H$_2$ production by catalytic methane decomposition on Cu based catalyst

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ABSTRACT:

The thermocatalytic decomposition (TCD) of methane has been investigated in a laboratory scale fixed bed reactor using a copper dispersed on γ-alumina as a catalyst. The usefulness of a fluidized bed operation instead of a fixed bed one has been assessed in terms of methane to hydrogen conversion, amount of carbon accumulated on the catalyst, possibility of the catalyst regeneration. The results highlight some promising features in using fluidized bed reactors in the TCD process.

KEYWORDS : hydrogen production, methane catalytic decomposition, fluidized bed, copper based catalyst

1. Introduction

The thermocatalytic decomposition of methane (TCD) is an attractive process to produce hydrogen. In addition as result of the absence of oxidants, no carbon oxides are expected to be formed in this process. An additional feature of TCD process is the possibility to produce significant amount of carbon, which could be used in different applications, but, of course, it requires a separation step to remove carbon from the catalyst. On the other side, carbon has itself catalytic properties with reference to TCD process, but, in this case, relatively low methane conversions, lower than 30%, have been observed [1, 2].The use of fixed bed reactors has been proposed in the past in different published papers [3, 4, 5, 6]. However, some issues have been highlighted: relatively high pressure drops, further increased during operation by the accumulation of carbon in the bed [3, 4]; impossibility of a continuous operation due to the necessity to unload carbon and in turn to regenerate the catalyst. To overcome these drawbacks Choudhary et al. [4] proposed the use of two parallel fixed bed catalytic reactors in which gas feed was alternately changed from methane to steam, with the goal of obtaining the catalyst regeneration by gasification of carbon. On the other hand, fluidized bed reactors have been recently proposed [1, 7] as a useful solution to operate with lower pressure drops and to carry out a continuous production of hydrogen.

With reference to catalyst options, those containing Ni [5] and Fe [6] have largely been tested in the past. The first has a maximum operative temperature of 600°C, above which it is deactivated by sintering of Ni particles. The Fe based catalysts are stable up to 800°C. For both catalysts, deposited carbon has generally a filamentous form (nanofibres or nanotubes), characterized by the presence of metal particles on their tips. This is an undesirable feature with reference to application in fluidized bed reactor where attrition is likely to remove the active metal phase away from the support, resulting in a decrease of hydrogen production and consumption of expensive metals of the catalysts [8].

On the basis of the above considerations fluidized bed reactors are suitable for the design a continuous process for hydrogen production based on a two-stage process including decomposition of methane and catalyst regeneration, even if some issues are to be actually answered. One these is the set-up of a catalytic system able to work at elevated temperatures in order to improve methane conversion (thermodynamically limited) and at the same time stable to repeated decomposition and regeneration operations.

In this work, a γ-alumina dispersed copper catalyst was used in fixed bed reactor in order to characterize its effectiveness in CH$_4$ decomposition at 800°C, first step required to use this catalytic system in the future in a cyclic process of hydrogen production carried out by means of fluidized bed reactors. The same catalyst has been also employed in the fluidized bed reactor and a comparative analysis of two different laboratory scale, fixed and fluidized bed, reactors during methane TCD tests has been performed on the basis of methane to hydrogen conversion and amount of carbon accumulated on catalyst particles.

2. Experimental

The catalysts were prepared by wet impregnation by dissolving the required amount of copper acetate in aqueous solution and adding a suitable ammount of γ-Al_2O_3 as reported in [9] and calcined for 3h in air flow at 800°C. The applicability of this copper based catalyst for fluidized bed operations, concerning its mechanical stability, has been reported by the same Authors. The copper contents were determined using a 7500CE Agilent ICP-MS after dissolving the sample in HCl and HNO_3 solution at 80°C. A PW 1100 Philips diffractometer was employed for the X-ray diffraction (XRD) patterns. BET surface areas were measured by N_2 adsorption at 77 K with a Carlo Erba 1900 Sorpomatic instrument. Thermogravimetric analysis was performed with a Perkin-Elmer TGA-7 coupled with a Perkin-Elmer spectrum GX FTIR for the analysis of the released gases, heating the sample 10°C min^{-1} in Ar up to 800°C and, when the weight of the sample is stable, adding methane (5%vol.) to the feed. Scanning Electron Microscopy (SEM) was performed with a Philips XL30 apparatus equipped with an EDAX instrument.

The experimental apparatus used consists of a 2.6 cm ID stainless steel reactor, equipped with a gauze type gas distributor, an electrical oven surrounding the reactor employed to heat up the reactor at the reaction temperature and to provide enough heat for methane decomposition, a device for collecting fine particles larger than 300nm escaping from the reactor in the exit gases. The same reactor has also been used under conditions of fixed or fluidized bed by moving gas feed from the top to the bottom of the bed and vice versa respectively. Bed temperature and pressure drops were measured by means of thermocouples horizontally inserted in the reactor and pressure transducers respectively. The inlet and outlet streams were analyzed by an on line continuous analyzer Hartmann & Braun URAS 14 for the analysis of CO, CO_2 and CH_4 and CALDOS 17 for H_2.

H_2 Temperature Programmed Reduction (TPR) experiments were carried out in an experimental apparatus equipped with a fixed bed quartz micro-reactor (11mm ID) operating under atmospheric pressure. The inlet and outlet streams were analyzed by the on line continuous analyzer Fischer-Rosemount NGA 2000 equipped with a TCD detector. The sample was reduced by a 2% H_2/N_2 mixture heating 10°C min^{-1} up to 800°C. The space time was 0.12 g·s·Ncm^{-3}. The analysis of carbon deposed on the catalyst was performed by the elemental analyzer CHN2000 LECO. Carbon balance was closed within 4% error in all experiments.

3. Results and discussion

3.1 Catalyst characterization

The copper amount of the catalyst is 8.4 wt%.

The surface area of catalyst (156m^2/g) is very close to that of support (164m^2/g) suggesting a good dispersion of the active phase in agreement with a copper content lower than that corresponding to monolayer coverage, estimated about 10wt.% Cu for an alumina support powder with similar surface area [10]. In agreement with this result no signals corresponding to CuO, in addition to those corresponding to the support, are present in the XRD spectra shown in Figure 1. The active phase probably corresponds to a surface $CuAl_2O_4$ spinel not detectable by XRD analysis.
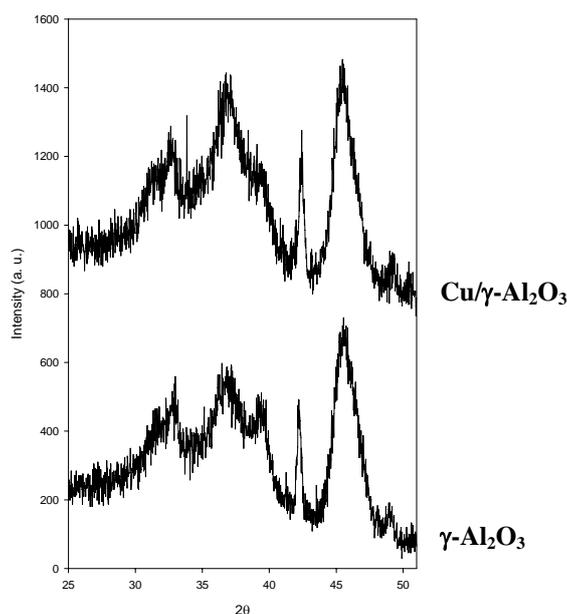

Figure 1   XRD spectra of support and catalyst.

3.2 TPR measurements

In Figure 2 the curves of H_2 consumption obtained during the H_2 TPR on the catalyst and temperature are reported as a function of the time.

A single peak with a maximum at about 270°C is present in the H_2 TPR curve.

This signal has been related to a surface $CuAl_2O_4$ spinel as reported in [9, 10] and confirms the formation of this active phase.
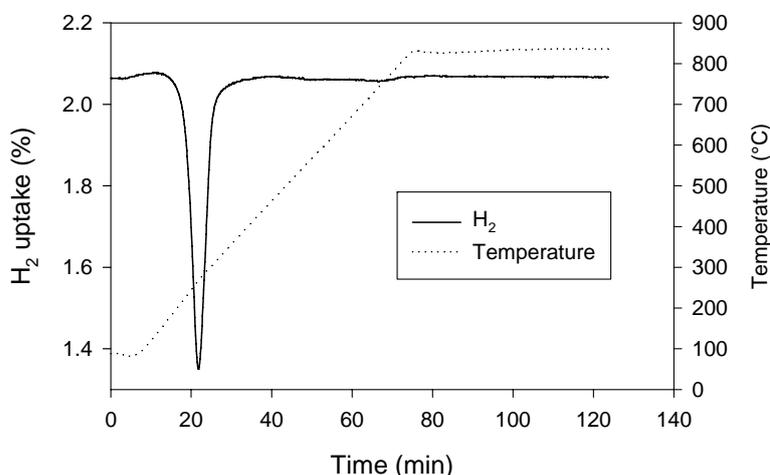

Figure 2 H_2 TPR. Feed composition: H_2 2%vol in N_2, heating rate=10°C/min, W/F= 0.12gs/Ncm^3.

The H_2/Cu ratio obtained for the catalyst is lower than one (0.64), suggesting that not all the copper present in the catalyst is present in the from Cu^{2+} or that the hydrogen is not able to reduce all the copper present in the catalyst to metallic one (Cu^0) at 800°C.

3.3 TG analysis

The effectiveness of this catalyst with respect to methane decomposition has been previously verified by the thermogravimetric analysis. In Figure 3 the curves of weight variation of sample obtained during the experiment and temperature are 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 added to the feed. The loss of weight observed under nitrogen is due both to the desorption of adsorbed species and to the condensation of OH group; the weight loss is in good agreement with the OH density typical of alumina ($3.6 \cdot 10^{-6}$ mol/m^2) as reported in [11]. When the methane is introduced a rapid decrease of weight of the sample due to the reduction of catalyst and the formation of CO_x has been observed. Subsequently the sample weight increases due to the accumulation of the carbon produced by methane decomposition on the catalyst surface. The change of the slope of the curve, observed at about 300 minutes is probably due to deactivation of catalyst and the residual activity of the deposited carbon.
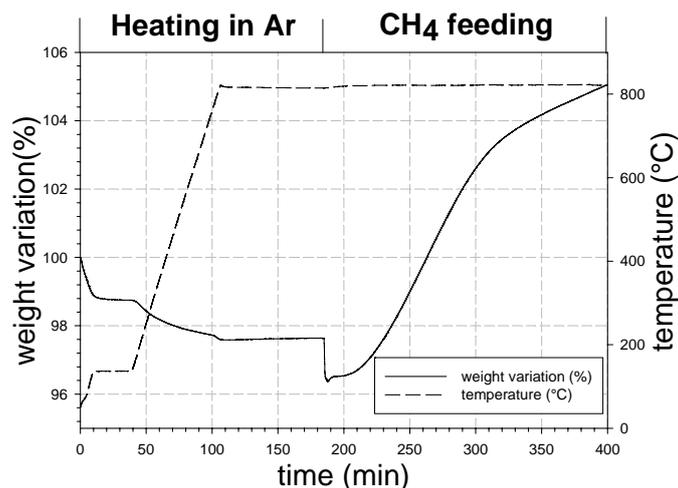
Figure 3   Weight variation of catalyst during the thermogravimetric test. Heating rate 10°C/min from 50°C to 800°C in Ar. Mixture composition 5%vol. CH_4 /Ar, F_{tot}= 50 Nml/min, temperature=800°C.

3.4 Catalytic test

Typical curves of CH_4 conversion and of H_2 production obtained during a TCD test carried out in the fixed bed reactor are reported in Figure 4 as a function of time. At time t=0 an inlet gas made of methane (5% vol.) and nitrogen is fed to the reactor.
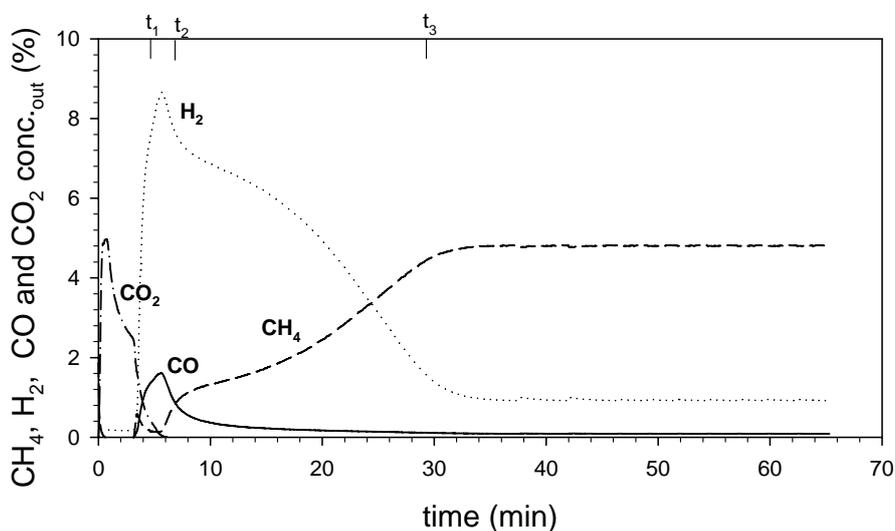
Figure 4   Typical catalytic activity test in the fixed bed reactor. Feed composition: CH_4 5%vol in N_2; T_r=800°C;; w_{cat}=25g; F=60Nl/h.

The figure shows an initial stage, $0<t<t_1$, in which all the methane is converted to CO_2 and water reacting with a part (about 60%) of the oxygen O_s present in the oxidized catalyst (linked to the copper) according to the total oxidation reaction:

$$4\ O_s + CH_4 \rightarrow CO_2 + 2\ H_2O. \qquad\qquad\qquad \Delta H^0 = -\ 803kJ/mol_{CH4} \qquad (1)$$

This reaction is faster than those of decomposition and partial oxidation. This behaviour is in agreement with the loss of weight observed during the TG experiment when the methane is injected on the sample.

At time $t_1 < t < t_2$ CH_4 still reacts with the residual oxygen O_s of the catalyst but the total oxidation reaction (1) is suppressed and CO_2 and water are not produced, probably due to the reduced O_s availability; CH_4 partial oxidation becomes favourite and CO is produced according to the reaction:

$$O_s + CH_4 \rightarrow CO + 2\,H_2 \qquad\qquad \Delta H^0 = -36\,kJ/mol_{CH4} \qquad (2)$$

At this time the decomposition reaction also occurs and H_2 is produced according to reaction (2) and to reaction of methane decomposition:

$$CH_4 \rightarrow 2\,H_2 + C. \qquad\qquad \Delta H^0 = +75\,kJ/mol_{CH4} \qquad (3)$$

This justifies the initial observed hydrogen peak.

The H_2 production is probably promoted by presence of reduced copper obtained by reduction of the catalyst with methane. In fact, the CO_2 and CO ratios obtained are in quite good agreement with those expected on the basis of the amount of surface oxygen of active phase (O_s) present in the oxidized catalyst.

At time $t_2 < t < t_3$ CH_4 is mainly decomposed according to the reaction (3) while the partial oxidation reaction is quite suppressed because O_s availability is poor; as a consequence rather limited CO concentration is measured. As time increases decomposition rate decreases as a result of the decrease of catalyst activity due to carbon deposition.

Finally, at time $t > t_3$ CH_4 conversion does not drop to zero and a relatively low value is observed. This residual activity could derive from a residual catalyst activity in CH_4 decomposition played by the deposited carbon [1, 7, 12].

As regards the energy balance it must be noted that apart from the time intervall $t < t_1$ the process requires energy.

In Figure 5 the curves of CH_4 consumption and of H_2, CO and CO_2 production obtained during the experiments of CH_4 decomposition carried out in fixed and fluidized beds are reported as a function of time.

In both cases similar CH_4 and H_2 profiles are obtained. However, there are some important differences obtained under similar operative conditions and fixed or fluidized bed regimes: a shorter deactivation time, a lower H_2 production and larger pressure drops (ΔP) across the bed have been obtained in fixed bed
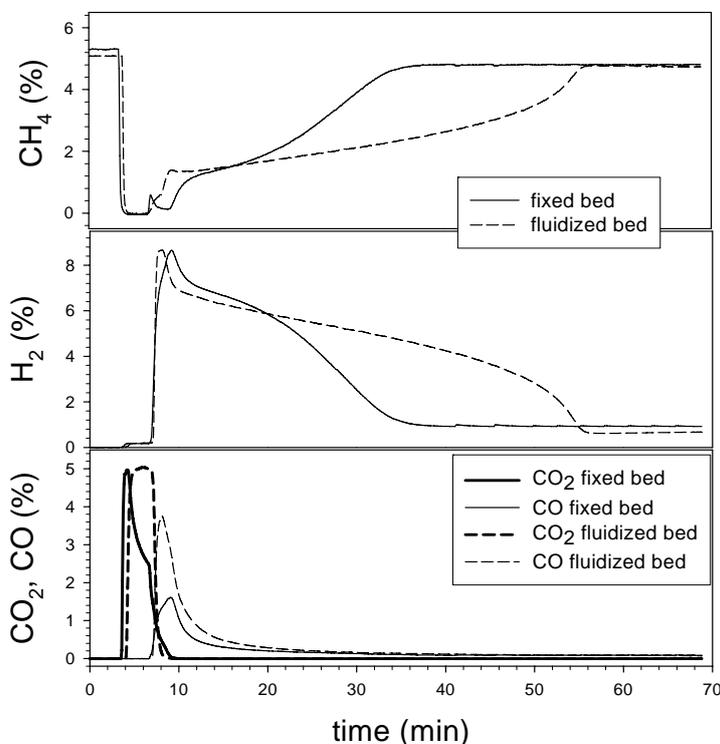
Figure 5   Comparison of catalytic activity test in fixed (continuous line) and fluidized bed (dashed line) reactors. Feed composition: CH_4 5%vol in N_2; T_r=800°C; w_{cat}=25g (H/D=2.5); F=60Nl/h (u_0/u_{mf}=4).

conditions. Deactivation times of 30min and 50min and H_2 production of 2.5mmol/g_{cat} and 4.0mmol/g_{cat} and ΔP=130mmH_2O and 40mmH_2O have been obtained in fixed and fluidized bed conditions respectively.

A regeneration treatment (2%vol O_2 at 700°C) in fluidized condition completely restores the initial activity of the catalyst by oxidation of the carbon deposited on the catalyst surface. In the Figure 6 the results obtained on the fresh and regenerated catalyst have been compared in terms of hydrogen production.
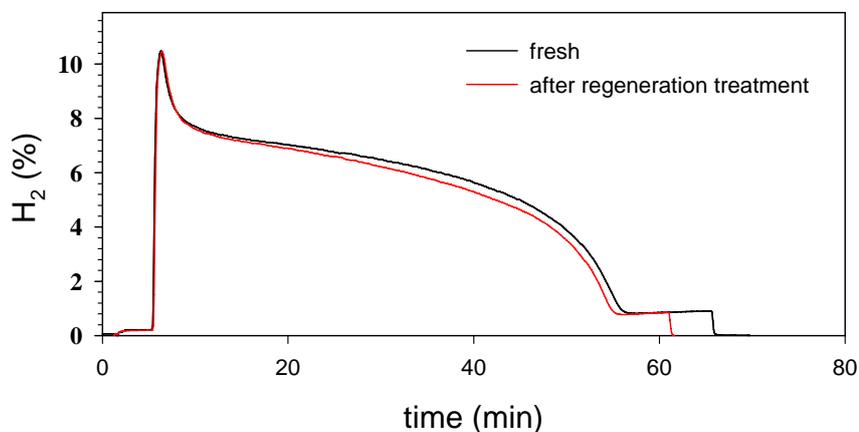

Figure 6 H_2 production as function of time of stream obtained in fluidized bed on the fresh and regenerated catalyst. W/F=1.96gs/Ncm^3 (w_{cat}=25g, F=45Nl/h); Feed composition: CH_4 5% vol. in N_2; T=800°C.

3.5 SEM and Carbon elementary analysis

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 produced during the decomposition is uniformely dispersed on the surface of the catalyst as is possible to see in the Figure 7 where the immagines of internal surface before (7a) and after (7b) the reaction are reported.
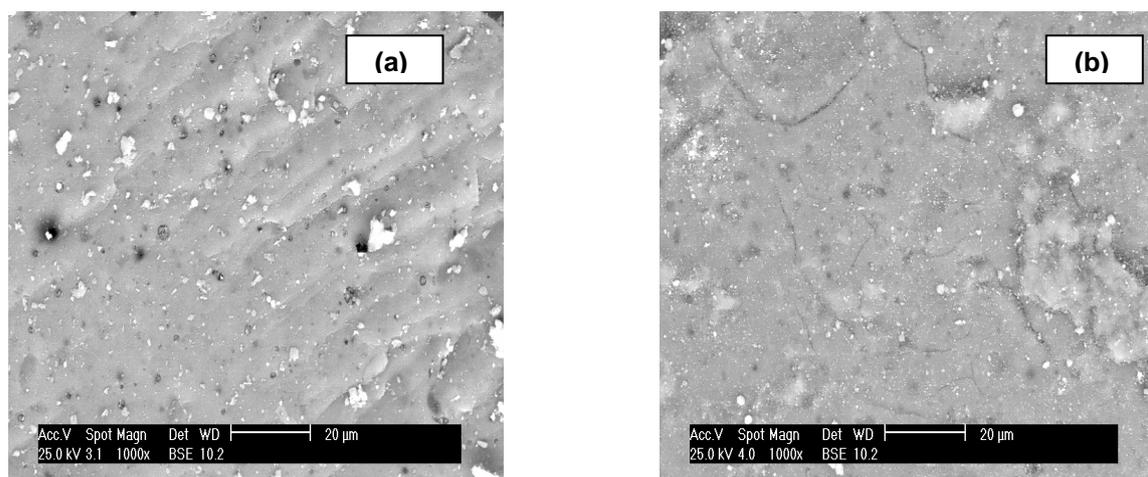
Figure 7. SEM imagines of catalyst internal surface before (a) and after (b) the methane decomposition test.

The amount of carbon deposed on the samples after methane decomposition tests determinated by carbon elementary analysis of samples is in agreement with the stochiometric amount calculated by the H_2 produced during the CH_4 decomposition tests according to reaction (3). This analysis also shows that deposited carbon is very poor hydrogenate (H/C ratio is very close to zero).

When the catalyst undergoes to a rigeneration treatment (2%O_2 in N_2 at 700°C) the surface is completely clean and all the carbon is removed as determined by SEM and carbon elementary analysis perfomed on the regenerated sample.

4. Conclusions

The Cu/Al catalytic system, active in the decomposition of methane at 800°C, has been tested for the thermocatalytic decomposition (TCD) of methane in a laboratory scale fixed bed reactor.

The reduced copper is the active phase of the catalyst for the methane decomposition. No carbon nanofibers are produced on the surface of catalyst up to 800°C. The system is more active than a carbon catalyst and it is stable under decomposition-regeneration cycles (the activity of catalyst is completely restored after an oxidizing treatment).

These aspects, in addition to its high mechanical resistance, make this catalytic systems very promising to its application in a fluidized bed reactor for continuous hydrogen production.

The use of catalyst in the fluidized bed reactors shows that a better performance in a fluidized bed reactor compared to that of a fixed bed could be achieved in terms of methane to hydrogen conversion and amount of carbon accumulated on catalyst particles. In any case, high methane conversions have been obtained even if several hundreds of ppm of CO were produced.

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The total Full Text length should not exceed 10 to 12 pages. English language must be used.

Insert all figures and tables in the text. The figures must be easy to read and understand.

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