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Cu/γ-Al_2O_3 catalyst for the combustion of methane in a fluidized bed reactor

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Abstract

The applicability of a catalyst based on copper dispersed on γ-Al_2O_3 spheres (1 mm diameter) for fluidized bed catalytic combustion of methane has been assessed. Catalyst properties have been determined by physico-chemical characterization techniques and fixed bed activity tests revealing the presence of a surface $CuAl_2O_4$ spinel phase, still active and stable in methane combustion after repeated thermal ageing treatments at 800 °C. Methane catalytic combustion experiments have been performed in a 100 mm premixed fluidized bed reactor under lean conditions (0.15–3% inlet methane concentration), showing that complete CH_4 conversion can be attained below 700 °C in a fluidized bed of 1 mm solids with a gas superficial velocity about twice the incipient fluidization velocity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; Fluidized bed; Methane

1. Introduction

Catalytic combustion of methane stems out as a clean and efficient alternative to conventional flame combustion [1–3] promoting full oxidation of methane on suitable catalysts at relatively low temperatures, and thus reducing NO_x, CO and unburned fuel emissions. Moreover, catalytic combustion enables burning of air/fuel mixtures well outside the flammability limits, a very attractive feature for safer domestic applications or for energy recovery from diluted hydrocarbon streams (VOC combustion) [4,5].

Noble metal-based catalysts—especially PdO—are by far the most active for catalytic combustion applications [1,2]. However, the activity of transition metal oxides, both simple and mixed-type systems, in total oxidation of hydrocarbons has also been investigated in the past and is still pursued because of their lower cost compared to noble metals [6–8]. One of the most compelling issues for the application of catalytic combustion is the effectiveness of heat withdrawal from the catalyst as compared with the rate of heat release, which affects catalyst over-heating and, in turn, thermal deactivation [2]. This issue is closely related to the need for catalytic systems with enhanced thermal stability, since high temperatures (above 800 °C) are easily reached in energy production systems even under very lean conditions. Unfortunately, poor thermal resistance is exhibited by noble metal-based catalysts because of their high volatility. Furthermore, PdO decomposes into the much less active metallic Pd above 800 °C [3]. In practice, the use of palladium can only be envisaged at lower temperatures or in hybrid systems, where fuel combustion is partly performed over the catalyst (up to 800 °C) and partly as gas-phase homogeneous reaction.

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Transition metal oxides such as CuO, Co_3O_4, NiO, Mn_3O_4 and Cr_2O_3 also display significant activity for hydrocarbon oxidation [9]. Among them, copper-based catalysts have been already successfully employed in VOC abatement processes [5]. Perovskite-type mixed oxides and hexa-aluminates show better thermal stability compared to the noble metals, but exhibit significant catalytic activity only above 500 °C (perovskites) or 800 °C (hexa-aluminates).

It has been suggested that heat extraction from the catalytic combustion system can be conveniently accomplished by carrying out the process in a fluidized bed reactor [10–12]. This technology has been recently investigated though the operating conditions adopted have discouraged its application. In particular, unconverted fuel by-pass has been recorded in fluidized beds operated in the bubbling regime with separate feed for reactants [11], whereas operation of fluidized beds in the turbulent fluidization regime is characterized by more efficient contact between the catalyst and the reactants, but brings about exceedingly large loss of noble metal-based catalyst due to in-bed attrition [12].

The present paper addresses catalytic combustion of methane in a bubbling premixed fluidized bed of transition metal catalysts. A Cu/γ-Al_2O_3 catalyst has been prepared, characterized and tested with the aim of studying thermal and mechanical stability, transport phenomena ruling reactor performances and to preliminarily assess a process for energy production at the domestic scale.

2. Experimental

The catalyst was prepared by wet impregnation by dissolving copper acetate in aqueous solution and then adding a suitable amount of spherical γ-Al_2O_3 particles supplied by Sasol (1 mm in diameter). Water was evaporated at 40 °C in a Heidolph Laborota 4002 rotative evaporator at 110 mbar and 60 rpm. Catalyst spheres were then dried for 12 h at 120 °C and calcined for 3 h in air flow at 600 °C. Copper content was determined by atomic absorption. A Carlo Erba 1900 Sorpomatic instrument was used for measuring BET surface area by N_2 adsorption at 77 K. XRD analysis was performed with a Philips diffractometer PW 1100. A Philips XL30 SEM equipped with an EDX instrument was used to study particle morphology and copper distribution. Thermo-gravimetric (TG) analysis was performed with a Perkin-Elmer TGA7 thermo-balance equipped with a high temperature furnace and coupled with a Perkin-Elmer Spectrum GX FTIR spectrometer for the analysis of released gases. TG analysis was carried out by heating the sample at 10 °C min^{-1} up to 800 °C in air flow. A DRIFT accessory installed in the spectrometer was used for the IR analysis. Temperature programmed reduction (TPR) experiments were performed using a Micromeritics TPD/TPR 2900 analyser equipped with a TC detector and coupled with a Hiden HPR 20 mass spectrometer. Catalyst (100 mg) was preheated in air at 600 °C for 2 h and, after cooling at room temperature, it was reduced with a 2% H_2/Ar mixture by heating at 10 °C min^{-1} up to 800 °C.

Fixed bed catalytic activity tests were carried out by feeding a gas mixture of CH_4 (0.5 vol.%) and air to an isothermal microreactor previously described [13].

Fluidized bed combustion experiments were performed in a stainless steel premixed reactor (internal diameter 100 mm) containing 700 g of catalyst pre-aged at 800 °C under reaction conditions (0.5% CH_4 in air) and surrounded by an electrical oven. Methane and air flow rates were controlled using Bronkhorst mass flow meters. Inlet flow rate was adjusted depending on bed temperature in order to realize effective gas velocities of 0.4 and 0.8 cm/s and CH_4 inlet concentrations between 0.15 and 3%. For the catalyst, minimum fluidization velocity varied between 0.25 (at 400 °C) and 0.19 m/s (at 700 °C), as evaluated by literature correlation [14]. A porous distribution plate and a Raschig rings packing in the section below the distributor allowed to reach flat velocity and temperature inlet profiles. Reactor temperature was controlled with a chromel–alumel thermocouple directly inserted in the bed. The reaction products were analysed with a Hewlett-Packard series II 5890 GC equipped with thermal conductivity and flame ionization detector.

3. Results and discussion

3.1. Catalyst physico-chemical characterization

Cu content of the catalyst is 5.5 wt.%. XRD patterns of both fresh and aged catalysts show only

Table 1
Surface area, H_2/Cu ratio from TPR and kinetic parameters for different samples

Sample	Calcination temperature (°C)	Surface area ($m^2\,g^{-1}$)	H_2/Cu	T_{50} (°C)	k^o ($l\,h^{-1}\,l_{cat}^{-1}$)	E_{act} ($cal\,mol^{-1}$)
γ-Al_2O_3	–	180	–			
Cu/γ-Al_2O_3	600	170	0.59	525	1.11×10^{11}	21200
Cu/γ-Al_2O_3	800	144	0.45	540	0.91×10^{11}	21330

signals of γ-Al_2O_3 phase suggesting a good dispersion of the active phase and the absence of alumina phase transition for treatments up to 800 °C.

Characterization was performed either on the sample calcined at 600 °C or on that aged at 800 °C in order to investigate the stability of the system and to determine the transformations of both the support and the deposed phases occurring in the temperature range 600–800 °C.

Calcination at 600 °C very weakly affects the value of γ-Al_2O_3 surface area, while the ageing treatment at 800 °C causes a more significant surface loss, likely due to the elimination of support micropores starting at this temperature (Table 1). EDX analysis of copper distribution along the radius of spheres showed copper enrichment in the proximity of the catalyst surface for both fresh and aged samples. The non-uniform distribution of copper can be due to capillary effects during drying stage or the large size of support spheres which hinders a complete penetration of copper ions towards particle core, even if copper content is well below that corresponding to monolayer coverage, estimated at about 10 wt.% Cu for an alumina support powder with a similar surface area [15]. In the SEM micrographs of the internal catalyst section, white spots appear for the sample treated at 600 °C (Fig. 1a) and results to be mainly constituted by copper, as revealed by EDX analysis. These spots could be attributed to copper oxide particles not detectable by XRD analysis, in agreement with Kim et al. [16] who detected the presence of finely dispersed CuO for a Cu/γ-Al_2O_3 sample calcined at 700 °C. The ageing treatment at 800 °C results in disappearing of these small copper oxide particles (Fig. 1b) likely due to surface reaction between copper and alumina. The homogeneous surface copper distribution of the aged sample is confirmed by the uniform green colour of the catalyst spheres compared to that of the sample calcined at 600 °C which appears partly black, i.e. the typical colour of copper oxide.

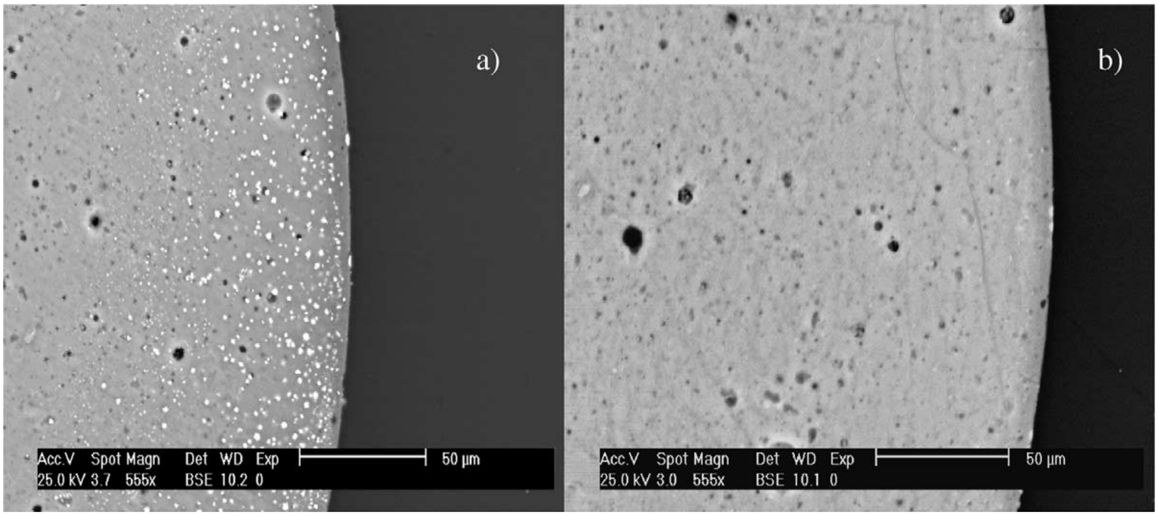

Fig. 1. SEM micrographs of catalyst section: (a) fresh sample, (b) aged sample.

TG analysis was carried out on both fresh and aged catalysts. Both samples start to loose weight at 30 °C and reach a stable weight at about 800 °C. However, the aged catalyst gives rise to a more significant weight loss (7.2%) compared to the fresh sample (2.3%), mainly due to CO_2 desorption at temperatures lower than 200 °C. CO_2 is constantly desorbed also by the fresh sample, even if in a very lower extent, together with some water almost absent for the aged catalyst. DRIFT spectra of fresh and aged samples confirmed the presence of carbonates (band at $1530\,cm^{-1}$) for the aged Cu/Al_2O_3 sample and adsorbed water for the fresh catalyst, as already observed by Hierl et al. [17]. After TG analysis of the fresh sample, a further TG cycle was performed. The superimposition with the curve obtained for the aged catalyst suggests that the high temperature and not the reaction mixture is responsible for the modifications undergone by the catalyst treated at 800 °C.

TPR profiles of both fresh and aged catalysts are reported in Fig. 2. It was verified that γ-Al_2O_3 gives a negligible contribution to H_2 consumption. Three signals are detectable in TPR curve of fresh catalyst, whereas the aged sample gives a single peak whose maximum (at about 200 °C) corresponds to the main signal in the curve of fresh Cu/Al_2O_3. The lower intensity of this peak in the fresh catalyst is balanced by the appearance of signals at a lower and higher temperature, respectively. This agrees well with the non-uniform composition of the deposed phase in the fresh sample evidenced by SEM/EDX analysis. Ferrandon et al. [18] also found a single peak centred at about 200 °C for a CuO–alumina system treated at 800 °C. This signal could be related to $CuAl_2O_4$ formed during the thermal treatment. The formation of a surface $CuAl_2O_4$ spinel has been reported also at temperature as low as 300 °C at low copper coverage [15,17,19] and its structure appears slightly different from that of bulk $CuAl_2O_4$ due to the occupation of most of the octahedral positions by copper ions [15]. On the other hand, a TPR experiment carried out on bulk CuO tenorite powder showed a signal with maximum at about 270 °C suggesting that the third signal observed in the TPR profile of the fresh catalyst can be attributed to the reduction of CuO particles, whilst the very easily reducible copper species responsible for the low temperature peak can be due to highly dispersed CuO [16]. The H_2/Cu ratio, reported in Table 1, is less than 1 for both the samples indicating that Cu^{2+} is not completely reduced to Cu^0 as found

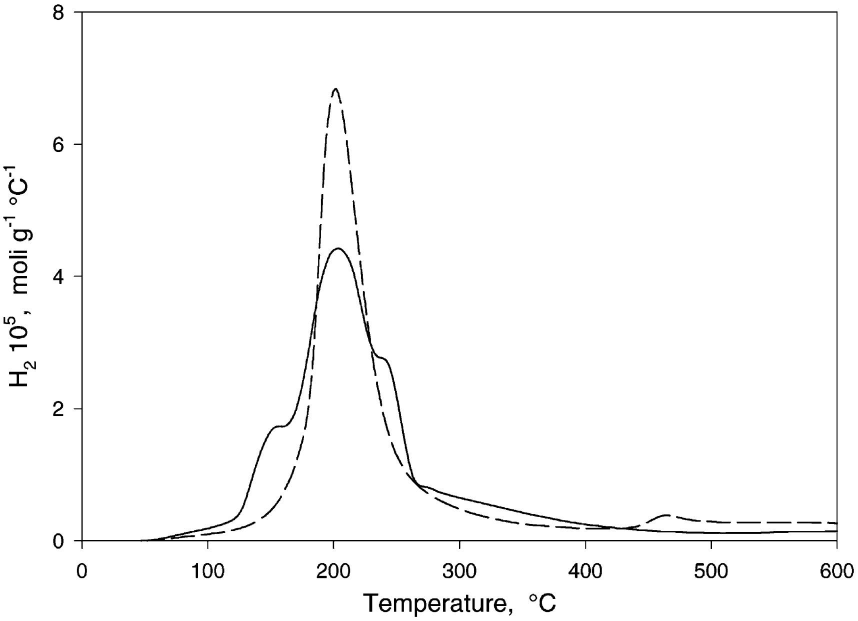

Fig. 2. Hydrogen consumption in the temperature programmed reduction (TPR) over Cu/Al_2O_3 catalyst pretreated at 600 °C (—) or aged at 800 °C (– – –). Heating rate: $10\,°C\,min^{-1}$, reductant gas composition: H_2 (5 vol.%) and balance Ar.

by others [15,18]. Fresh sample is slightly more reducible than aged catalyst in agreement with the less extensive formation of a surface $CuAl_2O_4$, as CuO is completely reduced to Cu^0 as confirmed by TPR tests carried out on bulk tenorite, whereas for $CuAl_2O_4$, copper in tetrahedral position is more reducible than that in octahedral position [17].

In conclusion, the results of physico-chemical characterization indicate that a thermally stable catalyst with a uniform composition of the deposed phase corresponding to a surface $CuAl_2O_4$ spinel can be obtained by treating Cu/γ-Al_2O_3 up to 800 °C under air or reaction mixture.

3.2. Catalytic activity measurements

The results of the catalytic tests carried out in fixed bed reactor reveal that the Cu/γ-Al_2O_3 catalyst calcined at 600 °C is slightly more active than the sample aged at 800 °C, thus confirming the previously reported assumptions about the higher activity of CuO compared to $CuAl_2O_4$ [6]. In Table 1, the temperatures for 50% methane conversion (T_{50}) are reported for both the samples. Fresh catalyst is more active than the aged sample, as the same methane conversion is obtained at a temperature which is 15 °C lower.

However, the possible modification of the catalyst from the fresh state (as prepared) to more and more aged forms has been followed by measuring the catalytic activity in methane conversion under repeated ageing treatments. In order to make such a comparison on the basis of kinetic parameters, conversion data were elaborated assuming a methane first-order rate equation and plug flow reactor behaviour in order to estimate the kinetic constant *k*. Fig. 3 reports *k* as a function of the inverse temperature for different

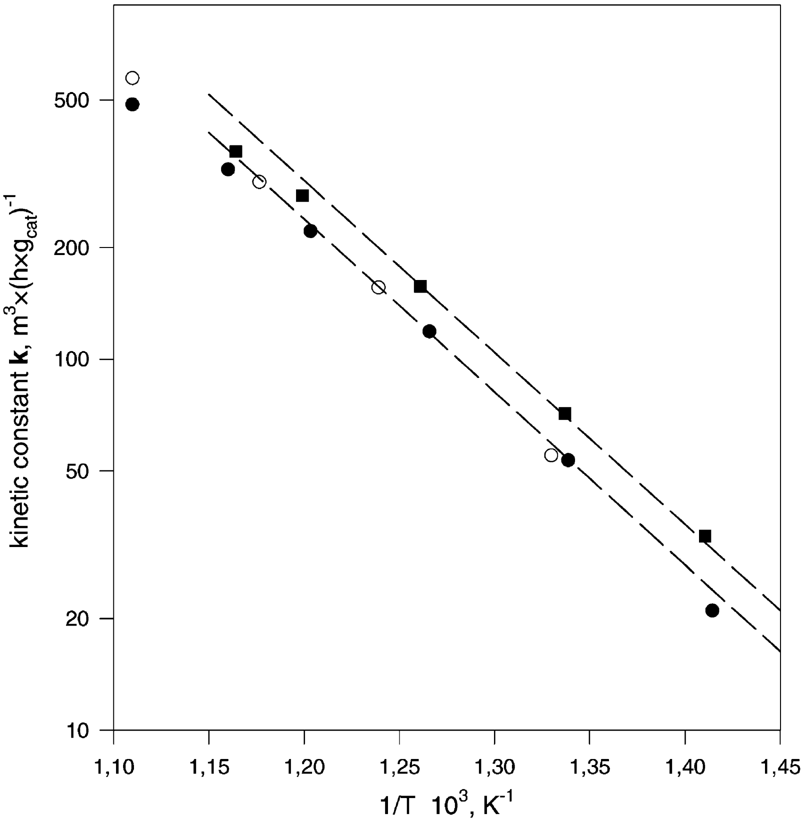

Fig. 3. Kinetic constant estimated for first-order methane combustion kinetics over Cu/Al_2O_3 catalyst after different ageing treatments: (■) 3 h at 600 °C in air flow; (○) 3 h at 800 °C under reaction conditions; (●) 20 h at 800 °C under reaction conditions. Tests conditions: 0.5 vol.% CH_4 (balance air), W/F = 0.06 g s Nm^{-3}.

treatments undergone by the sample. It is evident that ageing the catalyst at 800 °C for longer periods did not produce any further relevant deactivation effects, since no significant difference is observed in the kinetic constant estimated after 3 and 20 h of ageing treatment. The presence of diffusion limitations, indicated by the decreasing slope in the Arrhenius plot, cannot be neglected at temperatures higher than 600 °C. As a consequence, only low temperature conversion data have been used to obtain the Arrhenius parameters, which are reported in Table 1. The value of pre-exponential factor k^0 estimated for the fresh sample was about 20% higher than that evaluated for the aged catalyst, while the activation energy E_{act} remains

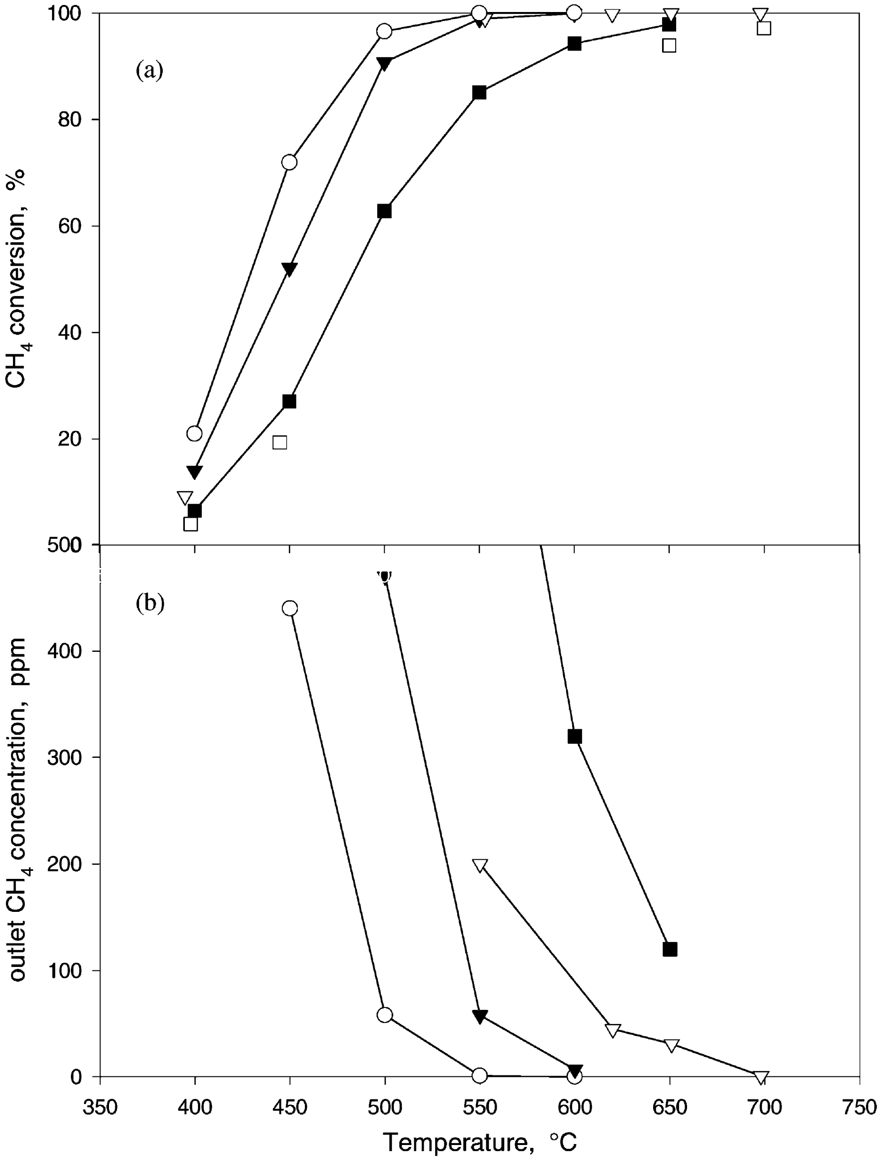

Fig. 4. CH_4 conversion (a) and CH_4 outlet concentration (b) as a function of reactor temperature at different superficial gas velocities and methane inlet concentrations ((○) 0.4 m/s and 0.15 vol.%; (▼) 0.4 m/s and 0.5 vol.%; (▽) 0.4 m/s and 3 vol.%; (■) 0.8 m/s and 0.5 vol.%; (□) 0.8 m/s and 3 vol.%).

constant. This suggests that the nature of the active site does not change and that the loss of activity of the latter sample can be attributed to surface area reduction. Table 1 evidences that, on the basis of the pre-exponential factor k^0 estimated, the reduction of catalytic activity could be quantified in a factor of about 20%, i.e. in the same order of magnitude of the corresponding loss of surface area.

3.3. Fluidized bed combustion tests

Results of steady state fluidized bed combustion tests carried out at different bed temperatures are reported in Fig. 4a for CH_4 inlet concentrations of 0.5 and 3 vol.%. For both the concentrations, the figure compares methane conversion obtained in tests carried out at gas superficial velocities (evaluated at reactor temperature) of 0.4 and 0.8 m/s. Methane conversion departs significantly from 0 at a temperature beyond about 400 °C and is complete at temperatures which strongly depend on the experimental conditions. In particular, a significant effect of gas velocity can be appreciated: methane conversion at 0.4 m/s is significantly higher than at 0.8 m/s for both inlet methane concentrations. It must be noted that in experiments with 3% CH_4 inlet concentration, only conditions corresponding to very low and very high values of methane conversion could be established at the pre-set temperature. For intermediate conversions, heat release associated with the methane oxidation was so large that the reactor temperature departed significantly from the set-up temperature.

Fig. 4b represents a close-up inspection of data points at high conversion degree. Results at gas velocity of 0.4 m/s are reported for 0.15, 0.5 and 3% CH_4 inlet concentrations. Results at gas velocity of 0.8 m/s are reported only for methane inlet concentration of 0.5% since at 3%, the methane content in the exhaust remains well above 2000 ppm even at very high temperatures. It can be noted that methane concentration below 10 ppm can be achieved at 0.4 m/s by temperatures $\leq$700 °C. In experiments at 0.8 m/s, methane content lies above 100 ppm even at relatively high temperatures.

It is concluded that at lower gas superficial velocity, methane contained in the uprising bubbles is effectively transferred to the dense phase where it reacts with the catalyst. Hence, by-pass of methane in bubble phase is negligible. This can be attributed to a combination of factors: the use of a premixed reactor, which maximizes the mixing of reactants, the smaller scale of the fluidized bed reactor which limits the bubble size, the use of solid belonging to group B–D of Geldart classification of particles [20], which enhances bubble-emulsion phase mass transfer.

At higher gas superficial velocity, the substantial amount of unconverted methane at the exhaust, even at high temperatures, might be explained both in terms of shorter space–time and more extensive bypass in the bubble phase. Further investigation at higher temperatures is in progress to elucidate the relative importance of these two effects.

Thermal stability of the catalyst was verified by reproducibility tests performed after about 200 h of operation showing that no deactivation occurred. Collection of fines elutriated from the combustor at the exhaust by means of sintered brass filters did not show appreciable loss of catalyst due to abrasion. In all the experimental conditions tested, no detectable ($\leq$1 ppm) NO_x and CO concentrations in the exit gas were measured.

4. Conclusions

A copper-based catalyst has been assessed for fluidized bed catalytic combustion. After ageing treatment of the catalyst at 800 °C, all copper is present as superficial $CuAl_2O_4$ spinel, which is stable towards further phase transformations. Fluidized bed catalytic combustion experiments show that with a gas velocity of 0.4 m/s, CH_4 emissions less than 10 ppm were reached below 700 °C at methane inlet concentration of 0.15 and 3%, while at 0.8 m/s and below 700 °C, significant amount of unreacted methane (above 100 ppm) was always present in the exhaust gas. This can be attributed to the lower gas contact time or by-pass effects of methane in the bubble phase. In all the experimental conditions tested, no CO, NO_x and particulates could be detected at the exhaust.

Acknowledgements

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