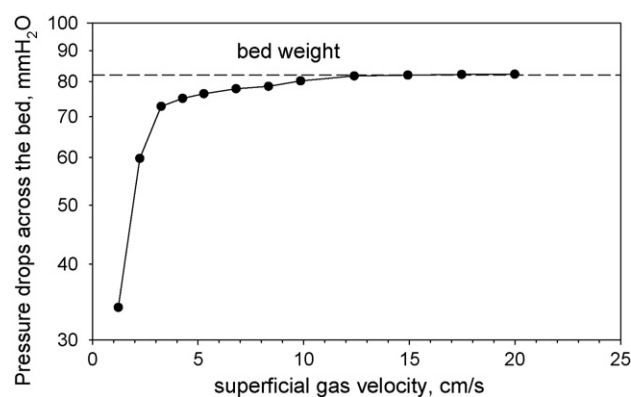


Fig. 9. Pressure drops curve of 8.4Cu/Al-800 catalyst (300–400 μ m) at 800 °C and atmospheric pressure in nitrogen flow.

of the bed particles they belong to the B group of Geldart classification of powders. Analysis of pressure drops curve as a function of the superficial gas velocity, reported in Fig. 9, suggested that a stable bubbling fluid-dynamic behaviour was established. The experimental data were worked out to calculate the value of the minimum fluidization velocity (u_{mf}) at bed temperature. The value obtained (2.9 cm s⁻¹) is in good agreement with that expected on the basis of Wen and Yu literature correlation [31].

As regards mechanical behaviour of the catalyst, an average attrition rate of $E_a = 1.5 \times 10^{-5}$ g/min has been obtained under the experimental conditions investigated. This very low value indicates a very low propensity of catalyst to generate fines avoiding the risk of a catalyst loss and environmental impact during fluidized bed operation.

Performances of this catalytic system in TCD of methane have been studied in an experimental campaign carried out in both fixed and fluidized bed reactor as reported elsewhere [32]. The results showed that, although a mechanical regeneration of surface catalyst by attrition was not possible, there are some promising features to carry out the TCD process in fluidized bed reactor for a continuous hydrogen production.

4. Conclusions

Alumina supported copper is active in the thermo-catalytic decomposition methane and CO₂ free hydrogen is produced starting from 600 °C provided that a pre-reduction treatment is carried out. The catalyst is stable up to 1000 °C.

The active phase has been identified as copper aluminium surface spinel, supported copper oxide having on the contrary a very poor activity.

The intrinsic activity of copper in the spinel structure increases with enhancing dispersion of the active phase, however, the catalyst with a copper load approaching that corresponding to the theoretical monolayer coverage, gives the best performances on the basis of total hydrogen production and catalyst duration before deactivation by carbon deposition. Moreover, the production of hydrogen enhances with the increasing copper load more than the production of CO.

The carbon deposited on the catalyst surface shows a residual activity. The absence of carbon nanofibres with the metal particle on their tips and the low attrition propensity of the 8.4Cu/Al-800 could represent promising features for the use of this catalyst in fluidized bed reactors to develop a continuous process for hydrogen production.

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