

# Co, Ni, Cu aluminates supported on mullite precursors via a solid state reaction

D. Mazza\*, A. Delmastro, S. Ronchetti

*Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico, Corso Duca degli Abruzzi 24, 10129 Turin, Italy*

Received 13 May 1999; accepted 3 July 1999

## Abstract

Finely dispersed Me-aluminates (Me = Ni, Co, Cu), stable up to 1000–1100°C, are obtained by diffusion and reaction with mullite precursors. The Me-aluminates are ‘reaction supported’, indeed these phases are synthesized in form of finely dispersed crystalline region in a supporting inert material, this latter providing high surface area together with thermal and mechanical stability. Two different preparative routes are exploited, the reactivity of Co, Ni is higher with route A, in which these metals diffuse and react with pre-formed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles to form the corresponding aluminates. Cu reacts in different way, promoting the formation of mullite, without being incorporated into its structure. For this reason the preparative route which employs impregnation of 400°C mullite amorphous precursor (route B) yields complete reaction of CuO with alumina to form Cu-aluminate, dispersed on a mullite substrate at the final temperature of 980°C. This material shows remarkable catalytic activity in CH<sub>4</sub> oxidation. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Aluminates; Catalysis; Mullite; Spinel; Surfaces; X-ray methods

## 1. Introduction

It has been shown in the past that Cr, Ti, V, Mn, Fe and Co<sup>3+</sup> can be relatively easily incorporated into the mullite structure, entering the octahedral sites of the same and substituting for Al<sup>3+</sup>.<sup>1</sup>

Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, due to their larger ionic size and lower valence, are not incorporated into the same structure; the same ions have however been shown recently to react at low (500–1000°C) temperatures with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> forming the corresponding metal aluminates MeAl<sub>2</sub>O<sub>4</sub> (with spinel structure) by means of solid-state diffusion and reaction of the Me ions into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> lattice, which has by itself a defective-spinel structure.<sup>2</sup>

On the basis of the above evidence, we studied the formation of Co, Ni, Cu aluminates obtained by diffusion reaction of Me-oxides within Al<sub>2</sub>O<sub>3</sub>, this latter being dispersed in a highly reactive amorphous xerogel having 3:2 mullite composition (3Al<sub>2</sub>O<sub>3</sub>:2SiO<sub>2</sub>). The aim is to obtain Me-aluminates highly dispersed and embedded in a relatively inert support (reaction supported) by means of a solid state reaction. This route is alternative to the simple deposition of metal oxides by

impregnation of inert ceramic support by wetting and finally drying-firing.

These materials are tested and found to be active in the field of heterogeneous catalysis as supported metal oxides with large surface area, stable at elevated temperatures.

## 2. Experimental

### 2.1. Preparation of support material

The mullite reactive precursors were obtained by wet chemical route, i.e. sol–gel synthesis. Starting materials were Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Fluka 99.9% purity) and tetraethylorthosilicate (TEOS, Aldrich). A measured volume of TEOS is added to an equal volume of ethanol (95%) and half a volume of distilled water. The pH of the aqueous alcoholic phase is adjusted to 0.5–1.0 with a few drops of HNO<sub>3</sub>. In this way a clear solution is quickly obtained after some minutes of stirring at room temperature. The ‘r’ factor (i.e. water moles/TEOS moles) reaches a value of about 7.

Under these conditions TEOS is firstly partially hydrolyzed to silanol monomers. An aqueous solution of Al nitrate in stoichiometric amount is then added to the proper quantity of the TEOS solution. The clear

\* Corresponding author.

solution, thus obtained, is then treated with excess aqueous ammonia (30 wt%). Condensation and cross-linking of silanol monomers rapidly occurs, whilst aluminum hydroxide precipitates, thus obtaining the complete gelation. The gel so obtained is first dried at 105°C then gradually heated up to 400°C, with the release of a part of the water and gaseous products formed by the decomposition of the nitrates and TEOS. The solids so obtained (xerogels) show, by X-ray diffraction, patterns with very broad fluctuations and they can still be classified as amorphous.

This material displays a very large surface area (about 400 m<sup>2</sup>/g) and monomodal pore size distribution. TG/DTA evidence indicates that weight loss continues up to 960°C, this being constituted by H<sub>2</sub>O loss from condensation of OH groups. The recombination of OH groups to H<sub>2</sub>O molecules has been demonstrated also for other sol-gel derived mullite precursors up to 900°C by FTIR.<sup>3</sup> At 980°C a first exotherm occurs, corresponding to the partial crystallization from the amorphous mass of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocrystals at this temperature, however, the specific surface has dropped to 160 m<sup>2</sup>/g. The stoichiometric 3:2 mullite only forms at 1250°C, as indicated by the second exotherms, by reaction of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with remaining amorphous SiO<sub>2</sub>. This behaviour, according to Aksay et al.<sup>4</sup> indicates that the scale of homogeneity of the amorphous precursor falls in the manometer range (1–100 nm). From XRD line broadening (Scherrer method) the crystal domains of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> result in about 15 Å.

## 2.2. Impregnation of the support material

Two preparative routes have been investigated, namely (A) and (B), summarized in Table 1. Both routes comprise the impregnation of a reactive support of 3:2

Table 1  
Summary of the A and B preparation routes for Me-aluminates

3:2 Mullite wet gel 150°C	⇒ Mullite-xerogel 400°C	⇒ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> dispersed in amorphous silica 980°C - 1h heating
	↓	↓
	↓(B)	↓(A)
	↓	↓
	Impregnation with Me-nitrates in aq. solution and gradual drying up to 150°C	Impregnation with Me-nitrates in aq. solution and gradual drying up to 150°C
	↓Direct heating	↓Stepwise heating
	↓up to 980°C	↓500–600°C
	↓in air	↓700–980°C
	Me-aluminate and $\gamma$ -Al <sub>2</sub> O <sub>3</sub> or mullite formation at 980°C	Ni, Co-aluminates formation by reactive diffusion or mullite formation (Cu)

mullite stoichiometry. This reactive support is constituted by a finely dispersed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in amorphous silica (mullite980 in Fig. 1) in route A or by an amorphous mullite precursor (mullite400 in Fig. 1) in route B. In both routes the reactive support is impregnated with a concentrated Me-nitrate aqueous solution at room temperature. The mole ratio Me:Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub> is 1:2.75 (Me/Al=6,0%) and the concentration of the solution is 0.034 Molar. Typically 2 g of mullite precursor were immersed in 50 cm<sup>3</sup> of Me-nitrate solution, then stirred at room temperature for about 30 min. The admixture is then heated up to 150°C and kept at that temperature for 10 h, thus obtaining finely dispersed metal nitrates on the surface. In the case of cobalt already after treatment at 150°C the diffraction lines of Co<sub>3</sub>O<sub>4</sub> are evident by XRD. The above procedure results to be efficient in dispersing the metal nitrates only with small amounts of reagents. A fourfold scale-up of the process quantities in the case of Cu nitrate, produced a less active material for the catalytic combustion of methane, as discussed later, because of the incomplete reaction of CuO, as resulting from X-ray evidence.

## 2.3. Formation of metal aluminates

In route A the 980°C xerogel, which already displays nanocrystals of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> dispersed in amorphous silica, is impregnated with metal nitrates and subsequently heated up to 500°C, at this temperature the nitrates decompose into oxides (Co<sub>3</sub>O<sub>4</sub>, NiO and CuO). Above this temperature the behavior of CuO differs from that of Ni and Co oxides. Indeed, Co<sub>3</sub>O<sub>4</sub> and NiO gradually diffuse and react inside the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles, producing increasing amounts of MeAl<sub>2</sub>O<sub>4</sub> along with temperature increases, as shown by PXRD evidence. This behavior is similar to that found by Bolt et al.<sup>2</sup> At 900°C the reaction is completed and Co, Ni-aluminates are formed (Figs. 2 and 3)

The crystal domains of these new phases can be estimated from line broadening of the same size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles (around 15 Å) in the case of Ni while with Co the particle size increases up to 60 Å (Scherrer method). Amorphous silica remains unreacted. The reaction of Co is apparently quicker than that of Ni, as found by Bolt et al.<sup>2</sup> The presence of CoAl<sub>2</sub>O<sub>4</sub> in the Co<sub>3</sub>O<sub>4</sub> deposited samples can not be established unequivocally by means of XRD; as CoAl<sub>2</sub>O<sub>4</sub> diffraction peaks have almost the same position as those of Co<sub>3</sub>O<sub>4</sub>. However, the enhancements of the relative intensities and the sharpening of the diffraction peaks (particularly those at  $d=2.84$  and  $2.43$  Å) and the appearance of the characteristic cobalt (II) blue color are strong indications of the formation of cobalt aluminates.

Al<sub>2</sub>O<sub>3</sub> shows a certain solubility in CoAl<sub>2</sub>O<sub>4</sub> (at 1000°C 40%) a fact that could suggest a concentration profile of this element, at least in the initial reaction at low temperature. A slight shift of the most intense

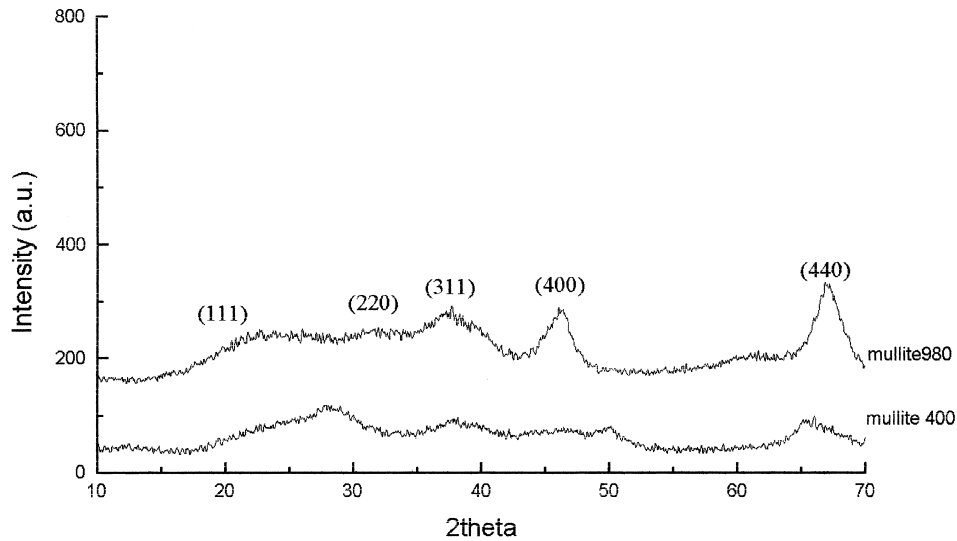


Fig. 1. X-ray diffraction patterns (monochromatized Cu  $K_{\alpha}$  radiation) of amorphous mullite precursor obtained at 400°C (below) and of the same material crystallized at 980°C for 1 h (above). Miller indexes of  $\gamma$ - $\text{Al}_2\text{O}_3$  in parentheses.

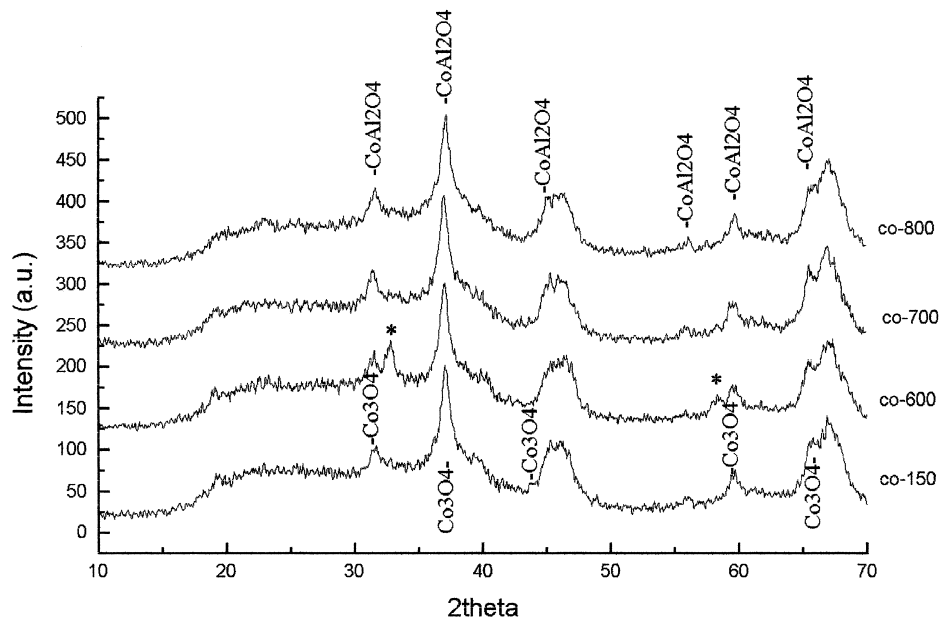


Fig. 2. X-ray diffraction patterns of supported Co-aluminates obtained through route (A) after 4 h heat treatments at the indicated temperatures (monochromatized Cu  $K_{\alpha}$  radiation) (peaks marked with asterisk are unassigned).

diffraction peaks along with the reaction, could be interpreted in this way.

The behavior of CuO is completely different. From experimental evidence it appears that this oxide promotes the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  with the formation of mullite, so that only a small amount of  $\text{Al}_2\text{O}_3$  is left to react with CuO to form Cu-aluminate, the main part of it reacting with  $\text{SiO}_2$  to yield mullite. These complex reactions occur between 800 and 900°C from the PXRD evidence at 900°C (0.5 h) the resulting phases are mullite (low-crystallinity),  $\gamma$ - $\text{Al}_2\text{O}_3$  with slightly shifted peaks to lower diffraction angles, a fact

that could indicate that a part of CuO can form a solid solution, thus increasing lattice constants of cubic cell, and traces of  $\text{CuAl}_2\text{O}_4$ . Even after 18 h of heating at 980°C the crystallization degree of the phases is not altered.

Route (B) comprises formation of mullite precursor (xerogel) at 400°C and its impregnation with the above described procedure. The obtained material is then directly heated up to 980°C in air. Again the behavior of CuO is different from Co, Ni-oxides. The promoter effect of CuO toward mullite formation is more pronounced by this route, as evidenced by the enhanced mullite

diffraction peaks (Fig. 4), moreover the Cu-aluminate formation is clearly evident by PXRD. The two phases are present with a relative abundance of 7 to 1, which roughly corresponds to the percentage deriving from the initial atomic ratio Cu/Al used in the preparation. As there is overall agreement in the literature that the Al/Si atomic ratio in mullite structure can not be lower than 3, either the metastable mullite is formed with Al/Si=2.64 or a part of silica remains unreacted. As the unit cell dimensions of mullite do not differ appreciably from ICPDS card  $\neq$ 15-776, the second hypothesis seems more realistic. DTA analysis shows a broadened exotherm

with onset temperature of 850°C ending at 950°C which indicates that both reactions occur simultaneously in this temperature interval.

Co and Ni-oxides do not promote mullite formation, therefore finely dispersed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is first formed at 980°C, as in the xerogel not impregnated, and only later these oxides diffuse and react with it thus obtaining NiAl<sub>2</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> as shown by PXRD (Fig. 5). Due to the delayed formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the aluminates of these two metals are formed in a slower manner than in route A. A quantitative determination of the relative abundance of aluminates and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is difficult, as many

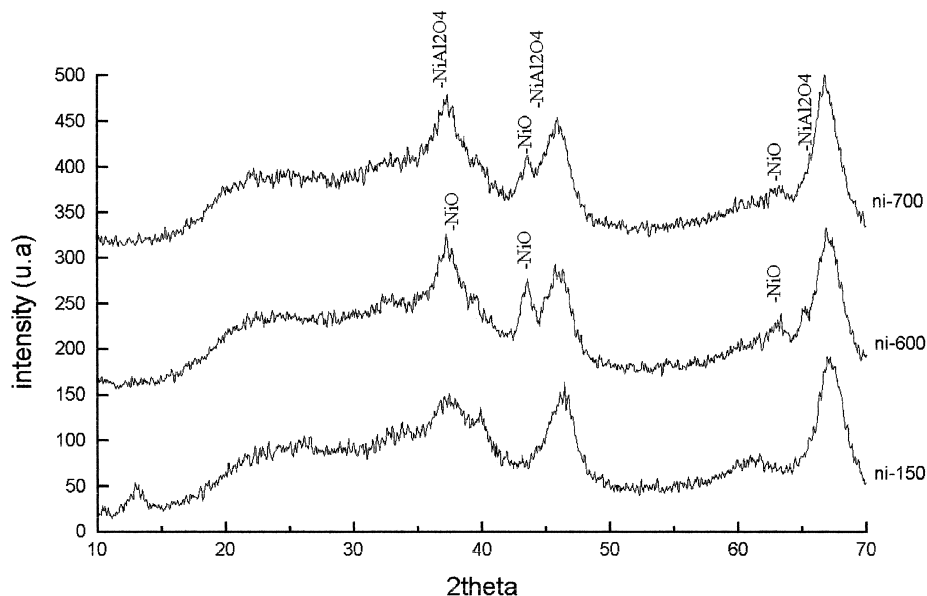


Fig. 3. X-ray diffraction patterns of supported Ni-aluminates obtained through route (A) after 4 h heat treatments at the indicated temperatures (monochromatized Cu  $K_{\alpha}$  radiation).

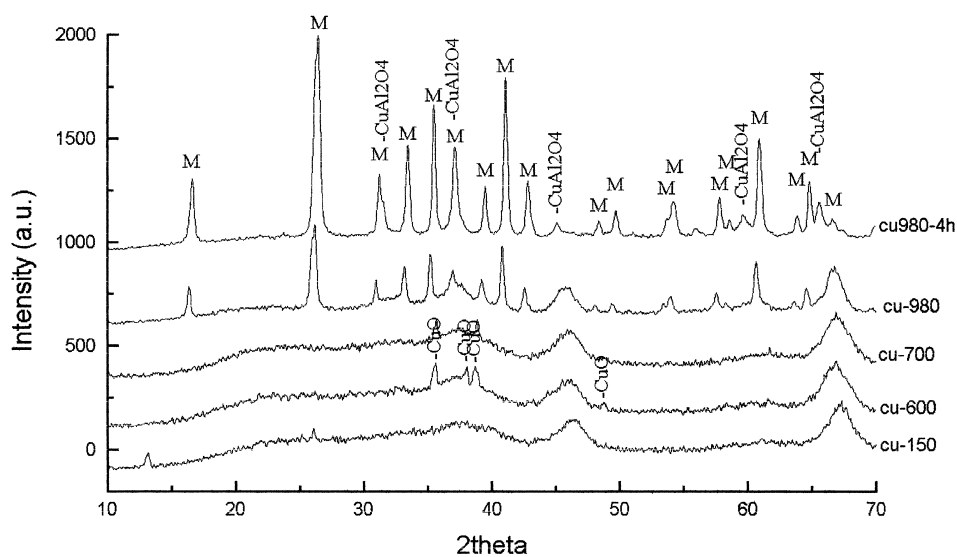


Fig. 4. X-ray diffraction patterns of supported Cu-aluminates obtained through route (A) after 4 h heat treatments at the indicated temperatures (cu-150, cu-600, cu-700, cu-980) and (above all) Cu-aluminate obtained by route (B) at 980°C for 4 h (cu-980-4h) (monochromatized Cu  $K_{\alpha}$  radiation).

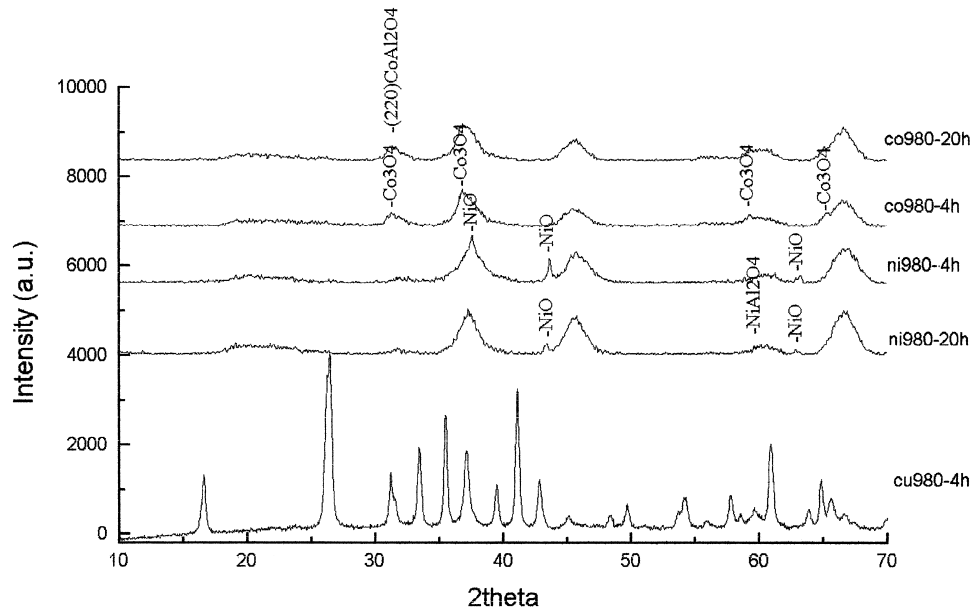


Fig. 5. X-ray diffraction patterns of supported Co,Ni-aluminates obtained through route (A) after 4 h heat treatments at the indicated temperatures compared with that of Cu-aluminate by route (B) (monochromatized Cu  $K_2$  radiation).

peaks are overlapping. With profile fitting procedures tentative results are obtained as reported in Table 2, from which it can be deduced that Co shows a higher diffusion and reaction rate than Ni. The FTIR absorbance patterns of these two materials do not differ significantly from that of mullite treated at 980°C (Fig. 6) thus confirming that the main constituent is  $\gamma$ - $\text{Al}_2\text{O}_3$  whilst that of Cu-mullite is different, due to the presence of the Cu spinel and  $\text{Al}_6\text{Si}_2\text{O}_{13}$  crystallized mullite.

Table 2

Atomic ratios between oxides and mullite after different heat treatment at 980°C in air

	Preparative Stoichiometry	From peak deconvolution after 4 h/980°C	From peak deconvolution after 20 h/980°C
NiO/mullite	6.0	$7 \pm 1\%$	$3.5 \pm 1$
Co $\text{O}_{1.33}$ /mullite	6.0	$5.5 \pm 1\%$	$2.0 \pm 0.5$

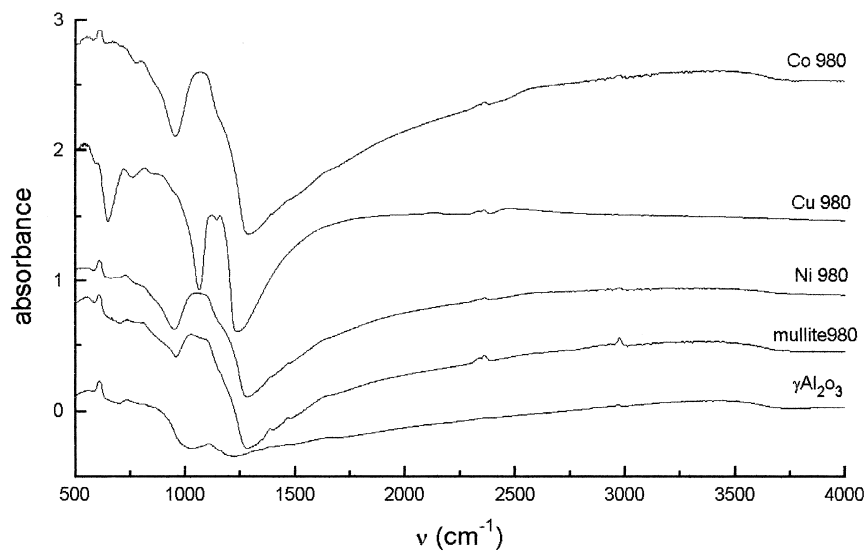


Fig. 6. FTIR absorbance patterns. Ni980, Cu980 and Co980 are from route (B). Mullite980 is unsupported and  $\gamma$ - $\text{Al}_2\text{O}_3$  is a commercial sample, inserted here for comparison sake.

The specific surface area (BET  $N_2$  adsorption) of the Co-material is very close to that of 980° unsupported mullite precursor (164 versus 160  $m^2/g$ ), while the specific surface of the Cu material drops to 34  $m^2/g$ . This is a further evidence of the stronger interaction of CuO with the amorph support. In spite of the lower specific surface, this last material has a remarkable catalytic activity, as discussed later.

### 3. Catalytic activity and microstructure

As these materials are stable at high temperature, a suitable model reaction for the catalytic activity of the reaction supported aluminates is methane combustion. 1 g of the material is pressed at 100 Mpa and then crushed

in pieces from 0.2 to 0.5 mm in diameter. A quartz tube (4 mm internal diameter) is then filled with this material and preliminarily heated up to 800°C under a controlled flow of 100 ml/min of the reactive gaseous mixture (2%  $CH_4$  + 18%  $O_2$  + 80% He). Inert gas is added in order to lie below flammability limits of methane. The heating is prolonged at 800°C for half an hour in order to clear the surface from adsorbed species or organic residues. During a controlled temperature decrement of 3°C/min down to 200°C the methane conversion is continuously monitored by  $CO_2$  IR absorption. 100% conversion is assumed at 800°C.

Co, Ni and Cu-aluminates obtained by route (B) were tested for catalytic activity, as shown in Fig. 7. Supported Cu-aluminate were heated to 980°C for 4 h, while Co and Ni-aluminates for 20 h. Two different preparation with 2 g of Cu-aluminate were tested for reproducibility (runs A and B); a third preparation with 8 g of material is shown as run C. Run D and E refer to Ni and Co-aluminates. As it is clearly evident from the figure, only Cu samples display catalytic activity, while the conversion curves for Co, Ni samples are nearly coincident with the uncatalyzed reaction curve (not shown). XRD pattern of sample C (not shown) revealed the presence of unreacted CuO and only small amount of  $CuAl_2O_4$ ; the lower activity of this sample is ascribable to the presence of CuO, which has a lower activity, if any, and to the lower amount of active  $CuAl_2O_4$ . The presence of CuO is related, in our opinion, to the scale-up of the starting materials (8 g of mullite precursor, 200  $cm^3$  of solution) which causes inhomogeneity in the deposition. The best activity is displayed by Cu-aluminates, free from CuO, obtained starting from 2 g of

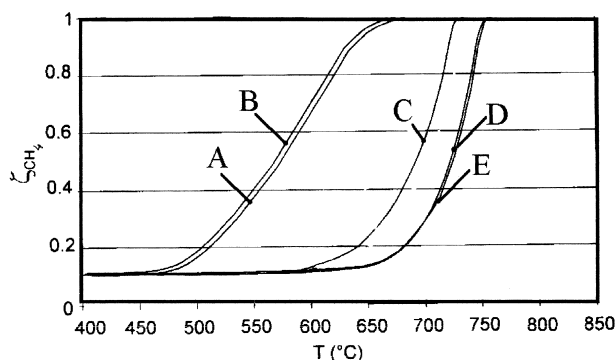


Fig. 7. Conversion curves for methane combustion. A,B=Cu-aluminate (2 g), C=Cu-aluminate (8 g), D=Ni-aluminate, E=Co-aluminate. All samples are obtained by route (B).

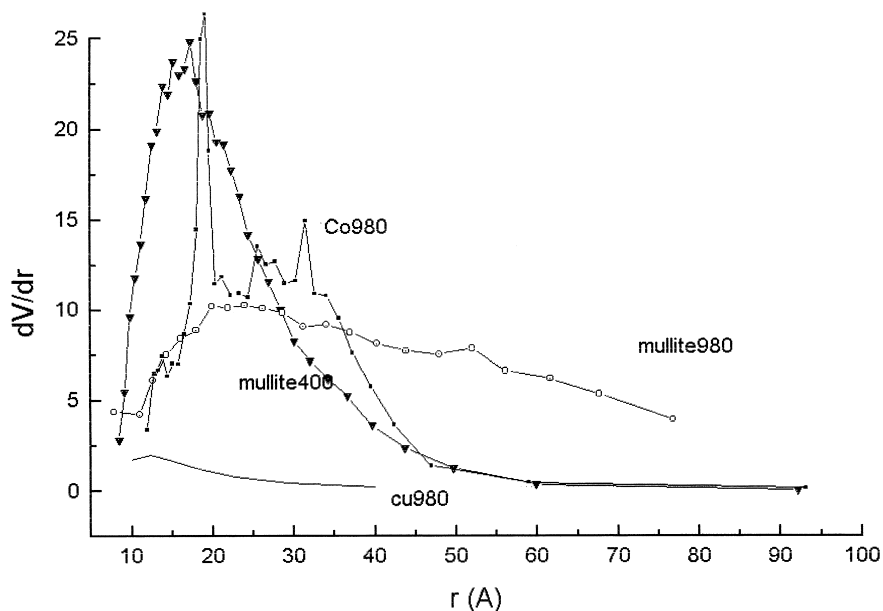


Fig. 8. Pore size distribution curves obtained by the standard model of Hasley from  $N_2$  desorption isotherms. Mullite980 and mullite400 are unsupported materials, Co980 and Cu980 are synthesized by route (B).

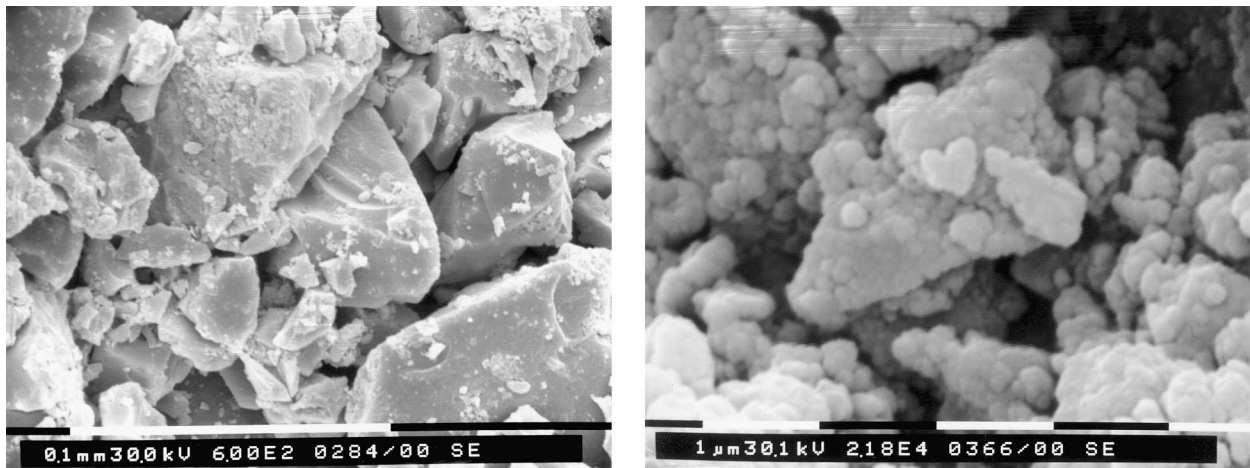


Fig. 9. SEM micrographs of Cu-aluminates on mullite obtained by route (B). Left 600 $\times$  and right 21 800 $\times$  on a detail of the fine  $\text{CuAl}_2\text{O}_4$  particles decorating the surface of mullite larger grains.

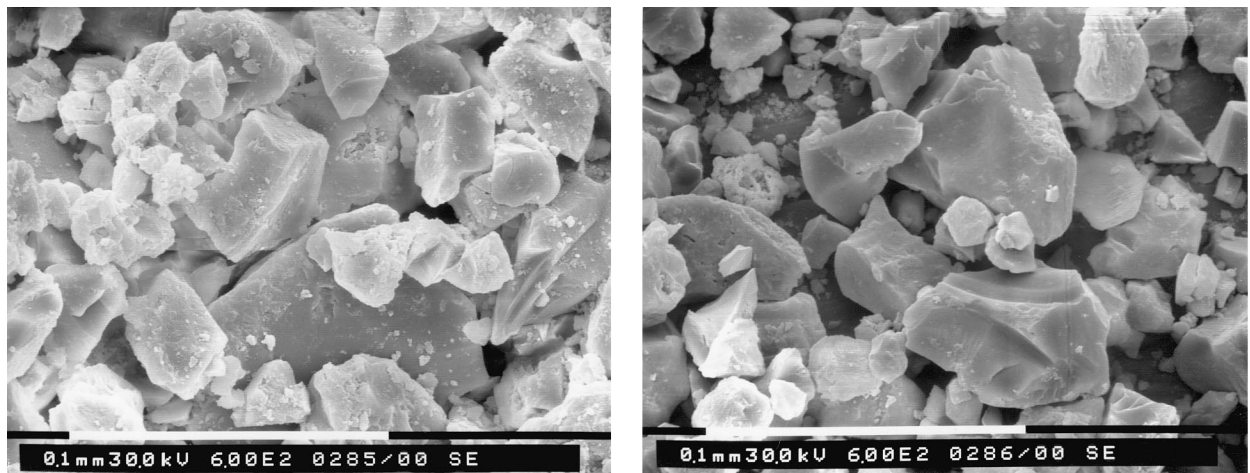


Fig. 10. SEM micrographs (600 $\times$ ) of Ni- and Co-aluminates (left to right) obtained by route (B).

mullite precursor; this activity is comparable or even better than other supported oxides, like transition metal perovskites supported on mullite foams.

The thermal stability of these reaction supported Cu-aluminates is, however, limited in temperature by the thermodynamic of the  $\text{CuO}$  conversion to  $\text{Cu}_2\text{O}$  and finally to metallic  $\text{Cu}$ . From literature equilibrium data  $\text{CuO}$  is stable in air up to 1025 $^\circ\text{C}$ , the stable phase between 1025 and 1050 $^\circ\text{C}$  is  $\text{Cu}_2\text{O}$ , and above is stable metallic copper. A sample of active Cu-aluminate, kept in air at 1200 $^\circ\text{C}$  for 2 h, displayed indeed by PXRD small but detectable peaks of  $\text{Cu}_2\text{O}$  and  $\text{Cu}$ , whilst  $\text{CuAl}_2\text{O}_4$  nearly disappeared.

As expected by the decrease in specific surface, 400 and 980 $^\circ\text{C}$  mullite-precursor have different pore size distribution curves (deduced by the standard model of Hasley from nitrogen 78K desorption data). The second material has a much broadened curve, while the first has

a maximum centered around 18  $\text{\AA}$  pore radius and a nearly monomodal distribution (Fig. 8).

Co-aluminate-980 $^\circ\text{C}$  (route B) shows two pronounced peaks (20 and 34  $\text{\AA}$ ) and a broad background from 15 to 45  $\text{\AA}$  pore radius. These characteristics, together with the high surface area (164  $\text{m}^2/\text{g}$ ) and thermal stability at high (1000–1100 $^\circ\text{C}$ ) temperatures, could be exploited in catalytic reaction were cobalt aluminates are active as CO hydrogenation to hydrocarbons<sup>5</sup> or alcohols<sup>6</sup> without the sintering effects, which impair surface area up to a value of 40  $\text{m}^2/\text{g}$  at 800 $^\circ\text{C}$  for pure  $\text{CoAl}_2\text{O}_4$  powders<sup>7</sup>.

Cu-aluminate-980 $^\circ\text{C}$  (route B) shows a flat distribution, as can be expected by its relatively lower surface area (34  $\text{m}^2/\text{g}$ ).

SEM observations on Ni-, Co-, and Cu-aluminates (route B, 980 $^\circ\text{C}$ ) show coarse grains with dimensions ranging from 10 to 90  $\mu\text{m}$  and concoid surface (Figs. 9

and 10). These are more or less decorated with much smaller particles (0.10–0.2  $\mu\text{m}$ ) of roughly spherical shape, often conglomerated. With Co and Ni-samples these particles are barely visible, whilst in the Cu-sample they cover a part of the coarse grain surface. They appear in detail in Fig. 8 right. EXAF analyses indicate that these particles are rich in transition metal, particularly for Cu-samples, with an atomic ratio Cu/Al equal or higher than 0.5. One can deduce, therefore, that, at least for Cu, these fine particles are constituted by Cu-aluminate, while the larger grains have mainly mullite structure.

#### 4. Conclusions

Finely dispersed Me-aluminates (Me = Ni, Co, Cu), stable up to 1000–1100°C, were obtained by diffusion and reaction with mullite precursors. Two different preparative routes were exploited, the reactivity of Co, Ni is higher with route A, in which these metals diffuse and reacts with pre-formed  $\gamma\text{-Al}_2\text{O}_3$ , nanoparticles. Cu reacts in a different way, promoting the formation of mullite, without being incorporated in its structure. For this reason the preparative route which employs impregnation of 400°C mullite amorphous precursor yields complete reaction of CuO with alumina to form Cu-aluminate, dispersed on a mullite substrate at the

final temperature of 980°C. This material shows remarkable catalytic activity in  $\text{CH}_4$  oxidation.

#### Acknowledgements

We wish to thank Ing. Isotta Cerri for the catalytic measurements and Prof Edoardo Garrone for helpful discussion and suggestions.

#### References

1. Rager, H., Schneider, H. and Graetsch, H., Chromium incorporation in mullite. *Am. Miner.*, 1990, **75**, 392–397.
2. Bolt, P. H., Habraken, F. H. P. M. and Geus, J. W., Formation of nickel, cobalt, copper and iron aluminates from  $\alpha$ - and  $\gamma$ -alumina-supported oxides; a comparative study. *J. of Solid State Chem.*, 1998, **135**, 59–69.
3. Voll, D., Beran, A. and Schneider, H., Temperature-dependent dehydration of sol-gel derived mullite precursors: an FTIR spectroscopy study. *J. Europ. Ceram. Soc.*, 1998, **18**, 1101–1106.
4. Aksay, I. A. and Wiederhorn, S. M., *J. Am. Ceram. Soc.*, 1991, **74**(10), 2341.
5. Blanchard, M., Canesson, P., de Werhier, P., and Chami, J., Proc. 9 Int. Congr. on Catalysis, Calgary, 1988, p. 767.
6. Courthy, P., Forestiere, A., Kawata, N., Ohno, T., Raimbault, C., and Yoshimoto, M. in: Industrial chemicals via Cl processes. Faehy, DR editor ACS, 1987 p. 42.
7. Busca, G., Lorenzelli, V. and Bolis, V., Preparation, bulk characterization and surface chemistry of high-surface-area cobalt aluminates. *Mat. Chem and Phys*, 1992, **31**, 221–228.