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# Methane combustion over unsupported iron oxide catalysts

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## Abstract

Bulk iron oxide, prepared by precipitation and by the citrates method, has been studied as an alternative catalyst for methane combustion. While hematite was the dominant phase in all the samples prepared, significant differences were observed regarding the activity and stability of the catalysts, depending on the preparation method. The catalysts prepared by precipitation presented higher surface areas and lower light-off temperatures. Catalyst deactivation is due to sintering under reaction conditions, and becomes more severe if the operating temperature exceeds the calcination temperature used in catalyst preparation. The best performance in terms of stability and steady-state conversion was obtained with the catalyst prepared by precipitation and calcined at 600°C. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Methane combustion; Iron oxide; Catalyst stability; Sintering

## 1. Introduction

In recent years an active search for alternative combustion catalysts based on non-noble metal oxides has been under way. The potential market for metal oxides in energy-generation applications is very high, spanning all the way from high-throughput, high-temperature turbines used in natural gas combustion to energy generation systems in domestic and small scale industrial applications. Most of the research on metal oxides has been focussed towards hexa-aluminate and perovskite-type compounds [1–7] which have been sometimes incorporated in the design of novel combustors [8,9]. Comparatively, little attention has been devoted to single oxide systems, which is in part related to their relatively easy deactivation by sintering. There are, however, exceptions to this rule; thus, $Fe_2O_3$ presents a relatively high sintering temperature and effective energy for cation diffusion [10], which makes it suitable for medium-high temperature applications.

Among the few studies dealing with the use of iron oxides in methane combustion applications, Kobayashi et al. [11] noted the activity of $Fe_2O_3$ supported on silica for total combustion to $CO_2$ when the iron content reached values above a certain level, and Sazonov et al. [12] showed the existence of a linear dependence of the rate of methane oxidation on the total iron content of the catalyst. On the other hand, Brown et al. [13] studied the methane oxidation activity of $Fe_2O_3$catalysts (with and without sulfation) prepared from different precursors, and found significant differences in the performance and catalytic properties, depending on the precursor used.

In this work, we have investigated the influence of the preparation procedure of bulk (unsupported) $Fe_2O_3$ catalysts on their activity and stability during the combustion of lean methane-containing mixtures. Special attention has been paid to the calcination temperature used during catalyst preparation in relation to the operating temperatures reached.

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## 2. Experimental

### 2.1. Catalyst preparation

Two different synthesis methods were used. In the first, termed the citrates method [16], the catalysts were prepared by adding excess citric acid to an aqueous solution containing $Fe(NO_3)_3$. After evaporation at 100°C for 12 h, a sponge-like precursor was obtained, which was calcined at a fixed temperature (between 500 and 800°C) for 6 h. The second method involved the addition of an ammonium hydroxide solution over an aqueous solution containing $Fe(NO_3)_3$. A colloidal precipitate was obtained ($Fe_2O_3 \cdot 3H_2O$), which was dried at 100°C for 12 h. The resulting dry powder was subjected to the same calcination protocol as the samples prepared by the citrates method.

In the remainder of this work, the catalyst samples will be designated as Fe-p$T$ or Fe-c$T$, where p and c indicate the method of preparation (precipitation or citrates), and $T$ the calcination temperature.

### 2.2. Catalyst characterisation

The iron content of the catalysts was measured using inductive coupling plasma (ICP) analysis. The BET surface areas were determined using a dynamic Micromeritics (Chemisorb 2700) equipment. The crystalline phases present were determined using X-ray diffraction (XRD) analysis, performed in a Rigaku/Max System difractometer (Ni-filtered Cu Kα radiation, graphite monochromator, scan rate 0.03°/s).

Temperature-programmed reduction (TPR) experiments were carried out at atmospheric pressure in a quartz reactor loaded with 200 mg of a freshly calcined sample, under a mass flow-controlled stream containing 6% $H_2$ in $N_2$. The sample was heated at 10°C/min, from room temperature to 1000°C.

The reactivity of lattice oxygen in the catalysts employed was tested in transient experiments carried out in a quartz micro-reactor loaded with 200 mg of catalyst. After oxidation in air for 20 m at 600°C the catalytic surface was swept with He and then pulses containing 3% $CH_4$ in He were passed over the catalyst. The conversion of the methane in the pulses was followed by on-line mass spectrometry (Hiden HAL 2/201). In order to compare the conversions between anaerobic and aerobic conditions the same experiment was repeated using pulses containing 3% $CH_4$ in $O_2$.

### 2.3. Steady-state reaction tests

Combustion experiments were performed in a quartz tubular reactor, in which 150 mg of catalyst were loaded between two quartz wool plugs. A mass-flow controlled (Brooks) mixture containing 3 vol% methane in air was passed over the catalyst with a total flow rate of 90 ml (STP) min$^{-1}$ ($W/F = 1.66 \times 10^{-3}$ g min [ml(STP)]$^{-1}$). The GHSV was around 25 000 h$^{-1}$. On-line gas chromatography was used to analyse the product stream for unreacted methane, CO and $CO_2$. The sensitivity of the analysis was increased using a methanator coupled to the FID detector in the gas chromatograph. Carbon mass balance closures were always within 4% and usually within 2% for the experiments reported in this work.

The reaction temperatures reported below are steady-state temperatures measured by a thermocouple within a quartz thermowell directly embedded in the catalyst bed (i.e., they are not inlet gas temperatures). The reaction temperature was kept at the desired value by means of an external electrical furnace (PID controller). Typical reaction experiments were carried out by measuring the conversion at successively increasing (or decreasing) temperatures, after a stabilisation period needed to achieve steady state. Some extended catalyst stability experiments were also carried out during which a fixed catalyst temperature (600°C) was maintained.

## 3. Results and discussion

Table 1 gives some of the main characteristics of the catalysts used in this work (preparation method, calcination temperature, XRD characterisation, Fe content as measured by ICP analysis, and BET surface area). It can be seen that the catalysts prepared by precipitation have specific surface areas which are around three times higher than the corresponding catalysts prepared by the citrates method. As will be shown below, this leads to a lower activity (on a mass basis) and higher light-off temperatures (measured at 50% methane conversion) for the catalysts prepared by the citrates method, with the exception of those calcined

Table 1
Some characteristics of the fresh catalysts used in this work

| Catalyst | Preparation method | Calcination temperature (°C) | XRD structure | $L$ (nm)[a] | BET area ($m^2/g$) | Iron content (wt.%) |
|---|---|---|---|---|---|---|
| Fe-c500 | Citrates | 500 | n/a | n/a | 9.9 | 66.2 |
| Fe-c600 | Citrates | 600 | $\alpha$-$Fe_2O_3$ | 50 | 5.9 | |
| Fe-c800 | Citrates | 800 | $\alpha$-$Fe_2O_3$ | 108 | 1.2 | |
| Fe-p500 | Precipitation | 500 | $\alpha$-$Fe_2O_3$ | 21 | 27.2 | 61.2 |
| Fe-p600 | Precipitation | 600 | $\alpha$-$Fe_2O_3$ | 31 | 18.5 | |
| Fe-p800 | Precipitation | 800 | $\alpha$-$Fe_2O_3$ | 59 | 9.0 | |

[a] Characteristic length calculated from the main XRD band.

at 800°C. Increasing the calcination temperature had a more marked effect on the catalyst prepared by the citrates method: in spite of the already low values of BET area of these catalysts when prepared at 500°C, increasing the calcination temperature to 800°C resulted in a loss of 88% of the specific area; in the co-precipitated catalysts roughly one-third of the area was preserved after the same temperature increase.

The XRD patterns of the catalyst samples calcined at 600 and 800°C are shown in Fig. 1. They show that $\alpha$-$Fe_2O_3$ was obtained in all cases, independently of the preparation method or the calcination temperature. Also, a clear increase of the crystallinity can be observed for the higher calcination temperatures. Table 1 gives the characteristic crystallite size, as calculated from the width of the hematite peak at $2\theta = 38°$. It can be seen that increasing the calcination temperature has a stronger effect on the catalyst prepared by the citrates method: a change in the calcination temperature from 600 to 800°C increases the mean crystallite size from 50 to 108 nm. In the same interval the mean crystallite size of the precipitated catalyst increases from 31 to 59 nm. This correlates well with the results on reduction of the surface area given in Table 1.

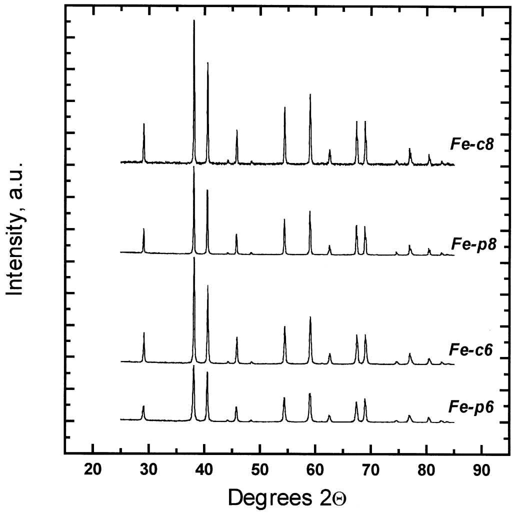

Fig. 1. X-Ray diffraction patterns of catalysts calcined at 600 and 800°C.

### 3.1. Catalyst reducibility

The results of TPR experiments (not shown) were similar for the different catalysts. A first reduction band was clearly visible around 400°C which can be ascribed [14] to the reduction of $Fe_2O_3$ (hematite) to $Fe_3O_4$ (magnetite). Since magnetite (containing a mixture of $Fe^{2+}$ and $Fe^{3+}$) is less active for combustion than hematite, this transformation would entail some reduction of the catalytic activity. At higher temperatures (450–850°C), a broad band appeared with two unresolved peaks. These are attributed to the reduction of $Fe_3O_4$ to FeO and then to Fe [15]. A progressive displacement of the reduction peaks towards higher temperatures as the calcination temperature increases could be observed for both catalysts. Again, this indicates a process of catalyst sintering: larger crystallites present a higher resistance to hydrogen diffusion and therefore require more time for reduction. Under a fixed temperature ramp in the TPR experiments this translates into a higher apparent reduction temperature.

The ability of $CH_4$ to reduce the catalyst at the reaction temperatures was tested in separate transient experiments. Fig. 2 shows the results of experiments in which 20 pulses containing 3% methane in He were sent over the Fe-p600 catalyst at 600°C. In spite of

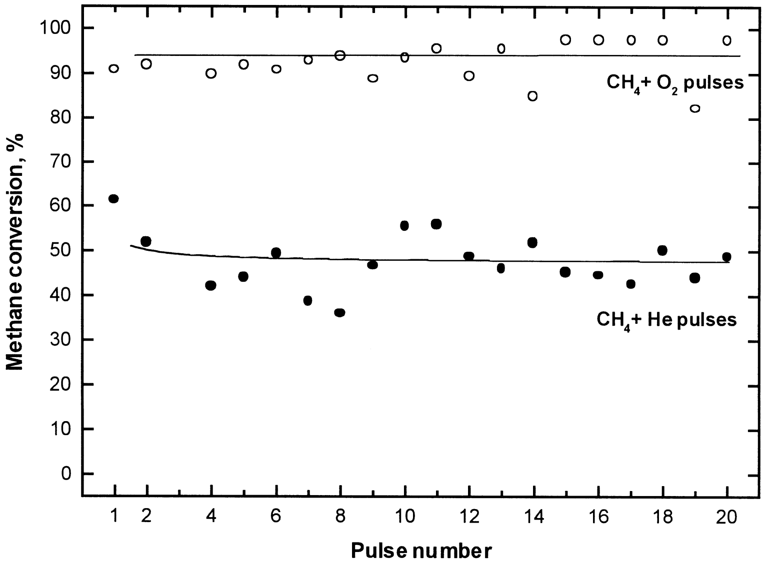

Fig. 2. Methane conversion in pulse experiments at 600°C, as determined from continuous mass-spectrometry monitoring. Fe-p600 catalyst, experimental conditions given in the text.

some dispersion it can be seen that the conversion of methane stayed relatively constant around 50%, indicating the ability of methane to reduce the catalyst lattice at this temperature. This approximately constant conversion is explained because oxygen consumption in these first 20 pulses represents less than 2% of the oxygen available in the catalyst. The conversion observed in the absence of gas phase oxygen would indicate that the catalyst uses primarily lattice oxygen in the methane combustion reaction. However, the presence of oxygen in the gas phase increases the reaction rate considerably: when a large excess of gas phase oxygen was present the conversion of methane was roughly doubled (upper curve in Fig. 2).

### *3.2. Catalytic activity*

The bulk iron oxide catalysts used in this work behaved selectively in methane combustion. Under the conditions used, only $CO_2$ was detected as a product below 700°C. Above this temperature some CO was formed, but the yield to CO was always below 1%. Blank experiments carried out without catalyst in the reactor (only quartz glass plugs) indicated that at temperatures of 700°C and higher homogeneous combustion was significant, with a high selectivity to CO. It seems therefore likely that the observed CO production in the presence of $Fe_2O_3$ is primarily due to homogeneous combustion in the void space of the reactor.

The light-off curves for the first three tests with the different catalysts employed are shown in Fig. 3. The first curve, on the left side of the graph for each catalyst corresponds to the experiment carried out with the fresh (after calcination) catalyst. After the first experiment was carried out with increasing temperatures, a second experiment was performed with decreasing temperatures, which produced the middle curve of each graph. The third and final test was performed with increasing temperatures. For each of the two preparation methods used there is a clear displacement of the light-off curves towards higher temperatures as the calcination temperature increases (see Fig. 3 and also Table 2).

The evolution of combustion temperatures on the different catalyst samples during the first three tests of Fig. 3 shows that with each experiment the light-off curve moves towards higher temperatures as a result of catalyst deactivation by sintering. The rate of sintering is significant, given the limited exposure of the catalysts to high temperatures (the cumulative time on stream for each catalyst sample during the first three

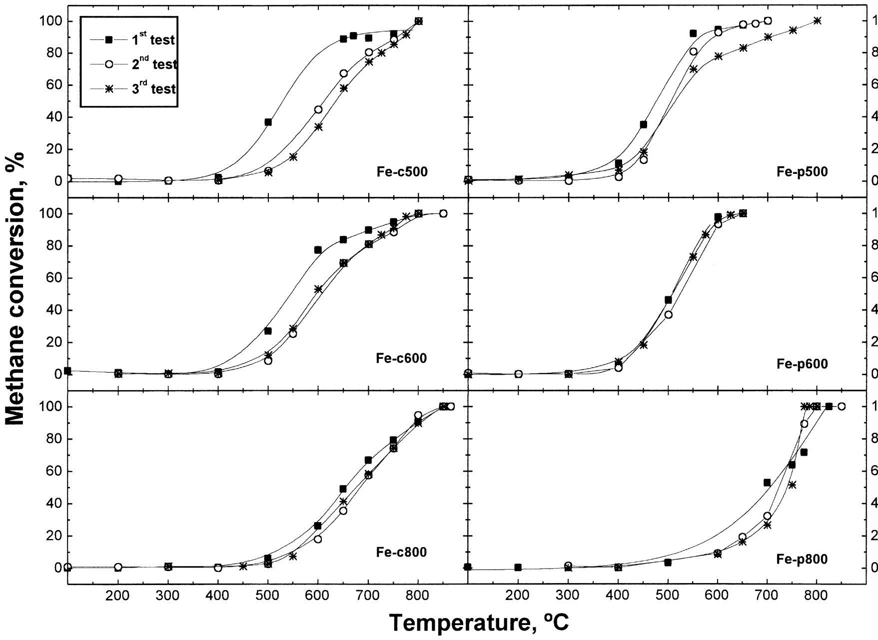

Fig. 3. Light-off curves for methane combustion. Conditions given in the text.

tests is between 22 and 30 h). The area of the hysteresis loop between the first and the third test can be used as an indication of the extent of sintering undergone by each catalyst. As could be expected, this is largest for the catalysts calcined at 500°C, especially for the catalyst prepared by the citrates method. Also (in spite of some scatter of the data), the stability is highest for the Fe-c800 and Fe-p800 catalysts, which were calcined (and therefore pre-sintered) at 800°C.

The light-off temperatures for the first reaction test (Table 2) increase as the calcination temperature increases. This is expected, since the initial specific surface area is inversely proportional to the calcination temperature (Table 1). However, a closer examination of Table 2 and Fig. 3 reveals some unanticipated results. Because the evolution of each catalyst sample with use during the first three tests is different, in the third reaction test the light-off temperatures of the cat-

Table 2
Evolution of catalytic activity

| Catalyst sample | Light-off temperature (°C)[a] | | | Catalyst deactivation[b] | | |
|---|---|---|---|---|---|---|
| | First test | Second test | Third test | Conversion at $t = 1\,\mathrm{h}$ (%) | Conversion at $t = 100\,\mathrm{h}$ (%)[b] | Specific activity at $t = 100\,\mathrm{h}$[b,c] |
| Fe-c500 | 529 | 613 | 634 | 80.2 | n/a | n/a |
| Fe-c600 | 527 | 596 | 600 | 77.4 | 41.5 | 3.35 |
| Fe-c800 | 653 | 674 | 683 | 26.6 | 11.5 | 0.92 |
| Fe-p500 | 475 | 505 | 513 | 94.8 | 68.5 | 5.50 |
| Fe-p600 | 504 | 507 | 521 | 97.6 | 79.4 | 6.38 |
| Fe-p800 | 706 | 724 | 741 | 21.0 | n/a | n/a |

[a] Defined as the temperature required for 50% methane conversion.

[b] The first 22–25 h on stream for each catalyst sample correspond to the combustion experiments of Fig. 3.

[c] Given in (mol $CH_4$/g catalyst·min)×$10^4$.

alysts prepared by the citrates method do not follow the order of calcination temperatures; instead, the lowest values correspond to the catalyst calcined at the intermediate temperature of 600°C (Table 2). Also, in the precipitated catalyst the samples Fe-p500 and Fe-p600 present similar light-off temperatures. The reasons for this behaviour will be explained below.

### *3.3. Catalyst stability*

The light-off curves in Fig. 3 indicate different degrees of instability of the iron catalysts when subjected to high temperatures. In order to further test catalyst stability, the evolution of methane conversion was followed in extended experiments (Fig. 4), in which after performing the first three tests as already described, the catalyst temperature was kept constant at 600°C and the evolution of activity was followed. These experiments were carried out on four catalyst samples displaying moderate sintering (as measured by the difference between the first and second tests of Fig. 3): Fe-p500, Fe-p600, Fe-c600 and Fe-c800. As could be expected, a very stable behaviour was displayed by the Fe-c800 catalyst, whose activity is stable after ca. 20 h in Fig. 4. However, this stability comes at the price of an important loss of surface area, which takes place mainly during calcination at 800°C (further use of this catalyst during the first three light-off tests had only a small effect on its catalytic activity, as already shown in Fig. 3). The two catalysts calcined at 600°C showed a moderate loss of activity, and after 100 h on stream the catalyst Fe-p600 gave the highest reaction rate (on a mass basis) of all the samples studied. A good level of long-term activity was also displayed by the Fe-p500 catalyst, but in this case the deactivation

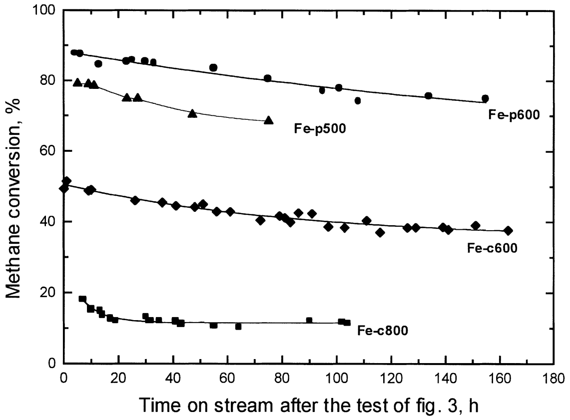

Fig. 4. Evolution of methane conversion at 600°C for different catalyst samples. Note: the figure starts after the experiments of Fig. 3, i.e., after the third test the sample temperature was kept constant at 600°C, and this corresponds to time = 0 in this figure.

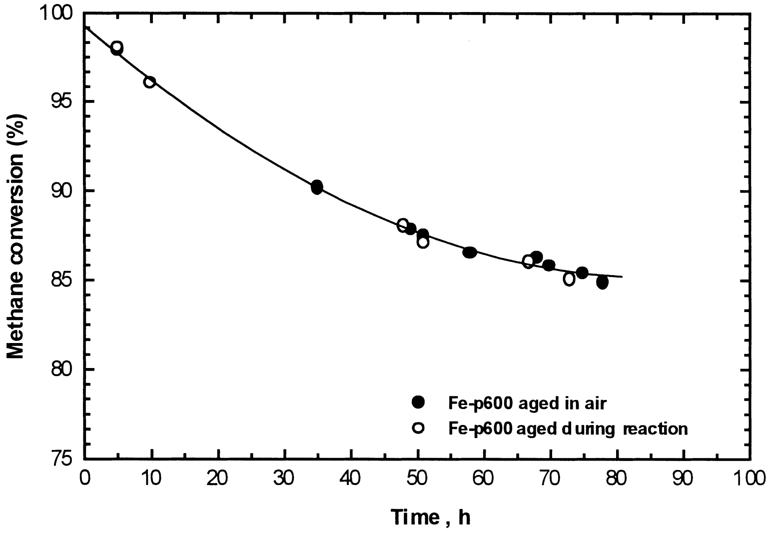

Fig. 5. Evolution of activity. Fresh Fe-p600 catalyst samples aged in air and during reaction.

during the first three tests was very significant. As a consequence, its initial activity in Fig. 4 (after the first three tests) is below that of the Fe-p600 catalyst.

Further stability testing was carried out on the sample giving the best performance (Fe-p600). Fig. 5 compares the ageing process at 600°C in the presence and in the absence of reaction (i.e., sintering in air). It can be seen that the evolution of activity is identical in both cases, which would indicate that deactivation is in this case a purely thermal process, unaffected by the chemical reaction or by the presence of reaction products (e.g. steam), at the concentrations present in these experiments. Fig. 6 shows the normalised loss of surface area (i.e. the ratio between the specific surface at any given time and the specific surface of the fresh catalyst) observed in a separate experiment where a fresh sample of Fe-p600 was aged in air at 600°C. Over the first 60 h on stream the fresh catalyst loses about 28% of its surface area, and then retains an approximately stable level. Fig. 5 shows that, in the same period, the loss of activity is of only 15%. This means that the catalytic activity is not exactly proportional to the BET area. Instead, the comparison of the results presented in Figs. 4 and 5 would indicate that some increase of the specific activity (on a surface area basis) takes place as the catalyst sinters.

The results discussed so far indicate that the iron catalysts undergo significant deactivation due to sintering; the loss of activity is more pronounced for the catalysts prepared by the citrates method and it becomes more severe when the catalysts are used at temperatures which are above those used during the calcination stage. This poses an interesting optimisation problem: the highest surface areas and initial activities correspond to $Fe_2O_3$ catalysts calcined at low temperatures. In this case, if the activity was such that a sufficiently high conversion could be reached at or below the calcination temperature, it is expected that catalyst behaviour would be stable. This is clearly not the case for the Fe-c500 and Fe-p500 catalysts, which required first-test temperatures considerably above 500°C in order to reach high methane conversions (Fig. 3). As a consequence their structure becomes unstable, and the light-off curve is displaced towards even higher temperatures in subsequent tests. On the other hand, it has been shown that the initial structure of catalysts prepared at high temperatures is stabilised by the pre-sintering process that takes during calcination. However, this loss of activity means that high temperatures are required to reach high conversions. If these operating temperatures are above the calcination temperature of the catalyst, further sintering is possible. Despite their stable behaviour and their low activity levels this occurs to a certain extent with catalysts Fe-c800 and Fe-p800 (Fig. 3).

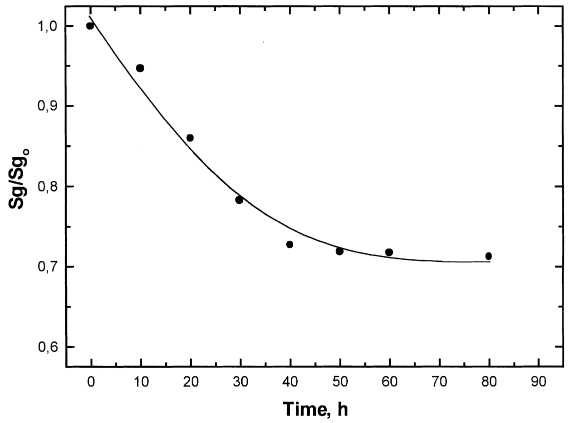

Fig. 6. Evolution of the normalised surface area with time on stream at 600°C. Catalyst Fe-p600.

The best results were obtained with catalyst Fe-p600. In this case the surface area retained after calcination was sufficiently high to yield total methane conversion at temperatures only moderately above the calcination temperature of 600°C (Fig. 3). Therefore only a limited amount of sintering is to be expected, which is in agreement with the results of Fig. 3 where the light-off curves for the first three tests are close to each other, and with the results of the extended experiments carried out with this catalyst. Postmortem analysis of Fe-p600 (after the carrying out the experiments of Fig. 4) yielded a surface area of 10.1 $m^2/g$ and a mean crystallite size of 42 nm, from 18.5 $m^2/g$ and 31 nm, respectively, for the fresh catalyst (Table 1). The equivalent data for the second best performing catalyst (Fe-p500) were 7.3 $m^2/g$ and 69 nm (compared with 27.2 $m^2/g$ and 21 nm for the fresh catalyst).

## 4. Conclusions

Unsupported iron oxide constitutes an interesting alternative catalyst for methane combustion. However, while the catalysts present a considerable initial activity, they undergo sintering at the operation temperatures. The preparation method strongly influences both the initial activity of the catalyst and its stability under reaction conditions. In particular, the calcination temperature plays a key role in determining some of the main catalytic properties (crystallite size, BET area, catalytic activity). If this temperature is too high, a catalyst with low activity results. If it is too low, the catalyst is not stable under reaction conditions and its catalytic activity plummets, following the collapse of surface area. The best results in this work were obtained with the catalysts prepared by the precipitation method, using a calcination temperature of 600°C.

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