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Catalytic combustion of methane on copper-substituted barium hexaaluminates

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Barium hexaaluminates partially substituted by copper have been synthesized by a sol–gel method. Formation of the parent $BaAl_{12}O_{19}$ and the mixed $BaCuAl_{11}O_{18.5}$ catalysts occurred during calcination at 1200 °C. XRD showed a good crystallinity of the structure and expansion of the unit cell parameter due to the presence of larger Cu^{2+} ions in place of Al^{3+} in tetrahedral sites. The presence of copper strongly enhances the catalytic activity in methane combustion, which should be due to the Cu^{2+} species evidenced by FTIR of adsorbed CO and by TPR. The introduction of a second copper ion in the structure was not possible, however, as revealed by the formation of copper (II) aluminate in addition to the Cu-substituted hexaaluminate phase.

Keywords: methane combustion, barium hexaaluminate, copper substitution, thermal stability, high temperature combustion catalyst

1. Introduction

As noted by Campbel [1], “electricity-generating plants have a basic anomaly for which catalysis offers solutions”. The production of primary energy by combustion of fossil fuels leads to the emission of nitrogen oxides, although careful chemical engineering can reduce the production of pollutants [2]. Catalytic combustion offers an attractive solution for zero NO_x emissions [3], and can be achieved by supported noble metals for which many studies have been published [4]. For high power output, a high thermal stability of the catalysts is required. Materials like hexaaluminates have been known as heat-resistant for more than seventy years [5], and have been used more recently as supports for noble metal [6] or new generation catalysts when doped with active cations [7]. Among transition metal oxides used as combustion catalysts, CuO is one of the most active [8]. It may be very valuable to combine the catalytic activity of Cu^{2+} ions with the thermal stability of the hexaaluminate structure: in this work, therefore, we substituted copper ions for aluminium ions in the hexaaluminate structure.

2. Experimental

2.1. Preparation of the catalysts

The catalysts are relative to the barium hexaaluminate phase, $BaAl_{12}O_{19}$, in which one or two aluminium ions have been substituted by copper ions, leading to a $BaCu_xAl_{12-x}O_{19-\delta}$ stoichiometry ($x = 1, 2$). They were prepared by a sol–gel method similar to that described by Arai et al. [9]. The preparation was performed under argon using standard Schlenk techniques. The alcohol used as solvent was dried and distilled before use. Metallic barium (1.7 g) and aluminium isopropoxide (31.8 g) were suspended in 400 ml of isopropanol. The suspension was refluxed for 3 h, then cooled to room temperature. Hydrolysis of the metal alkoxides mixture was performed with an under-stoichiometric amount of water ($xH_2O/M(OiPr)_x = 0.5$, in which $x = 2$ for M = Ba, and $x = 3$ for M = Al), diluted in isopropanol and dripped slowly. For the copper-containing solids, the required amount of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in a water/alcohol mixture and added during the hydrolysis step. A gel was formed rapidly, and kept at ambient temperature for 15 h. The solvents were evaporated under reduced pressure, and the powders obtained were dried at 120 °C for 3 h, followed by calcination in a quartz cell at 1200 °C under flowing oxygen for 24 h. This temperature was necessary to ensure the complete formation of the hexaaluminate phase [10]. The catalysts issued from this calcination will be referred to as “fresh catalysts”.

Further aging was performed at the same temperature (1200 °C) for another 24 h, in the presence of steam (6 vol%) added to an O_2/N_2 gas mixture (5 vol% O_2). Steam is well known for its tremendous effect on the sintering of oxides at high temperatures [11]. This procedure represents a quick simulation for the aging of a combustion catalyst under working conditions for long periods [10]. The resulting solids are referred to as “aged catalysts”.

2.2. Physicochemical analysis

Chemical analysis of the metals (Al, Ba and Cu) was performed by AAS after dissolution of the solids in a mixture of concentrated acids (HF + HCl + HNO_3).

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X-ray diffraction patterns were recorded with a Siemens D500 diffractometer using the nickel filtered Cu Kα1 line at 1.5406 Å. The spectra were recorded between 5 and 70° (2θ) with a scan rate of $1.2^\circ\,\mathrm{min}^{-1}$. Silicon powder (60 mesh, 5 wt%) was added to the powders as an internal standard. The phases were identified by comparison with the JCPDS-ICDD files. The cell parameters were calculated using a least squares method, on the basis of the positions of 16 to 24 peaks.

Specific surface areas were measured by nitrogen adsorption at 77 K using the multipoint BET method. The solids were desorbed at 500 °C under vacuum (10^{-5} Torr) for 2 h prior to nitrogen adsorption.

UV-vis-NIR diffuse reflectance spectra were recorded with a Perkin Elmer Lambda 9 spectrometer, with an integrating sphere allowing scanning from 200 to 2500 nm. $BaSO_4$ was used as reference.

CO adsorption on copper was studied by FTIR spectroscopy. The samples were pressed into thin disks (30–40 mg) treated in an IR cell allowing oxygen pretreatment at 500 °C for 12 h, followed by desorption at the same temperature. The spectra were recorded at room temperature with a Nicolet Magna 550 FTIR spectrometer (resolution set to 4 cm^{-1}).

Temperature programmed reduction (TPR) of the catalysts was performed under 1 vol% H_2 in argon, with a temperature ramp of $8\,^\circ\mathrm{C\,min}^{-1}$, starting from room temperature up to 1000 °C. Hydrogen consumption was monitored by an on-line TCD detector, and the percentage of copper reduction could be determined with an accuracy of 6–8%. The samples were pretreated in air at 400 °C for 1 h, then cooled to ambient temperature under argon before measurements.

The activity of fresh and aged catalysts for methane combustion was measured on 500 mg of powder in a quartz microreactor. The solids were first pretreated in O_2 at 400 °C during 1 h, cooled to 350 °C, then the reactant gas mixture consisting of 1 vol% CH_4, 4 vol% O_2 and 95 vol% N_2 was admitted. The total flow ($6.4\,\mathrm{l\,h}^{-1}$) corresponds to a GHSV of 15,000–25,000 h^{-1}.

3. Results

3.1. *$BaAl_{12}O_{19}$ matrix and monosubstituted catalyst $BaCuAl_{11}O_{18.5}$*

3.1.1. *Preparation and characterizations*

The X-ray diffraction pattern of the $BaAl_{12}O_{19}$ solid corresponds to that of the ICDD file 33-128, attributed to a $BaAl_{13.2}O_{20.8}$ phase which crystallizes in the hexagonal system. It is now well established that the so-called “barium β-aluminates” exist in a wide range of Ba/Al ratios [12]. The β_I-phase (Ba-poor) corresponds to the $BaAl_{14.66}O_{23}$ formula, and the β_{II}-phase (Ba-rich) to $BaAl_{9.15}O_{14.73}$. They have very similar diffraction patterns aside from some in the relative intensities of the lines [13]. These two phases coexist for intermediate Ba/Al compositions, and $BaAl_{12}O_{19}$ corresponds to a stoichiometric mixture of the β_I- and β_{II}-phases. The unit cell parameters (table 1) calculated for our solid are close to those published previously by Forzatti et al. ($a = b = 5.593$ Å; $c = 22.767$ Å) for a β_I–β_{II} mixture of composition $BaAl_{12.7}$ [13].

Table 1
Unit cell parameters calculated from powder diffraction pattern of the fresh solids.

Catalyst	a (Å)	c (Å)
$BaAl_{12}O_{19}$	5.587	22.743
$BaCuAl_{11}O_{18.5}$	5.615	22.654

Table 2
Weight percentages of the metals obtained by chemical analysis.[a]

Theoretical formula	Ba	Al	Cu	Experimental formula
$BaAl_{12}O_{19}$	17.9 (th)	42.3 (th)	–	
	17.3 (exp)	41.9 (exp)		$BaAl_{12.33}O_x$
$BaCuAl_{11}O_{18.5}$	17.1 (th)	37.0 (th)	7.9 (th)	
	15.5 (exp)	39.4 (exp)	7.3 (exp)	$BaCu_{1.02}Al_{12.94}O_x$

[a] th = theoretical composition; exp = experimental value.

Table 3
Specific surface areas ($\mathrm{m}^2\,\mathrm{g}^{-1}$) of fresh and aged catalysts.

Solid	Fresh state	Aged
$BaAl_{12}O_{19}$	10	9
$BaCuAl_{11}O_{18.5}$	11	6

The diffraction pattern of the copper-substituted hexaaluminate corresponds to the same ICDD reference file (33-128), together with a few weak lines attributed to traces of α-Al_2O_3. No copper-containing phase is observed. The diffraction lines are slightly shifted compared to the pattern of $BaAl_{12}O_{19}$, because of a cell expansion due to the larger size of Cu^{2+} ions compared to that of Al^{3+} ions. This effect is demonstrated for the a parameter (table 1), although on the opposite the c parameter decreases, which will be discussed later.

The chemical analyses of Ba, Al and Cu (when present) are in good agreement with the theoretical formulae (table 2). A slight aluminium excess is observed in the case of the $BaCuAl_{11}O_{18.5}$ solid, while the Ba/Cu ratio is correct. This is in accordance with the presence of α-Al_2O_3in the XRD pattern, whose source is the slight aluminium isopropylate excess introduced during the synthesis.

The specific surface areas of fresh and aged solids are presented in table 3. The BET area is 10 $\mathrm{m}^2\,\mathrm{g}^{-1}$for fresh $BaAl_{12}O_{19}$, and 9 $\mathrm{m}^2\,\mathrm{g}^{-1}$ after aging. Thus, the aging treatment under oxygen and steam at 1200 °C induces only a moderate surface loss (10%). As previously reported by several authors [7], the hexaaluminate structure resists well to thermal sintering. The surface area is not modified upon introduction of copper in the barium hexaaluminate lattice (11 $\mathrm{m}^2\,\mathrm{g}^{-1}$). The thermal stability of the matrix is not

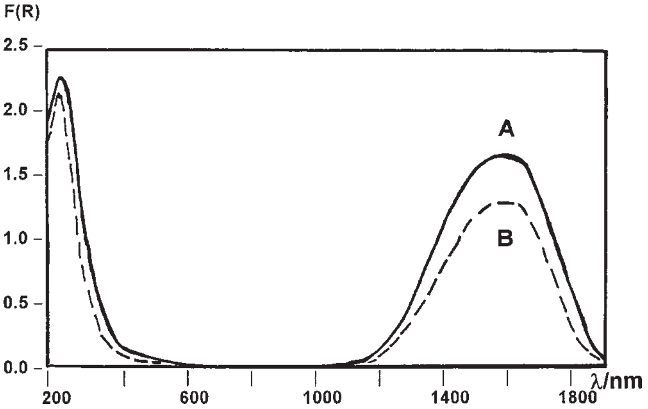

Figure 1. UV-visible spectra of the $BaCuAl_{11}O_{18.5}$ catalyst (A = fresh state; B = after aging).

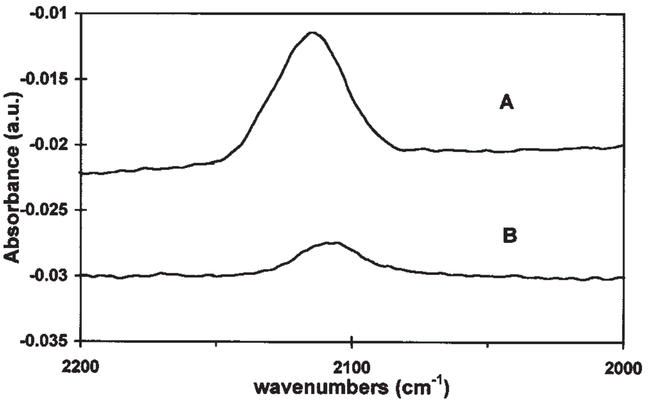

Figure 2. FTIR spectra of CO irreversibly adsorbed at room temperature onto the $BaCuAl_{11}O_{18.5}$ catalyst (A = fresh state; B = after aging).

fully preserved, however, since the surface area of aged $BaCuAl_{11}O_{18.5}$ is only 6 $m^2\,g^{-1}$.

Figure 1 shows the UV-visible spectra of both fresh and aged $BaCuAl_{11}O_{18.5}$ solids. Aging has almost no effect on the general aspect of the spectrum, except for a slight decrease of the NIR band (20%). The spectra present two bands at 250 and 1550–1600 nm. The first one is due to Cu–O charge transfer. The broad band in the 1550–1600 nm region is characteristic of the tetrahedral CuO_4 chromophore [14,15]. No absorption is observed in the 700–850 nm region, which would correspond to the octahedral CuO_6 chromophore [14,15]. This suggests that the copper ions are exclusively located in tetrahedral positions of the hexaaluminate structure.

Figure 2 depicts the IR spectra of CO irreversibly adsorbed at room temperature on fresh and aged $BaCuAl_{11}O_{18.5}$. A single νCO band is observed at 2115 cm^{-1} for the fresh catalyst, which after aging is shifted to 2110 cm^{-1} and is of lower intensity. This band is characteristic of CO adsorbed on oxidized copper species. The optical densities, expressed in absorbance units per gram of catalyst and normalized to 1 wt% Cu, are 0.061 for fresh $BaCuAl_{11}O_{18.5}$, and 0.014 for the aged solid. The aging treatment reduces the number of surface sites available for CO adsorption by a factor of approximately 4.

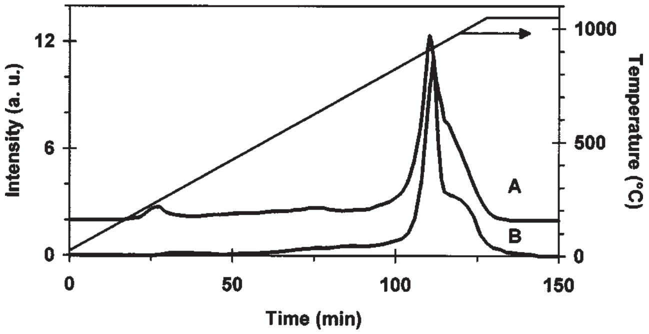

Figure 3. TPR profiles of the $BaCuAl_{11}O_{18.5}$ catalyst (A = fresh state; B = after aging).

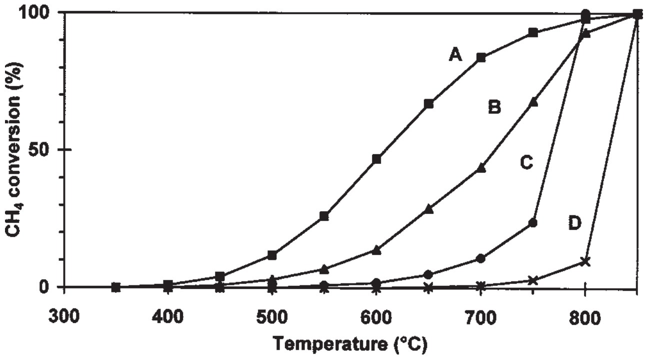

Figure 4. Catalytic combustion of methane over hexaaluminate based catalysts: A = $BaCuAl_{11}O_{18.5}$ fresh state; B = $BaCuAl_{11}O_{18.5}$ after aging; C = $BaAl_{12}O_{19}$ fresh state; D = empty reactor.

TPR experiments performed on the $BaAl_{12}O_{19}$ matrix show the absence of hydrogen consumption up to 1000 °C. The TPR profiles of fresh and aged $BaCuAl_{11}O_{18.5}$ are shown in figure 3. The amount of hydrogen consumed between 25 and 1000 °C corresponds to the total reduction of Cu^{2+} into metallic copper for both solids. This reduction occurs in a single step, without intermediate Cu^{+} formation. The main reduction peak appears at high temperature (between 800 and 1000 °C), and should not be related to species involved in the catalytic reaction, since at this temperature the methane conversion is total (see figure 4). The TPR profiles were divided into three zones related to the catalytic activity: a first zone between ambient temperature and 400 °C, the temperature at which the conversion of methane starts; a second zone between 400 and 800 °C, which corresponds to the whole methane combustion domain (from the beginning up to total conversion); and a third zone for temperatures higher than 800 °C, at which the conversion of methane is total. The percentages of copper reduced in these three zones are presented in table 4. The reduction occurring at low temperature (below 400 °C) concerned only a very small number of copper ions. For the fresh catalyst, only 3.5% of copper is reduced before 400 °C, 28.5% between 400 and 800 °C, and 68% after 800 °C. After aging the proportion of copper reduced before 400 °C falls to 1.7%, while the main part of the reduction (80%) occurs between 800 and 1000 °C. This suggests that most of the copper introduced in the hexaaluminate structure does not participate to the catalytic reaction, probably because it is located in positions inaccessible to the reactants. The aging treatment seems to induce the further migration of copper into these positions.

3.1.2. Catalytic activity in methane combustion

The unsubstituted $BaAl_{12}O_{19}$ phase exhibits some activity (figure 4) compared to an empty reactor. Methane conversion starts at 550–600 °C, at a lower temperature than the gas phase reaction. The activity of the aged matrix is only slightly lower. An apparent activation energy of 120 $kJ\,mol^{-1}$ was calculated for the fresh solid, and 110 $kJ\,mol^{-1}$ for the aged one, whereas a value of 175 $kJ\,mol^{-1}$ was found for the homogeneous reaction. In both cases, however, the selectivity towards CO_2 is not always 100%; up to 40% CO is detected at low conversions. The temperatures corresponding to 10, 50 and 90% methane conversion are reported in table 5. In table 6, the activity at low conversions (in moles of CH_4 converted per minute and per square meter of catalyst) has been calculated at various temperatures.

The introduction of Cu^{2+} ions in the hexaaluminate structure strongly enhances the activity: the T_{50} temperature is shifted down by about 150 °C (table 5), and CO_2 is the only product detected in the whole temperature range. At low conversions (550, 600 °C), the activity is roughly 30 times that of the non-substituted hexaaluminate (table 6). After aging, a deactivation is observed: the activity is reduced by a factor of about 2, independent of the surface area of the solids, and the temperature of half conversion increases from 610 to 730 °C. The decrease in activity is greater than the decrease in surface area (from 11 to 6 $m^2\,g^{-1}$), which is consistent with a loss of surface copper sites by migration into inaccessible positions.

Table 4
Percentages of Cu^{2+} ions reduced by hydrogen upon TPR experiments between ambient temperature and 1000 °C.

Catalyst	25 → 400 °C	400 → 800 °C	800 → 1000 °C
$BaCuAl_{11}O_{18.5}$ (fresh)	3.5%	28.5%	68%
$BaCuAl_{11}O_{18.5}$ (aged)	1.7%	18.3%	80%

Table 5
Temperatures corresponding to 10, 50 and 90% of methane conversion.

Solid	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
$BaAl_{12}O_{19}$ (fresh)	675	765	780
$BaAl_{12}O_{19}$ (aged)	725	760	780
$BaCuAl_{11}O_{18.5}$ (fresh)	510	610	740
$BaCuAl_{11}O_{18.5}$ (aged)	580	730	770

3.2. Preparation of a bi-substituted catalyst $BaCu_2Al_{10}O_{18}$

In the attempt to increase the amount of catalytically active copper in the hexaaluminate structure, a catalyst was synthesized in which two Cu^{2+} ions should replace aluminium ions. After calcination at 1200 °C under oxygen, the XRD pattern showed the presence of copper aluminate $CuAl_2O_4$ together with the hexaaluminate phase. Variation of the cell parameters of the hexaaluminate phase was comparable to that observed in the case of the monosubstituted solid, and led to the conclusion that the substitution of aluminium is limited to about one copper ion. The activity of this solid was between those of fresh and aged $BaCuAl_{11}O_{18.5}$, in terms of conversion temperatures, and in agreement with its lower surface area (5 $m^2\,g^{-1}$ for fresh $BaCu_2Al_{10}O_{18}$, compared to 11 $m^2\,g^{-1}$ for fresh $BaCuAl_{11}O_{18.5}$). When calculated per surface area of catalyst (table 6), however, the activity of the bi-substituted catalyst is slightly higher than that of the mono-substituted one, which suggests that more active sites are present per surface area unit, and that a little more than one copper ion per unit cell can be accommodated in the hexaaluminate structure.

4. Discussion

4.1. Properties of the $BaAl_{12}O_{19}$ matrix

Hexaaluminates, also called β-alumina, possess a particular hexagonal layered structure composed of alumina spinel blocks separated by M_2O or MO planes, where M stands for alkaline or alkaline-earth metals [16]. Prepared by a sol–gel method, the hexaaluminate phase is quickly obtained; however, a temperature of 1200 °C is required for its formation. The XRD pattern shows the presence of a single phase, which corresponds to the $BaAl_{13.2}O_{20.8}$ structure in the ICDD files [17]. As already mentioned, the Ba/Al ratio may vary between 9.2 and 15 in hexaaluminates, with only very slight modifications of the XRD patterns [12]. The cell parameters calculated in our case, with an Al/Ba ratio close to 12, are in agreement with a mixture of both β_I- and β_{II}-phases in almost equal concentrations [13,18].

Table 6
Relative reaction rates at various temperatures, expressed as μmol CH_4 converted per minute and per square meter of surface area (μmol CH_4 $min^{-1}\,m^{-2}$).

Solid	500 °C	550 °C	600 °C	650 °C	700 °C	E_a ($kJ\,mol^{-1}$)
$BaAl_{12}O_{19}$ (fresh)	0.033	0.076	0.200	0.473	1.076	120
$BaAl_{12}O_{19}$ (aged)	0.033	0.067	0.144	0.302	0.709	110
$BaCuAl_{11}O_{18.5}$ (fresh)	0.983	2.117	3.833	–	–	98
$BaCuAl_{11}O_{18.5}$ (aged)	0.483	1.142	2.283	–	–	98
$BaCu_2Al_{10}O_{18}$ (fresh)	1.450	3.167	5.975			85

Barium hexaaluminate is known for its exceptional resistance to sintering at elevated temperatures. This is confirmed here, since upon aging at 1200 °C in the presence of steam, the surface area decreases only from 10 to 9 $m^2\ g^{-1}$.

The solid shows a moderate activity in the combustion of methane, which is clearly higher than the simple gas phase reaction: the reaction starts at 550–600 °C, and the full conversion is obtained at 800 °C with a T_{50} of 765 °C. CO is formed in large amounts at moderate temperature, however. This type of activity has been already observed for mixed oxides like $MgAl_2O_4$ [19]. It may be supposed that some oxygen anions with a basic character could lead to methane coupling into ethylene on oxides containing either alkaline or alkaline-earth ions. Ethylene is then quickly combusted. In the case of barium hexaaluminate, Busca et al. [20] have indeed shown that the surface has a medium-strong basic character, probably due to the preferential exposition at the crystallite surface of the so-called "mirror planes" containing the barium ions. Another point worth considering is that anisotropic oxygen self-diffusion in this mirror plane has been observed in single crystals of barium hexaaluminate by secondary-ion mass spectrometry [21], suggesting a high mobility of the surface oxygen ions.

4.2. Copper-substituted barium hexaaluminates

4.2.1. Effect of copper introduction on the hexaaluminate structure

Substitution of one copper ion for aluminium in the hexaaluminate phase does not induce a severe structural stress, since the structure is preserved despite the different valences of these two ions. The XRD lines are shifted to lower 2θ values, however, revealing an enlargement of planes distances, although for some of them shorter distances were calculated. It is surprising that copper introduction leads to an increase of the a cell parameter, while c becomes shorter. The effective ionic radii of Al^{3+} and Cu^{2+} ions in tetrahedral coordination are 0.39 and 0.57 Å, respectively [22]. Thus introduction of copper should result in an increase of the M–O bond by roughly 25%, which is very high. This explains the increase of the a parameter. It is well known that copper complexes exhibit a Jahn–Teller effect leading to lower symmetry. The tetrahedron deformation may occur along the three-fold axis, leading to a C_{3v} symmetry like for Cu^{2+} in ZnO [23], for which the axial Cu–O bond is slightly *shorter*. If another tetrahedral deformation along the (111)-axis occurs, there is a flattening of the tetrahedron leading to D_{2d} symmetry [24] with the same effect: the z-component of the tetrahedron diminishes, whereas the x- and y-components increase. Thus introduction of copper ions in the hexaaluminate, i.e., in tetrahedral sites of the alumina spinel blocks, may result in an expansion of the three Cu–O bonds near the xy-plane (a expansion), and to the shortening in the axial Cu–O bond along the z-axis (c lowering).

Diffuse reflectance spectra of both fresh and aged $BaCuAl_{11}O_{18.5}$ present the characteristic band of Cu^{2+} ions in tetrahedral coordination. In comparison, the spectrum of the parent $BaAl_{12}O_{19}$ shows no absorption down to 200 nm in the UV range. The copper ions occupy tetrahedral sites of the spinel block. Analysis of the barium hexaaluminate crystal structure has shown that the T_d sites represent about 40% of the total Al^{3+} sites, while 60% are octahedral sites [25], and that three types of T_d sites exist. This must have some incidence on the activity: active sites should be tetrahedrally coordinated superficial Cu^{2+} ions. It must be noted that if Cu^+ ions are present they will escape DRS analysis since they do not absorb in the visible and near-infrared range. This is unlikely, however, according to the preparation procedure (Cu^{2+} precursor, calcination under oxygen at 1200 °C), and the hydrogen consumption in TPR experiments supports the presence of Cu^{2+} ions.

Incorporation of copper in the hexaaluminate structure can lead to a combustion catalyst with high resistance to sintering, providing there exist surface copper sites which can chemisorb the reactants of the gas phase. IR spectroscopy of irreversibly adsorbed CO was used to prove the existence of these sites. The νCO band observed at 2115 cm^{-1} on the fresh catalyst can be attributed to CO adsorbed on partially oxidized copper [26], although its attribution to reduced or oxidized copper species is still a matter of controversy [26–30]. As pointed out by several authors [28,30], oxidized copper species can be reduced by CO at room temperature. Recently, Balkenende et al. [29] showed that oxidized and reduced copper cannot be distinguished by their CO absorbance frequency: on a 20% Cu/SiO_2 catalyst reduced at increasing temperatures, the CO absorption band shifts from 2135 cm^{-1} after mild reduction (573 K) to 2095 cm^{-1} after severe reduction at 873 K for 16 h; on the fully oxidized catalyst the νCO band is observed at 2120 cm^{-1}. In the case of our $BaCuAl_{11}O_{18.5}$ fresh catalyst, CO adsorption allowed us to demonstrate the presence of surface copper species responsible for the methane combustion reaction. It is interesting to note that the intensity of the νCO band is fairly low (0.061 absorbance units per gram catalyst, normalized to 1 wt% Cu) with respect to the amount of copper introduced (about 8 wt%). For comparison, CO adsorbed in the same conditions on a CuO/Al_2O_3 catalyst (4.8 wt% CuO) gave a νCO band of 3.017 (in the same unit), about 50 times more intense [31]. This suggests that only a small fraction of the copper introduced in the hexaaluminate structure is accessible to the gas phase, probably because of the preparation method in which the copper is not deposited on the surface of a support, but incorporated in lattice positions into the whole catalyst structure.

The substitution of Al^{3+} ions by divalent Cu^{2+} seems to be limited to about one copper for one aluminium, since the incorporation of a second copper failed. The charge compensation for the different valences of these two ions is probably not sufficient to allow further copper incorporation in the structure without loss of stability leading to phase separation.

4.2.2. Effect of copper introduction on the resistance to aging

The surface area of the aged $BaCuAl_{11}O_{18.5}$ catalyst is lower than that of the $BaAl_{12}O_{19}$ matrix aged in the same conditions, which suggests that the hexaaluminate matrix is somehow destabilized by the presence of copper. This is not surprising since divalent copper is substituted for trivalent aluminium, which requires charge compensation by the oxide lattice. This compensation seems to be possible for one copper ion, but probably not much more. The resistance to sintering of the hexaaluminate structure has been attributed to a strong crystal shape anisotropy, which results in the inhibition of crystal growth in one direction (along the c-axis, perpendicular to the Ba-containing mirror planes) [18]. This has been attributed to the preferential diffusion of oxygen ions in the mirror plane, which plays a key role in the transfer of constituent ions from bulk to surface [21], and leads to grain growth in the $-c$ direction. It appears that the introduction of copper in the hexaaluminate matrix, leading to the creation of defects in the structure, will probably influence oxygen diffusion and the sintering process.

The UV-vis spectra show the decrease of the band due to tetrahedral copper (by 20% roughly). This can be attributed to the sintering, which increases particle size, leading to a decrease in light diffusion. The aging treatment may also induce the migration of copper in other tetrahedral sites of the hexaaluminate structure (three types of T_d sites), but no octahedral sites become occupied.

IR spectroscopy of adsorbed CO shows that less surface copper sites are available on the aged $BaCuAl_{11}O_{18.5}$. The intensity of this band (in O.D. per gram catalyst, normalized to 1 wt% Cu) is decreased by a factor roughly 4 when compared to fresh $BaCuAl_{11}O_{18.5}$, which means that upon aging the number of surface sites adsorbing CO has been reduced by the same factor. This is not only related to the loss of specific area, which is decreased only by a factor of about 2. It is worth noticing that the νCO band, when expressed per square meter of catalyst (0.040 a.u. for fresh catalyst, 0.017 for the aged one), is decreased by a factor 2.4 upon aging, which is in the same order as that of the activity per square meter of catalyst (see table 6, reaction rates at 550 and 600 °C). Thus, the activity is directly related to the superficial copper sites adsorbing CO.

4.2.3. Effect of copper introduction on the catalytic activity

The introduction of Cu^{2+} ions in the hexaaluminate structure leads to a fairly active catalyst in methane combustion. The T_{10} and T_{90} temperatures are 510 and 740 °C, respectively (table 5). For comparison, Arai et al. [32] obtained similar values with a $BaMnAl_{11}O_{19}$ catalyst (540 and 740 °C, respectively), at a slightly higher space velocity than our conditions, however (48,000 h^{-1}).

The TPR study of the $BaCuAl_{11}O_{18.5}$ catalysts (figure 3) clearly shows that most of the copper is reduced by hydrogen at high temperatures (>800 °C). This reduction represents 68 and 80% of the total amount of copper introduced for fresh and aged solids, respectively. Since at this temperature the total conversion of methane is reached, these species cannot be responsible for the catalytic reaction. They must correspond to Cu^{2+} ions located in the deep layers of the spinel block, in which the diffusion of hydrogen is difficult. For comparison, the reduction of copper ions of $CuAl_2O_4$ occluded in Al_2O_3 occurs in the 450–700 °C temperature range [33], and this solid is only weakly active in methane combustion.

We believe the fraction of copper reduced under 400 °C is responsible for the catalytic activity: it corresponds to the end of the first small reduction peak in the profile of the fresh catalyst (figure 3), and to the beginning of methane conversion (figure 4). These species represent only a very small fraction of the total amount of copper introduced (3.5 and 1.7% for fresh and aged $BaCuAl_{11}O_{18.5}$, respectively, table 4), and this amount cannot be increased since the synthesis of a $BaCu_2Al_{10}O_{19}$ solid is not possible. Upon aging, the fraction of copper reduced at <400 °C is decreased by a factor of 2, in agreement with the decrease in the activity between fresh and aged $BaCuAl_{11}O_{18.5}$.

On the whole, the active sites are likely to consist in tetrahedrally coordinated Cu^{2+} ions located on the uppermost layer of the spinel group of the barium hexaaluminate structure, at the limit of the Ba-containing mirror plane.

5. Conclusion

Barium hexaaluminate was prepared by a sol–gel method from the metal alkoxides, followed by calcination at 1200 °C under oxygen which led to a pure monophased solid. Its specific surface area of 11 $m^2\,g^{-1}$ did not vary with subsequent aging treatment in the presence of steam.

The substitution of one Al^{3+} ion by one Cu^{2+} ion, corresponding to the $BaCuAl_{11}O_{18.5}$ formula, is possible without structural stress, despite the different valence states. Crystallographic parameters are hardly modified, except for a slight expansion of the unit cell. All Cu^{2+} ions introduced occupy tetrahedral sites, although the octahedral positions in the hexaaluminate structure are more numerous. This solid is fairly active in the combustion of methane, and this activity cannot be improved by higher copper loading, since the introduction of a second copper ion in the structure is not possible. After aging at 1200 °C in the presence of steam, some deactivation is observed, but the solid remains active in this reaction. This justifies its use as a high temperature combustion catalyst.

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