Synthesis, structure and catalytic properties of Fe-substituted barium hexaaluminates

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A sol–gel method using Ba and Al isopropylates and iron nitrate has been used to synthesise barium hexaaluminate partially substituted with iron. After calcination under oxygen at 1200 °C the β-alumina structure was obtained. Formation of the mixed $BaFe_xAl_{12-x}O_{19}$ phase occurred for $x = 1$–4. XRD measurements showed a good crystallinity of the structure and expansion of unit cell parameters due to the presence of larger Fe^{3+} ions substituting Al^{3+} ones in octahedral sites only. Mössbauer spectroscopy revealed that Fe^{3+} ions are present in four different octahedral sites slightly distorted. Catalytic activity in methane combustion showed that an optimum was obtained for solid containing 2 Fe ions per unit cell: the increase of the amount of introduced iron was counterbalanced by the decrease of specific surface area. Intrinsic activities have been calculated for the four solids in both the fresh and aged states. It is observed that increasing iron content increases relative activities in the same ratio as the populations of iron located in two sites as deduced from Mössbauer spectroscopy. It is then tentatively assumed that activity is attributed to octahedrally coordinated Fe^{3+} ions in some specific sites.

Keywords: catalytic combustion, methane, iron, barium hexaaluminates, aging, Mössbauer spectroscopy

1. Introduction

Due to new stringent regulations concerning waste emissions, catalytic combustion of gaseous fuels appears as a very promising alternative for the production of primary energy [1]. The catalytic combustion of hydrocarbons is certainly one of the cleanest ways to obtain thermal energy without emission of NO_x [2]. For specific applications like gas turbines [3], catalysts of very high thermal stability are required because of the high temperatures reached for high efficiency [4]. The hexaaluminates-based catalysts (also called β-alumina) [5] are one family of heat resistant materials for this type of application.

They have a lamellar structure which consists of layers of spinel blocks separated by a monolayer of oxides issued from either bulky alkaline cations, or bulkier alkaline-earth ones [5]. In both cases direct contact between spinel layers is impossible and alkaline-earth ions act as a separation avoiding sintering by stacking all the spinel layers. Spinels consist of a fcc structure of oxygen anions, where both octahedral and tetrahedral sites are more or less filled [6]. On the other hand, α-alumina has an hcp structure of oxygen anion with aluminium cations occupying $2/3$ of octahedral sites only [7]. Formation of α-alumina at the expense of other forms (γ, δ, η, θ, etc.) needs a restructuring of anion layers. This is not possible at all for β-alumina due to the blocking introduced by the alkaline(-earth) cations [8]. So alumina transformation cannot occur and sintering is hindered: these complex oxides are exceptionally stable [9], but also poorly active in any catalytic process. The introduction of transition metal ions into the structure leads to a material active in complete oxidation [10], since such cations possess at least two different oxidation states. Nevertheless, the substitution may induce a loss in thermal stability because of charge and radius stress locally created.

The aim of the present work is to synthesise Fe-substituted hexaaluminates of the $BaFe_xAl_{12-x}O_{19}$ type and to evaluate their properties in catalytic combustion of methane in fresh and aged states.

2. Experimental

2.1. Preparation

A sol–gel method, derived from that already published by Arai [11], was used. Five different solids have been synthesised: the parent barium hexaaluminate $BaAl_{12}O_{19}$, and the solids containing 1 to 4 Fe^{3+} ions and 11 to 8 Al^{3+} only.

The required amounts of metallic barium and aluminium isopropoxide (Aldrich Chemicals) were suspended in 2-propanol. The suspension was refluxed for 3 h at 80 °C, then cooled at room temperature. Hydrolysis of the metal alkoxides was performed with an under-stoichiometric amount of water, i.e., the $x H_2O/M(iPrO)_x$ ratio is equal to 0.5 according to Machida et al. [10] who showed this ratio led to better results. For the iron-containing solids,

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Table 1
Chemical analysis.[a]

Catalyst	wt% Ba		wt% Al		wt% Fe		Formula
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	
BaO, $6Al_2O_3$	17.9	15.84	42.3	40.35	–		$BaAl_{13}O_{20.5}$
$BaFeAl_{11}O_{19}$	17.3	16.79	37.3	37.10	7.15	6.52	$BaFe_{0.95}Al_{11.25}O_{19.22}$
$BaFe_2Al_{10}O_{19}$	16.7	15.53	32.8	31.15	13.8	12.46	$BaFe_{1.97}Al_{10.20}O_{19}$
$BaFe_3Al_9O_{19}$	16.1	14.68	28.5	27.7	20.0	18.15	$BaFe_{3.03}Al_{9.6}O_{19}$
$BaFe_4Al_8O_{19}$	15.6	15.16	24.3	25.20	25.9	24.29	$BaFe_{3.94}Al_{8.46}O_{19}$

[a] Theoretical (Theor.) and experimental (Exp.) values.

the required amount of $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved into a water/2-proponal mixture and added during the hydrolysis step. A gel was rapidly formed; it was kept at room temperature for 15 h. Solvents were removed by evaporation under reduced pressure. The obtained powders were dried for few hours at 120 °C in an oven. They were finally calcined under flowing oxygen at 1200 °C for 24 h. Such a treatment leads to “fresh catalysts”.

The thermal stability of the catalysts was investigated after a treatment at 1200 °C for 24 h under a O_2/N_2 mixture (5 vol% + 95 vol%) containing 6 vol% steam. This severe treatment is systematically experienced in our tests for every heat-resistant catalyst. It simulates real conditions experienced by solids acting as catalysts when a full conversion of 9% of natural gas in air is reached. For each sample, 3 g of catalyst were treated under a flow of 10 $\mathrm{l\,h^{-1}}$ of the aging mixture; the obtained solids will be named “aged catalysts”.

2.2. Characterisation of the catalysts

Results concerning chemical analysis are reported in table 1 where chemical formulae are also indicated as deduced from analysis. Elements (Al, Ba and Fe) were analysed by AAS after dissolution of the samples in a mixture of concentrated acids ($HF + HCl + HNO_3$).

X-ray diffraction measurements were performed with a Siemens D500 diffractometer using the nickel-filtered Cu Kα1 line at 1.5406 Å. Diffraction peaks recorded for 2θ values between 5 and 70° have been used for two purposes, first to identify the obtained structure and, secondly, to calculate the unit cell parameters values. Silicon powder (60 mesh, 5 wt%) was added as an internal standard. The JCPDS-ICDD files (Copyright 1993) were used for phases identification. The unit cell parameters of the $BaAl_{12}O_{19}$ parent and substituted ones were calculated with the help of the least-squares functions of a spreadsheet using the values of the positions of the 16 most intense peaks.

Specific surface area (SSA) was measured by using the multipoint BET method of nitrogen adsorption at 77 K. Prior to nitrogen adsorption, the solids were evacuated at 500 °C for 2 h.

Valence states of introduced iron cations along with local symmetry were deduced from Mössbauer spectroscopy. The spectrometer used a source of ^{57}Co γ emitter radioisotope inserted in a rhodium matrix which was mounted onto a vibrator device [12]. The latter was accelerated at constant rate, twice in a period for which speed was inverted. The sample, placed between the source and the detector, was put into a cylindrical pellet of 16 mm in diameter and 1 mm in thickness: pellets were made in a die normally used for producing KBr pellets in conjunction with a press delivering 2 tons/cm^2. In order to avoid a too strong absorption, powder samples were diluted with α-alumina (each fifty percent in weight). All values reported here were calculated from polycrystalline α-Fe as a reference. The parameters δ, W and Δ are all expressed in speed unit (mm/s) and correspond to isomer shift, peaks FHW and quadrupolar separation, respectively.

2.3. Catalytic activity measurements

The activity of fresh and aged catalysts in methane combustion was measured on 500 mg of powder put onto a frit of a U-shaped silica reactor. Solids were first pretreated in O_2 at 400 °C for 1 h, cooled down to 350 °C and then contacted with the reactants mixture consisting of 4 vol% O_2 and 1 vol% CH_4 in nitrogen.

Temperature was measured with a Ni–Cr thermocouple inside an Inconel® sheath (2 mm OD) located outside but close to the reactor. The total flow (6.4 $\mathrm{l\,h^{-1}}$) corresponds to a GHSV of 15,000–25,000 $\mathrm{h^{-1}}$. Excess of oxygen was used in order to avoid any coke deposit or methane reforming when insufficient mixing of a stoichiometric mixture occurs.

3. Results

3.1. Physicochemical characterisations

Powders were analysed before the calcination step in order to make easier the acidic attack needed for the dissolution. At this stage no reaction occurred and solids were totally amorphous. Previous experiments have shown that digestion of solids calcined at 1200 °C is time consuming and not total. Thus some elements can be missing although weight ratios are always correct. The results reported in table 1 showed that stoichiometry was obtained in each case: the Fe/Ba and Fe/Al ratios are very close to the theoretical ones. Since oxygen has been never analysed, formulae reported here correspond always to 19 oxygen atoms per

Table 2
BET surface area in $m^2\,g^{-1}$.

Catalyst	Fresh	Aged	Δ ($m^2\,g^{-1}$)	Δ (%)
BaO, $6Al_2O_3$	10.0	8.9	1.1	10
$BaFeAl_{11}O_{19}$	14.1	11.9	2.2	16
$BaFe_2Al_{10}O_{19}$	11.8	9.2	2.6	22
$BaFe_3Al_9O_{19}$	9.5	6.6	2.9	30
$BaFe_4Al_8O_{19}$	6.0	4.6	1.4	23

Table 3
Crystallographic phases observed by XRD.

Fresh catalysts	Phases[a]
BaO, $6Al_2O_3$	$BaO{\cdot}6.6Al_2O_3$
$BaFeAl_{11}O_{12}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
$BaFe_2Al_{10}O_{19}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
$BaFe_3Al_9O_{19}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
$BaFe_4Al_8O_{19}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
Aged catalysts	**Phases**
$BaFeAl_{11}O_{12}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
$BaFe_2Al_{10}O_{19}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
$BaFe_3Al_9O_{19}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3
$BaFe_4Al_8O_{19}$	$BaO{\cdot}6.6Al_2O_3$, $BaO{\cdot}6Al_2O_3$, α-Al_2O_3

[a] α-Al_2O_3 diffraction peaks are of very low intensity.

molecule, although analysis should correspond to values slightly different from 19.

The SSA for all synthesised solids were between 5 and 14 m^2/g depending upon the iron content and the thermal treatment (table 2). The introduction of iron leads to an increase of BET area from 10 m^2/g for the parent hexaaluminate to 14 m^2/g for $BaFeAl_{11}O_{19}$. Further increase in the iron substitution leads to a decrease of the BET area; its value is 6 m^2/g for $BaFe_4Al_8O_{19}$. Aging has a limited effect because all iron-containing samples lose SSA in the same extent irrespective of the initial values (ca. 2–3 m^2/g).

X-ray diffraction spectra showed that the structure corresponds to $BaAl_{13.2}O_{21.8}$ (BaO, $6.6Al_2O_3$) according to ICDD file no. 33-128; very small amounts of α-Al_2O_3 are sometimes detected. However, some faint peaks were ascribed to the presence of another phase, namely $BaAl_{12}O_{19}$ (BaO, $6Al_2O_3$) (ICDD file no. 26-135). In fact, the two hexaaluminate structures are identical and correspond to a slight difference of aluminium concentrations (*vide infra*). However, calculations of unit cell parameters were done on the main $BaAl_{13.2}O_{21.8}$ structure. Moreover, no significant difference could be observed between fresh and aged catalysts as far as the structure is concerned (table 3).

The a and c unit cell parameters have been calculated (table 4).

For fresh catalysts, the introduction of increasing amounts of Fe^{3+} cations inside the bulk leads to an increase of both parameters. However, this effect is well evidenced for the c parameter for which there is an almost linear increase of value with the iron loading (figure 1), whereas the a parameter value seems to be rather independent of the cation concentration.

Table 4
Unit cell parameters.

Fresh catalysts	a (Å)	c (Å)
BaO, $6Al_2O_3$	5.586	22.725
$BaFeAl_{11}O_{19}$	5.612	22.746
$BaFe_2Al_{10}O_{19}$	5.612	22.748
$BaFe_3Al_9O_{19}$	5.612	22.755
$BaFe_4Al_8O_{19}$	5.613	22.778
Aged catalysts	**a (Å)**	**c (Å)**
$BaFeAl_{11}O_{19}$	5.600	22.778
$BaFe_2Al_{10}O_{19}$	5.599	22.818
$BaFe_3Al_9O_{19}$	5.627	22.753
$BaFe_4Al_8O_{19}$	5.613	22.682

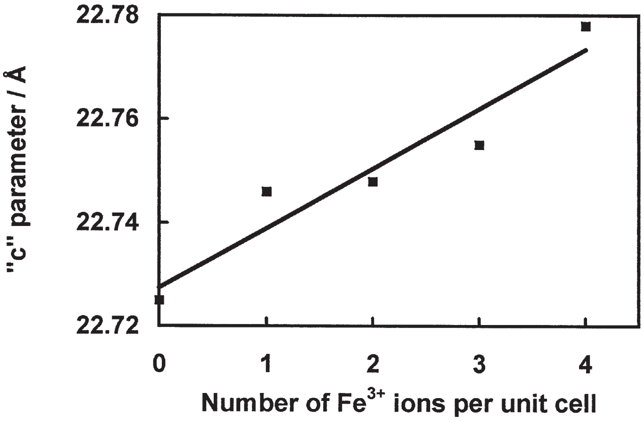

Figure 1. Variation of the c parameter values as a function of the number of iron cations per unit cell.

For aged solids, no simple trends of both a and c parameters could be deduced. Nevertheless, an increase in the values of both parameters with the iron content was globally observed.

In conclusion, the introduction of Fe^{3+} cations (radius = 0.61 Å) bulkier than Al^{3+} ones (radius = 0.53 Å) leads to a slight expansion of the unit cell, as already observed in other substituted hexaaluminates.

Iron Mössbauer spectroscopy has been used for determining the oxidation state of the cations as well as their locations in the hexaaluminate structure. Only fresh catalysts have been investigated (table 5).

Iron ions are exclusively in the 3+ oxidation state since no ferrous ions were detected by this technique. This result is deduced from the δ values (0.20–0.48 mm/s) which are much more related to Fe^{3+} species ($\delta = 0.30$–0.7 mm/s) rather than to Fe^{2+} cations, for which usual values of δ are closer to 1.1–1.3 mm/s [13]. This result is very important because Fe^{2+} ions are much bigger than Fe^{3+} ions. The presence of ferrous cations, whose radius for a 6 coordinance (0.76 Å) is roughly 50% larger than that of Al^{3+} ions, should induce a big stress in the lattice at high iron concentration and lead to important changes of a and c values. The small modifications of a and c parameters are

Table 5
Mössbauer parameters: δ, W and Δ are expressed in mm/s.

Solid	Site	δ	W	Δ	Population (%)	Number of ion per unit cell
$BaFe_1Al_{11}O_{19}$	S1	0.20	0.42	0.57	50	0.5
	S2	0.21	0.38	0.96	50	0.5
$BaFe_2Al_{10}O_{19}$	S1	0.20	0.31	0.49	38	0.76
	S2	0.21	0.38	0.85	42	0.84
	S3	0.14	0.26	2.43	5	0.1
	S4	0.48	0.29	0.55	15	0.3
$BaFe_3Al_9O_{19}$	S1	0.20	0.28	0.47	33	1
	S2	0.20	0.40	0.76	40	1.2
	S3	0.22	0.25	2.44	7	0.21
	S4	0.47	0.28	0.53	20	0.3
$BaFe_4Al_8O_{19}$	S1	0.20	0.25	0.43	25	1
	S2	0.19	0.34	0.67	40	1.6
	S3	0.21	0.29	2.34	10	0.4
	S4	0.47	0.28	0.53	25	1

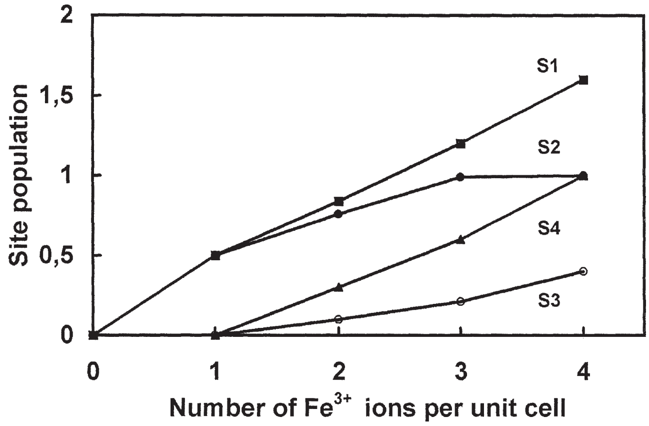

Figure 2. Mössbauer spectroscopy: occupancy of the different types of sites as a function of the number of iron cations per unit cell.

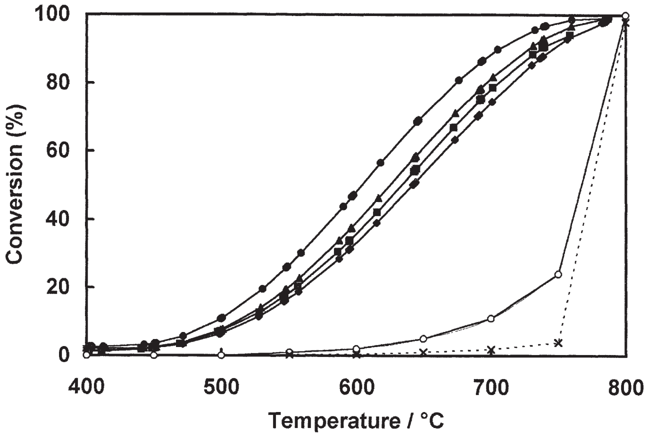

Figure 3. Catalytic activity of the fresh iron-substituted barium hexaaluminates $BaFe_xAl_{12-x}O_{19}$ solids in the combustion of methane ($x = 0$, 1, 2, 3 and 4): (▲) $BaFe_1$, (●) $BaFe_2$, (■) $BaFe_3$, (◆) $BaFe_4$, (○) support, (- - -) homogeneous reaction (empty reactor).

in agreement with the absence of iron in the 2+ oxidation state. The Δ values evidence slight deviations from cubic symmetries. In the hexaaluminate structure, cationic sites are either octahedral or tetrahedral and rigorous symmetries should lead to a Δ value equal to zero. In our samples, sites containing iron cations are not perfectly symmetrical and deformations occur. On the other hand, Fe^{3+} ions are rarely in tetrahedral environment when surrounded with oxygenated ligands [14] and prefer octahedral symmetry. Moreover, values of δ are also much more related to Fe^{3+} species in octahedral environment rather than in a tetrahedral one [13].

The global spectra of the studied solids showed Fe^{3+} ions are located in several sites. By resolving spectra, whose lines were asymmetrical, four different octahedral sites occupied by iron cations have been found; their occupancy depends upon iron concentration. In fact, iron cations do occupy four slightly different sites, each being a slightly distorted octahedron. Figure 2 shows the occupancy in each type of sites as a function of the number of iron cations introduced in the hexaaluminate structure.

The occupancy of the first site, noted S1, which is the most occupied, is almost linear with a cation concentration from 0.5 Fe^{3+} ion per unit cell for the $BaFeAl_{11}O_{19}$ sample to 1.6 Fe^{3+} ion for the $BaFe_4Al_8O_{19}$ sample. The second site, noted S2, is also occupied but its occupancy seems to reach a limit of 1 cation per unit cell. The two last sites, noted S3 and S4, are less occupied; their occupancy increases linearly and slowly with concentration and starts only for samples containing at least two Fe^{3+} ions per unit cell. Thus it seems here that S1 and S2 sites are slightly different from S3 and S4 sites, although they all have an octahedral symmetry.

3.2. Catalytic activity measurements

After synthesis, the activity of all the solids including parent barium hexaaluminate was measured in the complete oxidation of methane. The parent support is almost inactive, because conversion starts at 550 °C only and light-off is close to 770 °C. However, full conversion was obtained at 790 °C which is a temperature lower than that corresponding to homogeneous gas phase reaction, indicated as a dotted line in figure 3: support is not totally inert. When Fe^{3+}

Table 6
Isoconversion temperatures (in °C) corresponding to 10% (T_{10}), 50% (T_{50}) and 90% (T_{90}) of methane conversion for fresh (F) and aged (A) catalysts and activation energy (in kJ/mol).

Catalyst	T_{10}	T_{50}	T_{90}	E_A (kJ mol^{-1})
$BaFeAl_{11}O_{19}$ (F)	514	634	737	92
$BaFeAl_{11}O_{19}$ (A)	543	665	759	95
$BaFe_2Al_{10}O_{19}$ (F)	495	603	705	79
$BaFe_2Al_{10}O_{19}$ (A)	517	640	754	10
$BaFe_3Al_9O_{19}$ (F)	512	625	728	85
$BaFe_3Al_9O_{19}$ (A)	537	663	759	91
$BaFe_4Al_8O_{19}$ (F)	518	641	747	86
$BaFe_4Al_8O_{19}$ (A)	538	702	775	110

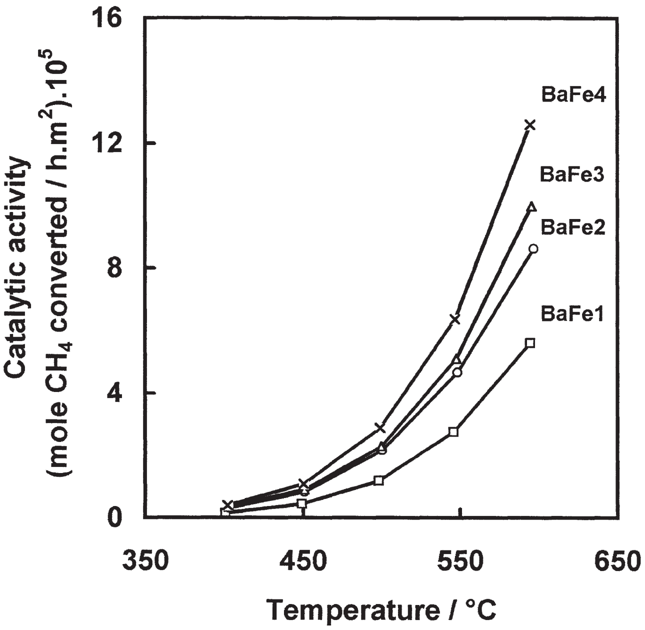

Figure 4. Intrinsic catalytic activity (mol h^{-1} m^{-2}) of the fresh iron-substituted barium hexaaluminates $BaFe_xAl_{12-x}O_{19}$ solids in the combustion of methane ($x = 0, 1, 2, 3$ and 4).

cations are introduced in the lattice the solids become much more active. However, it is observed that all the solids behave similarly whatever the iron concentration and the four T_{50} values are in the 605–640 °C range (table 6). However, it is observed experimentally that $BaFe_2Al_{10}O_{19}$ is the most active solid whereas $BaFe_4Al_8O_{19}$ is unexpectively the less active one, although it contains much more Fe^{3+} ions. Conversions, when compared for the same catalyst weight, are not in direct relationship with cation concentrations. The same is true also for aged solids where $BaFe_2Al_{10}O_{19}$ is still the more active catalyst. When comparing each catalyst in both fresh and aged states it is curiously observed that light-off temperature increased from 30 to 60 °C, and the higher the iron content the higher the difference between fresh and aged states.

In order to better compare activities for which catalysts have different specific surface areas, catalytic activities per square meter have been calculated at conversions sufficiently low (less than 20–30%) in order to be sure that reaction is under kinetic control. Figure 4 shows this behaviour. The activities of the fresh catalysts are expressed as mole of methane converted per hour and per m^2 unit area. The activity increases with cation content although there is no good proportionality. For example, at 600 °C activities are in the ratio numbers 1/1.6/1.8/2.3, whereas iron concentrations are in the ratio numbers 1/2/3/4. Thus either only part of iron introduced seems to be involved in catalytic combustion, or an increase in the cation loading leads to different geometry around Fe^{3+} ions which are not catalytically equivalent.

4. Discussion

There is a close relationship between catalytic activity and iron content as clearly evidenced by different physicochemical characterisations. However, and because of the sol–gel method used here, iron is supposed to be uniformly distributed inside the hexaaluminate structure. In addition, only accessible iron species are involved in the catalytic activity and because of the small SSA values only a small fraction of total iron should be normally accessible to reactants. Physicochemical characterisations experienced in this study refer essentially to bulk properties of the solid, whereas catalysis refers to surface only.

4.1. Structural properties

Synthesis appear to be quite reproducible. Five different solids were prepared by the sol–gel process whose calcination at 1200 °C leads always to strictly the same structure. The process has been already described by Machida and coworkers [15] and previously used in our laboratory [16]. A previous study performed by Kimura et al. [17], has demonstrated that for barium hexaaluminate Al/Ba ratio is varying between 9.2 and 15. According to Groppi et al. [18] all the barium hexaaluminates for which this ratio is comprised between 12 and 13.2 should in fact correspond to a solid solution of two structures mutually soluble each other, one being rich in aluminium noted β_I (Al/Ba = 15) and a second rich in BaO noted β_{II} (Al/Ba = 9.2). Moreover, Kimura et al. [17] have shown that both phases do have the same XRD diagram, with only relative intensities of some diffraction peaks allowing to chose between the two β_I and β_{II} structures. Moreover, the β_I and β_{II} phases lead to 5.586 and 5.601 Å for a, respectively, and 22.727 and 22.905 Å for c and it has been published also that the c/a ratio is varying from 4.07 to 4.12 when Ba/Al is increasing, i.e., when alumina content decreases [19]. For our solids the unit cell parameters a and c have been calculated and compared also to literature's values. The experimental values we calculated (5.586 and 22.725) and the c/a value (4.07) are values corresponding to an alumina rich β_I phase according to Kimura [19].

Substitution of Al^{3+} in spinel blocks by Fe^{3+} ions induces only minute modifications of the X-ray diffraction patterns. The same peaks were present with the same intensities: however, all the spectrum was shifted to low 2θ

values, i.e., there was a unit cell expansion. When comparing cation sizes it is quite evident that insertion of iron cation into the structure leads to an increase of some crystallographic distances, as experimentally observed. The effect is particularly important for the c parameter, its value increases almost linearly with cation concentration. The reason explaining the strong expansion of c and the slight one for a may be related with sites in which iron is located. According to the hexaaluminate structure the c parameter is directed along the z-axis, which is a ternary axis for all octahedral and tetrahedral sites of the hexaaluminates [5]. Incorporation of a larger ion into an octahedral arrangement of oxygen atoms is likely to slightly lower the symmetry and to increase distance between opposite faces of an octahedron. The result is that the two groups of three oxygen atoms (above and below iron ion) are a little bit more separated. But in the same time each of the three oxygen atoms of one group pertaining one oxygen plane does not need to separate the others: on the whole the a parameter has not to change a lot.

The values of the SSA are typical for hexaaluminates synthesised after calcination at 1200 °C [16]. In the present study, the higher the iron content the lower the area obtained, suggesting that bulkier cations introduce some stress leading to a partial destabilisation of the network. Chemical bonds of iron-containing oxides have more ionic character than that of alumina. So at 1200 °C under a humid atmosphere migration of Fe^{3+} becomes likely and some sintering cannot be avoided. However, this phenomenon is rather limited and consequently solids show very good resistance towards sintering. Thermal destabilisation that may occur is relatively limited because substitution is restricted to a maximum of $1/3$ of the total aluminium cations. This is the reason why barium hexaaluminate has been chosen for that purpose.

4.2. Catalytic activity

The present results show that the higher iron content leading to a better activity is limited to 2 cations per unit cell as far as conversion is taken into account, or when catalytic activity is relevant to mass unit. However, the whole study concerns a bulk unsupported catalyst for which main part of cation is inaccessible and so not active.

For the support itself the catalytic activity is almost nil because obtained conversion is comparable to that for homogeneous reaction (reactor filled with crushed silica). This residual activity has been already observed for other solids which should normally have been not active. This has been explained by a parallel reaction like oxidative coupling leading to some traces of ethylene that burn instantaneously [20]. For the four solids containing from 1 to 4 iron ions per unit cell, the activity is strongly increased, whereas the apparent activation energies have similar values close to 85 ± 6 kJ/mol for fresh catalysts and 95 ± 5 kJ/mol for aged ones (table 5). All this means that solids, whatever the iron concentration and whether the state be aged or not, behave similarly. The nature of active sites seems to be always the same inducing a reaction path with the same limiting step. Only the number of actives sites may vary due to iron concentrations inducing variation of activities.

As far as conversions are concerned the solid $BaFe_2Al_{11}O_{19}$ is the most active, and increasing the iron content is not valuable. This is partly due to BET areas which decrease almost linearly when iron concentration increases. A low concentration of foreigner active cations is beneficial for activity by increasing the number of active sites, but at the same time some stress is also produced due to the larger size of Fe^{3+} ions compared to that of Al^{3+} ones. If the iron concentration is too high, the latter induces a too strong constraint and breaks the structure, leading to loss of area after aging. Effect of active sites whose number increases with iron content is counterbalanced by lowering the SSA.

At a given temperature, the specific activity increases with cation content but was not proportional to it (figure 4). Thus for the solid containing 4 cations per unit cell activity was only 2.4 times that corresponding to a solid having 1 cation per unit cell. The same is true for aged solids. It is experimentally observed that after aging the percentage of loss of conversion for each solid is exactly the BET area loss percentage. The only effect of aging is to induce some sintering without changing the nature of sites the latter being not changed. From the non-proportionality of activity versus iron concentration it is concluded that either only a part of accessible iron cations are active, or that there is some gradient in iron concentration between the bulk and the surface. In fact, it seems that the second hypothesis is more valid because it might have changed with sintering that is not observed.

On the other hand, the relative activities of the four solids at a given temperature have been compared to the population of iron in the four sites as deduced from Mössbauer measurements. In order to avoid problems connected with heat and mass transfers, the temperature of reaction (550 °C) was selected to obtain methane conversion lower than 25%. The activity (calculated per area unit) of the $BaFe_1Al_{11}O_{19}$ solid at 550 °C has been chosen as a

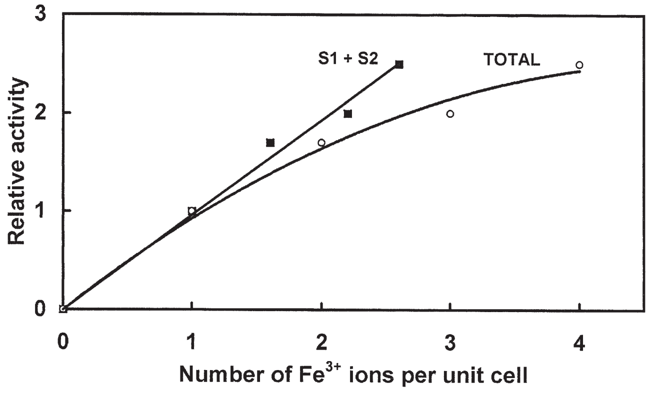

Figure 5. Relative catalytic activities of the fresh iron-substituted barium hexaaluminates as a function of the four sites occupancy factor deduced from Mössbauer measurements.

reference. The relative activities of the other catalysts was given by the ratio of the activity of a given solid to that of the $BaFe_1Al_{11}O_{19}$ one. Figure 5 gives the relative activities at 550 °C of the Fe-substituted barium hexaaluminate samples as a function of the $S1+S2$ sites population as well as a function of the number of iron cations per unit cell. Obviously, a linear relationship is observed between the number of iron cations in the S1 and S2 sites and the catalytic activity: the last property is strictly proportional to S1 and S2 population only. It is then concluded that catalytic activity in methane combustion is related to some Fe^{3+} ions octahedrally coordinated in sites we noted $S1 + S2$. Of course, only superficial $S1+S2$ sites should be concerned. By contrast, such a linear relationship is not observed by adding the S3 and S4 sites population to the $S1 + S2$ one, i.e., by considering the total number of iron ions present per unit cell. Moreover, the occupancy of such sites occurs only for solids containing already two iron cations per unit cell. It can be concluded that Fe^{3+} cations located into the S3 and S4 octahedral sites do not participate in the complete oxidation of the methane molecule.

Concerning the true nature of crystallographic sites, the S1 and S2 sites involved in catalytic combustion may be those noted 12k and $4f_{VI}$ by Dernier and Remeika [21], both being distorted octahedra as deduced from δ values issued from Mössbauer spectra. However, finer structural data are to be recovered before correct assignment of occupied cation sites [22], both inactive and active in methane combustion.

Recently, Groppi et al. [23] have prepared $BaFe_x Al_{12-x}O_{19}$ solids with $x = 1$, 3, 6, 9 and 12 by the method of carbonates precipitation. Despite the different method of synthesis, their samples are similar to the solids prepared in the present study. As a matter of fact, similar BET area values are obtained after the calcination of the samples at 1100 °C. In addition, these solids have been used in the catalytic combustion of methane. According to their experimental data, we have calculated an activity at 600 °C of 1.5×10^{-4} $\mathrm{mol\,h^{-1}\,m^{-2}}$ for their $BaFeAl_{11}O_{19}$ sample whereas our similar solid containing one iron per unit cell gives a value 2.5 times lower (6×10^{-5} $\mathrm{mol\,h^{-1}\,m^{-2}}$). Both values are very similar suggesting that the same types of sites are present with the same surface concentration on the two catalysts. The slight differences in activity may be accounted for by the preparation method.

Finally, the only but essential role of the strong thermally resistant barium hexaaluminate may be to immobilise active cations in accessible places (at least for those at the surface) without permitting them to migrate in any way, but changes in their valence state. In the limiting case it would be very worthwhile to synthesise divided $BaAl_{12}O_{19}$ and to only support epitaxially a thin layer of $BaFeAl_{11}O_{19}$. Both requirements, catalytic activity and thermal resistance would be fulfilled with minute amounts of active species. Finally, one can forecast that a lot of active transition metal cations might be introduced for generating new thermostable combustion catalysts.

5. Conclusion

Performing synthesis of iron-substituted barium hexaaluminates issued from a sol–gel method is a quite reproducible method. The process used is not too much time consuming and allows one to obtain homogeneous and monophased solids after calcining at 1200 °C. Introduction of 1–4 Fe^{3+} ions per unit cell is possible, and the obtained solid has always the same structure with some unit cell expansion due to bulkier cations introduced. Such iron-substituted hexaaluminates are very stable because whatever the number of cation introduced, a long duration aging with water and oxygen has almost no effect: no demixtion occurs and the only that occurs is a limited area loss. Contrary to manganese, for which substitution seems to be limited to 3 cations [15,20], substitution of aluminium by iron seems to have no limit. This is to be connected to the existence of parent hexaferrite structure which may be considered as an hexaaluminate for which total aluminium substitution by iron has occurred.

Catalytic activity is strongly enhanced by iron incorporation which is due to surface cations accessible to reactants. However, the increase of iron concentration occurs conversely to the specific surface area which decreases slightly, leading to the catalyst $BaFe_2Al_{10}O_{19}$ having the higher activity per mass unit. If specific activity is taken into account increasing iron content induces occupancy of sites which seem to be not accessible to reactants. Globally, when compared to manganese-substituted hexaaluminate [20], such $BaFe_xAl_{12-x}O_{19}$ solids have comparable activity associated with exceptional strong thermal resistance.

Mössbauer spectroscopy has been used for valency and coordination states determination. No ferrous ion was detected. Substitution of Al^{3+} occurs with Fe^{3+} only, even if calcination occurs at 1200 °C. Four different octahedral sites have been deduced from spectra containing Fe^{3+} cations. However, cations populations deduced from occupancy revealed that two slightly different sites consisting of octahedrally coordinated Fe^{3+} are connected with activity. These sites are present both in the bulk of hexaaluminate and at the subsurface of the uppermost oxygen layer. The latter are supposed to be responsible for the activity.

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