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# Catalytic combustion of methane on aluminate-supported copper oxide

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## Abstract

Copper oxide has been deposited onto high surface area magnesium aluminate spinel prepared from alumina and magnesium nitrate. The catalytic properties of such a solid have been investigated in methane combustion. At the laboratory scale a very good activity is observed (light-off of 530°C) and no CO is detected. Aging at 1000°C under water vapour has no influence on activity. The previous catalyst has been washcoated on monolith and tested on a rig either with methane or synthetic natural gas at very high GHSV under conditions close to those of a gas turbine. In that case also, a good activity was observed. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Copper oxide; Spinel support; Methane and natural gas combustion; Gas turbine

## 1. Introduction

Catalytic combustion of methane is one of the most promising processes for energy production due to two main attractive environmental requirements only obtained with this process: $CO_2$ evolved for identical energy production is reduced by one quarter when compared to combustion of octane [1], and $NO_x$ formation is prevented because of the temperature lowering [2]. In some cases catalytic combustion must be performed at high temperatures, i.e., for high power yields. Gas turbines or radiant reformers need more output energy efficiency associated with restricted volume, which means large gas consumption and high temperatures for the catalyst [3]. This high-temperature methane combustion requires thermally stable catalysts. Noble metals (Pd, Pt, etc.) supported on a carrier like alumina are not well adapted to the severe conditions usually encountered inside a turbine. Both the temperature, in the 700–1200°C range, and the water vapour content, about 6 vol%, induce a severe sintering of the metallic particles, as well as of the support [4]. A rapid deactivation is generally observed. The use of thermostable supports is of little value because the metallic phase sinters as soon as the temperature exceeds 1000°C [5].

First transition metal oxides are another class of catalysts for the total oxidation of hydrocarbons [6]. Although they are less active than noble metals, the active solid state phases that can be obtained are numerous [7]. Previous works concerning hydrocarbons catalytic combustion have been already published, mainly on cobalt [8], chromium [9] and copper [10] base oxides. It has been observed that copper oxide is one of the most attractive phases, due to its relatively high activity and fairly good stability.

CuO can be obtained in a fully dispersed state as $Cu^{2+}$ ions provided it is supported on a carrier like

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alumina [11]. However, as soon as temperatures of ca. 700°C are reached, a solid state reaction occurs leading to a partially deactivated catalyst (copper aluminate formation) [10]. It should be remembered that alumina is a spinel with cationic vacancies due to the trivalent state of the aluminium ions. These vacancies can be filled with $Cu^{2+}$ ions migrating inside the bulk of the alumina. One means to prevent such a cation migration is to use as support an aluminate instead of alumina [12]. In such a case two main advantages are obtained:

1. Aluminates (aluminium spinels) are thermally stable structures, much more than transition aluminas from which they have been synthetized [13].
2. $Cu^{2+}$ ions migration inside the bulk of the support is then limited due to cationic vacancies occupancy.

One of the most stable spinels is $MgAl_2O_4$, for which high specific surface areas can be obtained [14]. It may be valuable to support CuO on such a solid in order to obtain an active and thermostable oxidation catalyst.

In the present study the catalytic properties of CuO/$MgAl_2O_4$ were investigated in the complete oxidation of methane at various stages of aging. Changes in catalytic behaviour were connected with modifications with surface properties.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. $MgAl_2O_4$ support

$MgAl_2O_4$ synthesis needed three steps:

1. The first one consisted of impregnation of a Degussa alumina (100 $m^2/g$) with an aqueous solution containing the required amount of magnesium ions.
2. Water was then evaporated at 80°C under reduced pressure. The solid so obtained has been dried further overnight at 120°C, then crushed, and finally calcined under air in a muffle furnace at 500°C during 24 h after having raised the temperature at a rate of 1°C/min. This first calcination is necessary in order to decompose the magnesium nitrate into magnesium oxide supported onto the alumina.
3. The solid was put into a vertical tubular quartz cell (above a fritted) and allowed to be flushed with dry oxygen from room temperature to 1000°C during 24 h. This temperature has been reached after having been raised at a rate of 1°C/min. Both temperature and duration are needed for a complete alumina–magnesia solid state reaction.

#### 2.1.2. CuO/$MgAl_2O_4$

$MgAl_2O_4$ was contacted for 1 h at room temperature with a copper nitrate solution containing an amount of copper allowing a final CuO content of 5 wt%. After water elimination, drying at 120°C, the solid has been calcined under oxygen at 500°C during 24 h.

#### 2.1.3. Monolith washcoating

Cordierite honeycomb monolith samples (1 in.×1 in. length·diameter, 400 CPSI) have been used as support of the previous catalyst. The application process leads to monoliths containing about 10 wt% of active phase.

### 2.2. Physicochemical characterizations

#### 2.2.1. Analysis

Chemical analyses were performed using AAS. The results are given in Table 1.

#### 2.2.2. BET area

The specific surface area (SSA) has been measured using the BET method on samples previously treated under vacuum at 500°C for 2 h.

#### 2.2.3. X-ray diffraction (XRD)

The XRD spectra have been obtained for $MgAl_2O_4$, and CuO/$MgAl_2O_4$ in the fresh and the aged states. The obtained diffraction patterns were compared to the theoretical ones from the JCPDS files.

#### 2.2.4. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance spectra have been recorded at room temperature with a PE Lambda 9 spectrometer, equipped with an integrating sphere. The spectral range covers 200–2500 nm. The reference used was $BaSO_4$.

Table 1
Chemical analysis

| Catalyst | CuO (wt%) | Mg (wt%) | Al (wt%) | Al/Mg | Cu/Mg | Al/Cu |
|---|---|---|---|---|---|---|
| $CuO/MgAl_2O_4$ (fresh) | 4.9 | 14.9 | 33.8 | 2.0 | 0.10 | 20 |
| $CuO/MgAl_2O_4$ (aged) | 2.9 | 9.0 | 20.6 | 2.02 | 0.10 | 20 |
| $CuO/MgAl_2O_4$ (theoretical) | 5.0 | 16.2 | 36.0 | 2.0 | 0.09 | 21 |

### 2.2.5. Temperature-programmed reduction

Experiments have been performed according to the following experimental conditions:

- sample weight: 30 mg,
- gas feed: $H_2$ (1%) in Ar,
- total flow: 20 $cm^3$/min,
- temperature raising rate: 5°C/min,
- temperature range: 25–900°C, and
- pretreatment: Ar, 400°C, 1 h.

The hydrogen consumption was monitored by using an in-line gas chromatograph. The amounts of hydrogen consumed was deduced from the area of the TPR peaks within a 6–8% error.

## 2.3. Catalytic activity measurements

### 2.3.1. Powdered catalysts

The catalytic activity of solids has been measured in methane combustion according to the following experimental conditions:

- catalyst weight: 500 mg,
- reaction mixture: $O_2$ (4 vol%)+$CH_4$ (1 vol%)+$N_2$ (95 vol%),
- total flow: 6.4 l/h corresponding to a GHSV of 15 000–25 000 $h^{-1}$, and
- pretreatment: $O_2$, 400°C, 1 h.

For all the samples in fresh and aged states, carbon monoxide was never detected.

The activity of $CuO/MgAl_2O_4$, as well as the support itself, was measured for the fresh state (directly issued from the calcination at 500°C) and for aged states, either at 1000°C or at 1200°C. Comparison of the catalysts was performed using the $T_{50}$ temperature (light-off temperature) defined as temperature corresponding to 50% of methane conversion.

### 2.3.2. Aging procedure

Aging procedures at very high temperature with water vapour were necessary to investigate the thermal stability of the catalysts. The conditions of aging are as follows:

- catalyst weight: 3 g,
- geometric bed: cylindrical (h=2 cm, ø=2 cm),
- temperature: 1000°C or 1200°C,
- feed composition: $O_2$ (5 vol%)+$H_2O$ (6 vol%) in nitrogen,
- total gaseous flow: 10 l/h, and
- aging duration: 24 h.

### 2.3.3. Rig test with washcoated monolith (Fig. 1)

Catalytic activity test has been performed either with methane or with synthetic natural gas. In every case fuel was mixed with nitrogen and oxygen in order to ensure a nominal constant concentration of 1 vol% of combustible gas.

Conditions are as follows:

- $CH_4$ (or SNG) 1 vol%+$O_2$ (10 vol%) in nitrogen,
- synthetic natural gas: $CH_4$ (93 vol%)+$C_2H_6$ (5 vol%)+$C_3H_8$ (1.5 vol%)+$C_4H_{10}$ (0.5 vol%),
- GHSV: 300 000 $h^{-1}$ (50 l/min),
- monolith (cordierite): length=0.8 in, diameter=1 in,
- temperature range: from 250°C to 850°C,
- temperature increased by steps of 50–70°C. Duration of an isothermal step: 12 min, and
- four temperatures simultaneously measured: gas inlet and outlet, monolith inlet and outlet.

## 3. Results

### 3.1. Catalytic activity

### 3.1.1. $MgAl_2O_4$

The support is totally inactive below 550°C. However, a slight conversion of 20% is observed roughly at 700°C (Fig. 2(a)). This result is a surprising since both $Mg^{2+}$ and $Al^{3+}$ cations are inactive in total oxidation

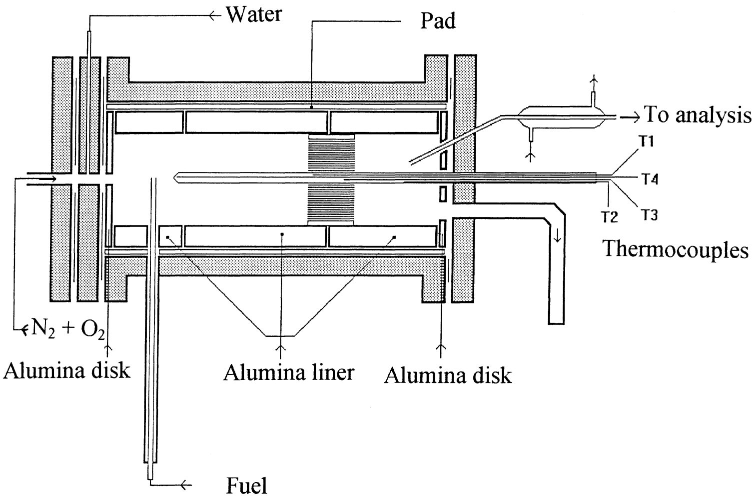

Fig. 1. GDF test rig.

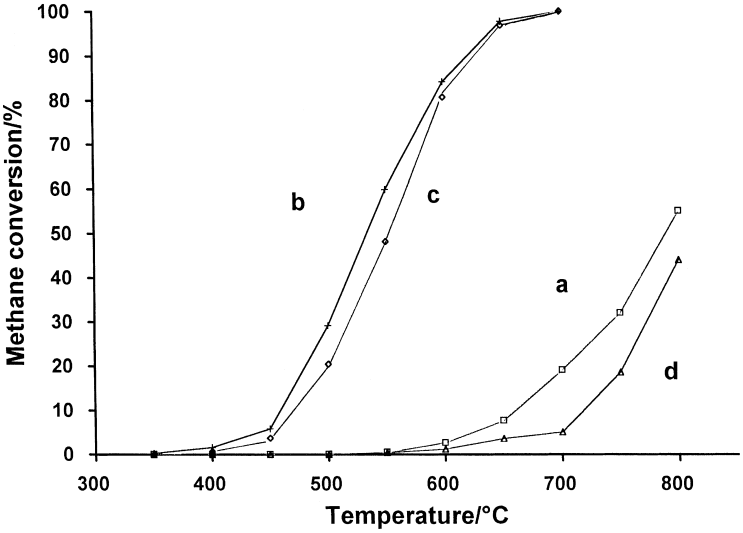

Fig. 2. Catalytic activity of $CuO/MgAl_2O_4$ in the methane combustion: (a) activity of the support alone, (b) activity of the fresh $CuO/MgAl_2O_4$ catalyst, (c) activity of the $CuO/MgAl_2O_4$ catalyst aged at 1000°C, and (d) activity of the $CuO/MgAl_2O_4$ catalyst aged at 1200°C.

($d^0$ cations). This small conversion at high temperatures may be explained by another parallel reaction (vide infra).

### 3.1.2. *$CuO/MgAl_2O_4$ (fresh state)*

Light-off temperature is 535°C (Fig. 2(b)), while the activation energy equals 120 kJ/mol. No change in activity with time has been observed in the full range of temperature.

### 3.1.3. *$CuO/MgAl_2O_4$ (aged states)*

When aged at 1000°C the solid showed an activity only slightly reduced, because the light-off temperature increased only by 20°C (Fig. 2(c)). Moreover when comparing the activity at low conversion, in the 350–500°C range, the activity was only reduced by a factor of 1.4. Such a value appears to be very small after the severe conditions of aging.

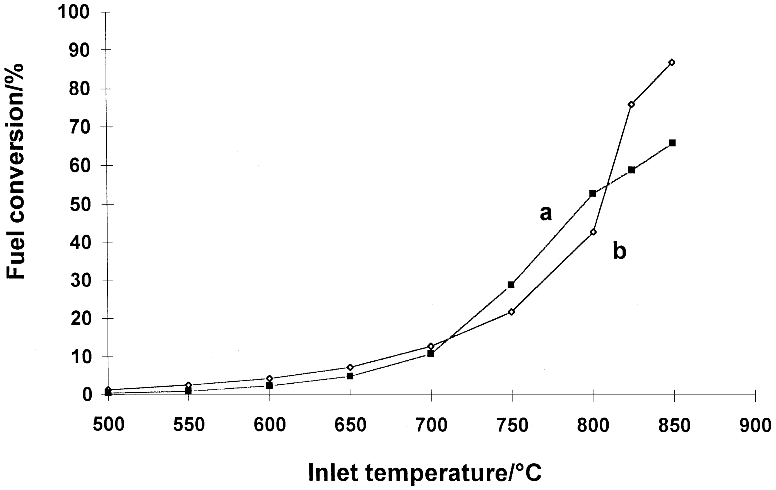

Fig. 3. Catalytic activity of the $CuO/MgAl_2O_4$ deposited onto cordierite honeycomb: (a) activity for methane combustion, and (b) activity for synthetic natural gas.

The same is not true when the solid was aged at 1200°C, since an almost inactive solid was obtained (Fig. 2(d)). This aged catalyst was even less active than the support alone itself.

### 3.1.4. *Monolith washcoated with $CuO/MgAl_2O_4$*

The catalytic behaviour of the monolith washcoated with 10% in weight of $CuO/MgAl_2O_4$ was the same whatever the fuel, i.e., methane or natural gas. Conversion curves are illustrated in Fig. 3 showing that the combustion started at roughly 500°C (1% conversion) and led to a light-off of 800°C. These temperatures may seem too high, but it should be remembered that the flow rate is very high (50 l/min) leading to very high velocity inside the monolith.

## 3.2. *Physicochemical characterizations*

### 3.2.1. *Chemical analysis (Table 1)*

Analysis performed by AAS reveals that elements ratios rather than elements weight percentages are indicative of constant composition. For catalyst aged at 1200°C, a fused solid appearing like clinker was obtained: consequently chemical attack for dissolution was so difficult that only part of this solid was really analysed.

### 3.2.2. *BET areas*

SSA values are reported in Table 2. Aging at 1000°C leads to some slight sintering, whereas aging at 1200°C leads to samples of very small specific areas.

Table 2
Specific surface area

| Catalyst | Treatment | SSA ($m^2/g$) |
|---|---|---|
| $MgAl_2O_4$ | None | 47.0 |
| $CuO/MgAl_2O_4$ | None | 44.7 |
| $CuO/MgAl_2O_4$ (A1000) | 1000°C+water | 33.1 |
| $CuO/MgAl_2O_4$ (A1200) | 1200°C+water | 2.2 |

### 3.2.3. *X-ray diffraction measurements*

Diffraction spectra of fresh and aged catalysts are reported in Fig. 4. In every case the diffraction lines of the spinel structure are clearly identified. In addition, the lines become sharper and more intense with increasing the aging temperature. This is to be related directly to the increasing crystal size also evident from the lowering of the BET area.

No peaks attributable to a transition alumina have been detected. Very small peaks corresponding to MgO (periclase) are observed for $MgAl_2O_4$. It has been reported that complete $MgAl_2O_4$ synthesis from magnesia and alumina is time consuming due to the kinetics of the solid state reaction [15], complete transformation is difficult to obtain.

For the fresh $CuO/MgAl_2O_4$ solid, the lines corresponding to MgO almost disappeared, whereas small

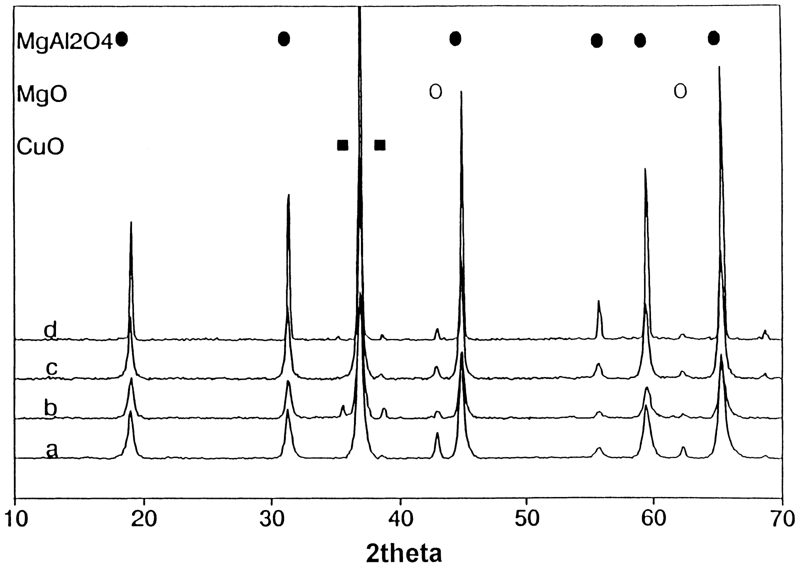

Fig. 4. X-ray diffraction patterns of $CuO/MgAl_2O_4$: (a) $MgAl_2O_4$ support, (b) fresh $CuO/MgAl_2O_4$ in the fresh state, (c) $CuO/MgAl_2O_4$ aged at 1000°C, and (d) $CuO/MgAl_2O_4$ aged at 1200°C. Symbols correspond to main diffraction peaks of $MgAl_2O_4$ (●) MgO (○) and CuO (■).

and wide ones corresponding to CuO were detected. This must be connected to the low copper loading as well as to a high dispersion state of CuO.

When aged at 1000°C the only difference in the XRD spectrum is the disappearance of the peaks due to CuO. At the same time the lines due to spinel become sharper.

After aging at 1200°C the spinel lines are very sharp because of the drastic sintering of the solid. Faint lines attributable to MgO are still observed.

### 3.2.4. *Diffuse reflectance spectroscopy*

The diffuse reflectance spectra of all the samples are reported in Fig. 5.

For the fresh sample the spectrum shows two mains features: (i) no absorption occurs in the near infrared, except weak and wide bands, hardly visible at ca. 1400, 1900 and 2100 nm, (ii) there is a large absorption from 200 to about 850 nm and responsible for the blue–grey colour of the solid. After the catalytic activity measurements up to 800°C, the following changes are observed: the absorption in the visible part of the spectrum is lowered leading to a well-defined band at 750 nm, and a second one of low intensity appears in the near infrared part at 1450 nm.

After aging at 1000°C the colour now turns pale yellow. The spectrum shows four separate bands. The most intense one occurs at 1450–1500 nm and seems to be symmetrical. The second one is weaker and is located at 750 nm. The third band is detected as a slight plateau at about 400 nm, while the last one is located at 250 nm. This latter band was also observed in the case of the fresh sample.

When aged at 1200°C the sample becomes almost white and significant changes of the absorption in the visible range are observed. The near infrared band located at 1500 nm decreases by about 60%. The most important change is the strong decrease (by ca. 85%) of the band located at 750 nm, which is hardly detected. The two other bands located in the UV range are not affected by such an aging at 1200°C. In conclusion the main effect of the increase in the aging temperature is the progressive disappearance of 750 nm band.

### 3.2.5. *Hydrogen reduction at programmed temperature*

The reduction profiles of copper oxide deposited on magnesium spinel are shown in Fig. 6, while Table 3 gives the hydrogen consumption, temperature maximum and $H_2/Cu$ ratio deduced from the TPR experiments.

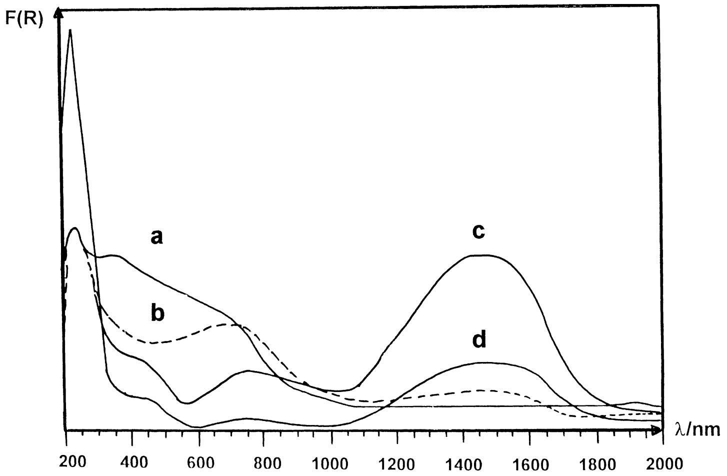

Fig. 5. Diffuse reflectance spectra of $CuO/MgAl_2O_4$: (a) fresh $CuO/MgAl_2O_4$, (b) after catalytic activity measurements up to 700°C, (c) CuO/ $MgAl_2O_4$ aged at 1000°C, and (d) $CuO/MgAl_2O_4$ aged at 1200°C.

The TPR results are not in accordance with the catalytic activity measurements. For the fresh catalyst (Fig. 6(a)), the reduction mainly consists of a double peak whose maximum is at 310°C, whilst a smaller shoulder is observed at ca. 230°C. After the main reduction peaks, a long tail is observed ranging from 350°C to almost 800°C. Thus for the fresh catalyst, TPR experiments evidence three types of copper ions.

When aged at 1000°C (Fig. 6(b)), the TPR profile has modified. The intensity of the main peak strongly decreases and two peaks at 210°C and 230°C are observed. When comparing the amount of hydrogen consumed below 350°C, only 1/4 of CuO initially present and easily reduced is still present. However, at the same time the catalytic activity is preserved, since no deactivation is observed after aging at 1000°C.

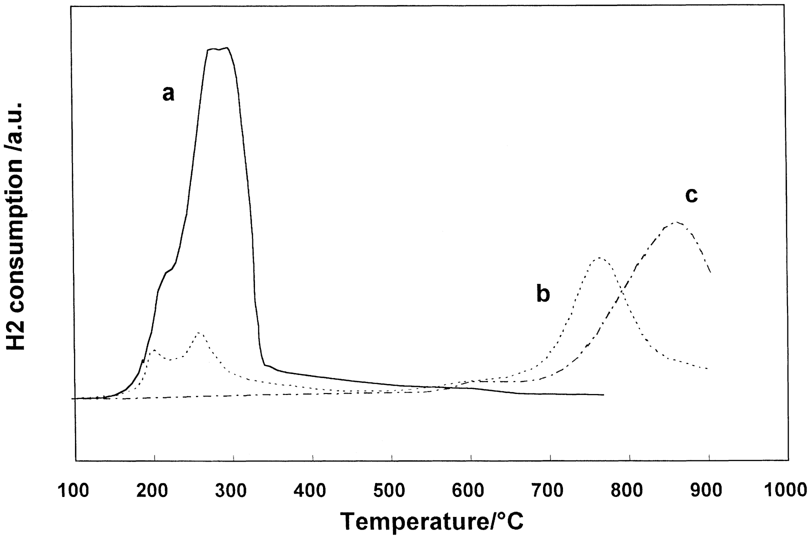

Fig. 6. TPR profiles of $CuO/MgAl_2O_4$: (a) fresh $CuO/MgAl_2O_4$, (b) $CuO/MgAl_2O_4$ aged at 1000°C, and (c) $CuO/MgAl_2O_4$ aged at 1200°C.

Table 3
TPR experiments: hydrogen consumption according to the temperature range

| Catalyst | 25°C<*T* <500°C | 500°C<*T* <1000°C | $H_2$ total/Cu |
|---|---|---|---|
| $CuO/MgAl_2O_4$ | 85% | 15% | 0.97 |
| $CuO/MgAl_2O_4$ (A1000) | 29% | 71% | 0.97 |
| $CuO/MgAl_2O_4$ (A1200) | 4% | 96% | 0.70 |

If aging is performed at 1200°C (Fig. 6(c)), additional changes are observed in the TPR profile. No $H_2$ consumption is observed below 550°C. Moreover, at the end of the experiment, when the final temperature is reached, only a fraction of the copper is reduced. The total $H_2$/Cu is now about 0.7 implying that copper was not completely accessible to hydrogen, or that the oxidation state has changed. XRD analysis showed that the $MgAl_2O_4$ structure is preserved, while no CuO phase was discussed. It is likely to think that the spinel, which has strongly sintered (2.2 $m^2/g$), has dissolved copper ions as reported in the literature for numerous transition metal ions [15]. For this sintered material having incorporated copper ions, hydrogen diffusion may be the limiting step of the reduction.

## 4. Discussion

One of the main facts of this study is the stability of the catalytic activity despite the disappearance of a great deal of copper as revealed by TPR, XRD and DRS. This may be due to the structure of copper oxide (vide infra)

### *4.1. Support properties*

The support is inactive below 550°C, but a slight conversion of 20% is observed at around 700°C, which may be explained by a second parallel reaction.

$MgAl_2O_4$ is not fully stoichiometric, since traces of MgO have been detected by XRD. According to the conditions of the preparation MgO is accessible to the reactants. In the case of the oxidative coupling of methane, the best catalysts are based on basic oxides (alkaline or alkaline-earth oxides) [16,17]. Thus for the $MgAl_2O_4$ support of the present study, methane may be activated by MgO leading to the formation of radical-anions. Due to temperature (500–700°C) and excess of oxygen, these are immediately oxidized to $CO_2$, because they are much more reactive than methane towards oxygen.

### *4.2. Fresh catalyst*

The diffuse reflectance spectroscopy shows that copper is only present as bulk CuO, whose spectrum is characteristic and different from that of isolated $Cu^{2+}$ ions. It consists of a band having a characteristic shape, i.e., a maximum located at ca. 700 nm decreasing linearly on the longer wavelength side and a tail ranging from 850 to the 2500 nm: The latter is due to some semi-conducting character of CuO (traces of $Cu_2O$?). The most important fact is the absence of a minimum. On the opposite the spectrum of isolated $Cu^{2+}$ ions deposited onto a support like alumina consists of a band whose maximum is at 760 nm, having a long side up to 1200–1300 nm and a characteristic minimum of absorption at 500–600 nm [10,11]. It is clear from the spectrum that the fresh catalyst contains almost exclusively CuO, although some isolated ions cannot be excluded because their spectrum would be submerged by that of CuO.

The XRD pattern shows also the presence of CuO (small peaks). Due to the low content of CuO (5 wt%) the appearance of lines suggests the presence of large crystallites of copper oxide.

The TPR profile also evidences the presence of such an oxide. In previous works performed on similar catalysts it has been shown that isolated $Cu^{2+}$ ions supported on alumina are reduced at 260–270°C, whereas the reduction of CuO occurred at 340°C [12]. So the main double peak must be assigned to the reduction of CuO. The double structure is probably due to a two-step reduction ($Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$) occurring at slightly different temperatures. The shoulder occurring at rather low temperature (230°C) is unusual for the reduction of $Cu^{2+}$ ions. It might be due to small amounts of species very hydrogen sensitive, for instance, small crystallites of CuO, or CuO in the form of bidimensional rafts.

### *4.3. Aged catalyst (1000°C)*

The drastic changes of the spectrum must be associated with a change of the nature of copper.

Both the 770 and 1450 nm bands, as well as the minimum at 550 nm, correspond now to isolated $Cu^{2+}$ ions, in octahedral and tetrahedral environment, respectively. This means that $Cu^{2+}$ ions have left the CuO network to enter that of the $MgAl_2O_4$ spinel. Previous studies have demonstrated that isolated $Cu^{2+}$ ions deposited onto alumina (spinel-like structure) are only octahedrally coordinated. Supported tetrahedral $Cu^{2+}$ ions have never been evidenced. In the case of tetrahedral coordination, copper ions must be necessarily located inside the bulk of alumina (copper aluminate formation) or at least just below the uppermost layer. In the case of the present CuO/$MgAl_2O_4$ catalyst, there are no data allowing the conclusion that the obtained new spinel is a superficial or a bulk one. However, one fact should be kept in mind: In TPR experiments, the reduction of the major part of the $Cu^{2+}$ ions (70%) occurs now at 750°C. This temperature level is not in accordance with a copper spinel located at the surface of the support for which reduction is expected at lower temperatures.

The XRD spectrum is of little value. It reveals that CuO has disappeared as oxide, while traces of MgO are still present. MgO may be formed by the following solid state reaction:

$$MgAl_2O_4 + CuO \Leftrightarrow CuAl_2O_4 + MgO$$

Such a reaction occurs partially between $MgAl_2O_4$ and FeO [15]. It can explain here both the disappearance of CuO as demonstrated by DRS, XRD and TPR and the appearance of MgO.

### 4.4. Aging at 1200°C

For the sample aged at 1200°C, the occurring changes are of another nature. In the diffuse reflectance spectrum both bands corresponding to $Cu^{2+}$ in tetrahedral and octahedral environments have decreased: 60% of $Cu^{2+}$ (Td) and 15% of $Cu^{2+}$ (Oh) are now missing, while a strong charge transfer is detected at 250 nm. Thus a change of valence state must be considered.

The XRD spectrum reveals only the presence of $MgAl_2O_4$ and MgO (traces). $MgAl_2O_4$ (support) and $CuAl_2O_4$ (partly formed) have the same unit cell parameter and they cannot be easily discriminated by the technique.

The TPR reveals that part of the copper is missing because the $H_2$/Cu ratio is now 0.70. This ratio may be explained by a partial decomposition of the Cu(II) spinel into a Cu(I) spinel. As a matter of fact, heating of $CuAl_2O_4$ at high temperatures leads to the formation of $CuAlO_2$ [14]. If partial reduction occurs, even in the presence of $O_2$ as mentioned in the literature, a simple calculation based on total $H_2$ consumption shows that there is now 60% of Cu(I) and 40% of Cu(II) according to the stoichiometry if all copper is assumed to be reduced. So 60% of $Cu^{2+}$ is now missing. This result has to be compared to that of DRS, which showed that 60% of tetrahedrally coordinated ions have disappeared along with 85% of octahedrally coordinated ones. In the $CuAl_2O_4$ spinel copper is located in both octahedral and tetrahedral sites. However, due to crystal field stabilization energy which is lower for tetrahedral symmetry, it is understandable that the disappearance of Cu(II) as revealed by TPR mainly concerns Cu(II) Td. Moreover, the Cu(I) ion having a $d^{10}$ electronic configuration, such as $Zn^{2+}$ ion, is likely to have the same preferential tetrahedral environment: reduction of Cu(II) Td into Cu(I) Td does not induce cation migration.

### 4.5. Relation between structure and activity

If the slight activity of the support is ignored, which is probably due to the oxidative coupling of methane [16,17], CuO supported on $MgAl_2O_4$ is a remarkable catalyst leading to a light-off at 530°C. Under the same conditions, a 2 wt% Pt/$Al_2O_3$ catalyst shows a $T_{50}$ of 480°C [18], i.e., only 50°C lower. All physicochemical characterizations clearly showed that only CuO is present as active phase, for which dispersion and texture are not known. Due to the type of exposed surface, an epitaxy between CuO and the $MgAl_2O_4$ spinel may be considered.

Copper oxide (tenorite) has a structure which is a distorted version of PtS. $Cu^{2+}$ has four Cu–O coplanar bonds corresponding to a strong octahedral modification [19]. The surface of CuO crystallites may well correspond to oxygen atoms arranged in a square planar arrangement. This is exactly the same for some spinels catalytically active, like $Co_3O_4$ and $Mn_3O_4$, for which only (1 1 1) and (1 1 0) low-index planes are supposed to exist at the surface [20]. Thus it is possible that the support and the

CuO structures match onto some planes leading to good anchoring of CuO. A high dispersion of the active phase would be expected, which is associated with a high catalytic activity.

In the same study [20] the authors have shown without ambiguity that no tetrahedral sites are present onto the spinel surface and that the activity is related to octahedral symmetry only. We proved the same here by DRS because no tetrahedral $Cu^{2+}$ are evidenced for the fresh catalyst, which is active.

No deactivation was observed after an aging performed at 1000°C revealing that the number of active sites is not deeply modified. The catalyst shows only a slight deactivation consisting of a rate reduced by a factor of 1.4 (conversions compared at low levels) and the $T_{50}$ shifts to higher temperature by only 20°C. This catalytic behaviour does not reflect at all the physicochemical characterizations, which show on the contrary profound modifications of the solid.

On the XRD pattern the slight peaks due to bulk CuO have disappeared, indicating either a redispersion of the oxide or a transformation. The BET surface area only decreased from 45 to 33 $m^2/g$, after aging at 1000°C. Moreover, when comparing the activity at low conversion, i.e., at a low temperature, it is valuable to note that the activity ratio (before and after aging) is strictly equal to the BET surface areas ratio ($r$=1.4). Thus aging seems to induce only slight sintering of catalyst particles, CuO anchored onto $MgAl_2O_4$. If aging had induced only a textural change, only a loss of CuO should have been observed either by XRD, DRS and TPR. Experimentally the opposite is observed.

The amount of $H_2$ consumed shows that 75% of copper present as CuO has disappeared, and that a second peak occurring at high temperature (760°C) corresponds to the copper aluminate. On the whole the stoichiometry $H_2/Cu$ has not changed at all between the fresh and the aged catalyst (see Table 2) and copper is still present as Cu(II) ions only. This resistance towards hydrogen reduction has been explained by the migration of copper inside the magnesium spinel forming a new copper aluminate. 25% of the initial copper content is still present in the form of CuO at the surface of the catalyst as revealed by TPR measurements. However, this low content of CuO is sufficient to exhibit an activity identical to that of the fresh catalyst. As a matter of fact the contradiction is only apparent and an explanation may be given according to a very simple model (Fig. 7).

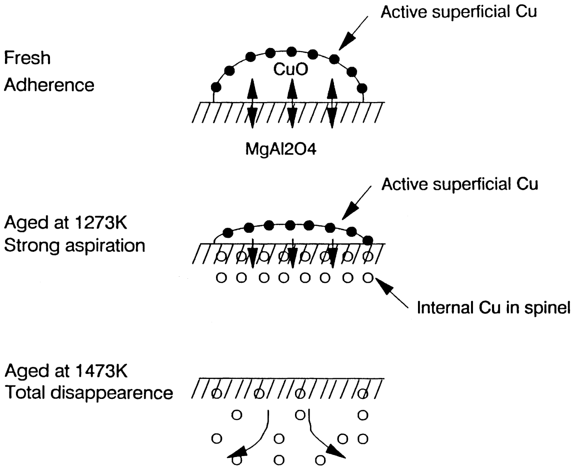

Fig. 7. Model for catalyst structure and aging.

$MgAl_2O_4$ is a spinel with a relatively high SSA. It is likely to think that the copper oxide particles have a quite large contact area with the $MgAl_2O_4$ support (epitaxy). A simple model consisting of CuO anchoring onto low-index planes (1 1 0) of spinel can explain the behaviour. At moderate temperatures the CuO particles lay onto the $MgAl_2O_4$ surface, because no sufficient driving force exists to enter the spinel. Aging at 1000°C induces a high mobility of Cu(II) ions, and a great deal of copper ions may migrate inside the bulk of magnesium spinel. It must be the copper ions at the CuO–$MgAl_2O_4$ interface, and the latter is not accessible to reactants. So up to three-fourth of the total CuO may disappear by such diffusion without changing the number of external copper ions (exposed surface sites). So the catalytic activity should not change, what is experimentally observed, whereas reducibility changes. Moreover, it is observed that tetrahedrally coordinated copper ions are now observed: these species are present only in the bulk of a mixed copper magnesium aluminium oxide.

When aged at 1200°C, copper oxide fully disappears, as revealed by TPR (no reduction occurring below 700°C) and by DRS (no $Cu^{2+}$ ions in octahedral symmetry). If no reduction by hydrogen is observed until 700°C, no reduction by $CH_4$ can occur because the reducing power of methane is lower than that of hydrogen: no activity is observed. According to our hypothesis of some CuO–$MgAl_2O_4$ epitaxy, when the last layer of CuO migrates a clean $MgAl_2O_4$ spinel surface is restored. Resulting activity is that of an inert and severely fritted support which is lower than that of the initial support. Moreover, the intensity of the bands due to $Cu^{2+}$ (Td) is reduced suggesting that some species are missing in the DRS analysis. This might be the case of $Cu^+$ ions for which the electronic configuration ($d^{10}$) leads to a totally non-absorbing species in UV–Visible. The formation of $Cu^+$ ions explains the decrease of the band observed by DRS as well as the value of the $H_2$/Cu ratio (Table 3).

DRS reveals that no octahedrally coordinated copper ions are now present and only tetrahedrally coordinated copper cations are observed. Study of catalytically active copper-containing spinel in hydrogenation reactions have revealed the "critical importance of the octahedral environment of cuprous ion" [21]. Finally octahedrally coordinated $Cu^{2+}$ions, pertaining here to CuO, are proved to be the active sites for methane combustion. When they disappear either as tetrahedrally coordinated $Cu^{2+}$ or as $Cu^+$ a decrease in the catalytic activity is observed.

## 5. Conclusion

$MgAl_2O_4$ may be easily prepared, with a reasonable surface area, from a high specific area alumina and magnesium nitrate. Deposition of CuO onto such a support leads to an efficient catalyst for the total oxidation of methane with a selectivity of 100% to carbon dioxide.

The catalytic activity is preserved after a thermal treatment at 1000°C in the presence of water and despite the partial formation of copper aluminate. In that sense it should be very valuable for medium-temperature application. After aging at 1200°C in the presence of water and oxygen, the reduction of the Cu(II) ions into Cu(I) species occurred, cuprous ions migrate into the magnesium aluminate bulk. A totally inactive solid is then obtained.

## References

[1] A.M. James, M.P. Lord, Macmillan's Chemical and Physical Data, Macmillan, London, 1992.

[2] L.D. Pfefferle, W.C. Pfefferle, Cat. Rev.-Sci. Eng. 29 (1987) 219.

[3] J. Saint-Just, J. der Kinderen, Catal. Today 29 (1996) 387.

[4] V. Labalme, E. Garbowski, N. Guilhaume, M. Primet, Appl. Catal. A 138 (1996) 93.

[5] P. Briot, Ph.D. Thesis, Université Claude Bernard Lyon I, no. 154–91, 1991.

[6] G.I. Golodets, in: J.R.H. Ross (Ed.), Heterogeneous Catalytic Reaction Involving Molecular Oxygen, Studies in Surface Science and Catalysis, vol. XV, Elsevier, Amsterdam, 1983.

[7] L.V. Azaroff, in: C. Klingsberg (Ed.), The Physics and Chemistry of Ceramics, Gordon and Breach, London, 1963, pp. 30–76.

[8] E. Garbowski, M. Guénin, M.C. Marion, M. Primet, Appl. Catal. 64 (1990) 209.

[9] S. Khairulin, B. Béguin, E. Garbowski, M. Primet, J. Chem. Soc. Faraday Trans. 93 (1997) 2217.

[10] M.C. Marion, E. Garbowski, M. Primet, J. Chem. Soc., Faraday Trans. 86 (1990) 3027.

[11] E. Garbowski, M. Primet, J. Chem. Soc., Chem. Commun. 11 (1991).

[12] M.C. Marion, E. Garbowski, M. Primet, J. Chem. Soc., Faraday Trans. 87 (1991) 1800.

[13] W.D. Kingery, Introduction to Ceramics, Wiley, New York, 1960.

[14] M.C. Marion, Ph.D. Thesis, Université Claude Bernard Lyon I, no. 02–90, 1990.

[15] P.P. Budnikov, A.M. Ginstling, Principles of Solid State Chemistry: Reactions in Solids, English transl.: Mac Laren & Sons, London, 1968.

[16] K. Aika, T. Nishiyama, Catal. Today 4 (1989) 271.

[17] J.A.S.P. Carreiro, M. Baerns, J. Catal. 117 (1989) 258.

[18] P. Briot, A. Auroux, D. Jones, M. Primet, Appl. Catal. 59 (1990) 141.

[19] A.F. Wells, Structural Inorganic Chemistry, 3rd ed., Clarendon Press, Oxford, 1962, p. 528.

[20] J.P. Jacobs, A. Maltha, J.G.H. Reintjes, J. Drimal, V. Ponec, H.H. Brongersma, J. Catal. 147 (1994) 294.

[21] L. Jalowiecki, G. Wrobel, M. Daage, J.P. Bonnelle, J. Catal. 107 (1987) 375.