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New Ni–Cu–Mg–Al-based catalysts preparation procedures for the synthesis of carbon nanofibers and nanotubes

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Abstract

Catalytic decomposition of methane to produce carbon nanofilaments, CNFs (nanofibers and/or nanotubes), and hydrogen was carried out on Ni–Cu–Mg–Al catalysts. The catalysts used as mixed oxides were obtained from the calcination at 1073 K of the corresponding lamellar double hydroxides (LDHs). The subsequent reduction at 1023 K of the calcined LDHs gave rise to Ni⁰ and Cu⁰ (and possibly Ni–Cu alloy) associated to an inorganic substrate with a MgO–MgAl₂O₄–NiAl₂O₄ mixed composition that were able to produce quality CNFs at 923 K. The size of metal particles and the carbon filaments as well as the nanofilament texture depends on the copper content of the catalyst. At a Cu content of 7.6 wt%, the carbon nanofilaments are nanofibers with a platelet texture, and the particles and CNFs sizes are widely distributed (50–400 nm). On the other hand, for a Cu content of 3.8 wt%, the size distribution is narrower and the CNFs are thinner (20–50 nm), nanofibers and nanotubes showing a 'herringbone' texture with twice the angle between the graphene layers and fiber axis, exhibiting values mainly in the range of 40°–60°. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

Nickel-based catalysts are well known for their activity in the decomposition of methane to produce hydrogen (alternative route to the steam reforming) and carbon. Sometimes this process is called catalytic chemical vapor deposition (CCVD). Among the numerous types of carbon nanomaterials able to be produced, nanotubes [1,2] and nanofibers [3,4] present a great interest and have been the subject of numerous research studies. Carbon nanofibers have received considerable attention, in particular because of their excellent adsorbent properties [5] and potential use as catalyst support [3,4] thanks to their mesoporosity and their relatively large surface area (between 100 and 300 m² g⁻¹). The latter properties result from their size and texture (orientation of graphene layers) which is a function of both the composition and structure of the catalysts used in the CCVD process.

One of the main advantages of Ni-based catalysts is that the decomposition temperature of CH_4 (873–973 K) is

approximately 300° lower than that of Fe catalysts. However, an important drawback is the deactivation of catalyst by sintering and/or by the deposition of amorphous and/or nonfilamentous graphene-based carbons which encapsulate the metal particles [6]. Previous studies showed that Ni–Al and Ni–Mg–Al catalysts suffer such a deactivation at temperatures higher than 850 K and that Cu enhances the activity and the stability of Ni–Al catalysts [7]. Whereas the presence of Cu can has a dilution effect on the metallic phase, thereby diminishing its reaction rate, the Ni–Cu–Mg–Al catalysts prepared in this study show increased resistance to deactivation because Cu favors a higher hydrogen mobility inhibiting the formation of encapsulating carbon deposit.

In order to maximize the inter-metallic interactions and to minimize the sintering effects, the catalysts were obtained from lamellar double hydroxides, LDHs [8]. Two modes of preparation of LDHs (Ni_xCu_{1-x}MgAl)(OH)₇(CO₃²⁻)_{0.5}, with $0 \le x \le 1$, were used: (i) the conventional method and (ii) the colloid mill co-precipitation method. After calcination of LDHs at 1073 K, the resulting (NiO)_{1-x}(CuO)_xMgO(Al₂O₃)_{0.5} mixed oxides were reduced in situ at 1023 K and then used in the decomposition of methane. This paper reports the results of the characterization of catalysts and carbon nanofilaments and

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the catalyst activity as a function of catalyst composition and preparation route.

2. Experimental

2.1. Materials

LDH samples with different Ni/Cu/Mg/Al compositions were prepared using two different methods, the conventional [8] and the colloid mill [9] co-precipitation methods, with appropriate amounts of Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Cu(NO₃)₂ 3H₂O, Ni(NO₃)₂·6H₂O, NaOH (to maintain pH constant at 9.5 \pm 0.2) and a slight excess of Na₂CO₃.

Then, in both cases, the catalyst precursors were calcined at 1073 K under a nitrogen flow during 11 h, then reduced in a thermobalance (C.I.Electronics) by a N₂/H₂ mixture (1/1; 150 ml min⁻¹) at 1023 K during 2.8 h. After 150 min at 923 K, methane (5%) was introduced along with N₂ (95%) (total flow rate of 750 ml min⁻¹) for 3 h. According to a kinetic study (to be published elsewhere), these reaction conditions were able to synthesize carbon nanofilaments with the highest carbon yield.

In the following, the catalysts will be noted as $Ni_{1-x}Cu_x$. MgAl (for example $Ni_{0.8}Cu_{0.2}MgAl$ for x = 0.2) the for the sake of simplification.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded in an INEL diffractometer using a curved position-sensitive detector and a monochromatic radiation (Cu K_{α} , 1.5406 Å).

XPS analyses were carried out in a Kratos spectrometer (model Axis Ultra) using a monochromatic Al K_{α} radiation (1486.6 eV), with the entry of its introduction chamber inside a glove box.

Temperature-Programmed Reduction (TPR) measurements of the samples were performed in a flow quartz reactor (GIRA, X-sorb model equipped with a TCD) with a hydrogen–argon mixture (5–95%) at a flow rate of 20 ml N min⁻¹ and $\beta = 10$ K min⁻¹.

The Raman spectra were performed using a Jobin Yvon T64000 confocal spectrophotometer with 514.5 nm Ar^+ ion laser as excitation source.

Transmission electron microscopy micrographs were recorded with either a Philips CM12 or CM30 microscope, LaB₆ electron source, operated at 120 and 150 kV, respectively, so that the irradiation damages are limited. Specimens for TEM were prepared by gently grinding the samples, making a sonicated suspension from the resulting powder, and depositing a droplet of the suspension onto a copper microgrid coated with a lacey carbon film.

3. Results and discussion

3.1. Characterization of catalysts

The catalysts are active in reduced state. TPR profile can indicate the degree of metallic phase present after activation treatment. The TPR profiles (Fig. 1) show two reduction peaks, the first at 440–500 K, the second at 970–1170 K.

The first peak corresponds to the reduction of copper $(Cu^{II} \rightarrow Cu^{0})$. High Cu content samples (x ranging from 0.5 to 1) present a single band with a FWHM of about 50 K. Lower Cu content catalysts present a double peak with smaller widths (~20 K), which indicates smaller particle sizes. The high temperature component (500 K) can be attributed to segregated CuO particles, the low temperature component (460 K) to copper oxide in interaction with the other metals [10], which can form Ni–Cu alloy. In this alloy, there is an electron donation from Cu to d orbitals of Ni, which can explain the easier reducibility of Cu [11]. The absence of a peak towards 770 K shows that CuAl₂O₄ was not formed [12].

The second region between 970 and 1170 K is associated with the reduction of nickel (Ni^{II} \rightarrow Ni⁰) since magnesium and aluminum oxides do not reduce below 1170 K. As in the case of copper peak, the broad band can be decomposed into two sub-bands centered at 1020 and 1120 K, respectively. The former should correspond to NiO particles in intimate contact with the support. The latter can be associated to the reduction of nickel aluminate. The presence of these types of nickel is confirmed by the XPS analysis of the samples reduced at 1023 K. For the high Ni content, when the copper is totally reduced (binding energy Cu2p^{3/2} at 932.5 eV), the Ni2p^{3/2} band indicates the presence of approximately 30% of Ni⁰ (binding energy at 852.5 eV) and 70% of Ni^{II} (binding energy at 855 eV). It seems that the ratio NiO/NiAl₂O₄ decreases with increasing Ni content. However, the total NiO content after the reduction step seems to reach its maximum for a composition



Fig. 1. TPR (293–1173 K) of the mixed oxides $(NiO)_{1-x}(CuO)_xMgO(Al_2O_3)_{0.5}$ obtained by calcination of corresponding LDHs at 1073 K.

with a value of x located in the range 0.1–0.2. According to TPR and XRD results (not shown here), the reduced catalysts prepared at 1023 K are composed of Cu^0 , Ni⁰, possibly Ni–Cu alloy, MgO, NiAl₂O₄ and MgAl₂O₄.

3.2. Carbon nanofilament growth

In agreement with the literature [7], an excess content of copper dramatically decreases the carbon yield and the catalysts with $x \ge 0.5$ show very little activity. Just as Al, Cu is relatively non-catalytic and has a dilution effect on the active sites of Ni. However, it enhances both the carbon diffusion and reaction rates and thus promotes the catalytic activity when it is incorporated in small quantities. In agreement with the literature [7], the maximal carbon yield is reached with Ni_{0.9}Cu_{0.1}MgAl, i.e. 3.8 wt% of Cu (Ni_{0.8}Cu_{0.2}MgAl, i.e. 7.6 wt% of Cu and Ni_{0.95}Cu_{0.05}MgAl, i.e. 1.9 wt% of Cu, are slightly less active).

The XRD patterns of the reaction products (not shown here) correspond exactly to the superposition of the diffractogram of reduced catalyst and of polyaromatic carbon typical of graphene-based materials such as carbon nanofibers and multi-walled nanotubes. Thus, it seems that the catalysts do not suffer any degradation during the first hours of reaction and sharpness of the related peaks indicates that the carbon formed presents a relatively high nanotexture, which corresponds to relatively large defect-free graphenes.

Beside its doping character, copper has a strong effect on the lifetime of the catalysts. This is shown by the comparison of carbon growth rates on $Ni_{0.9}Cu_{0.1}MgAl (x=0.1)$ and NiMgAl (x=0). While the latter decreases only after 15 min and is close to zero after 1 h, the former is quasi-constant during the whole duration of the test showing a high stability. The benefit of Cu has already been noted in the case of hydrogenation catalysts. Indeed, Cu favors a higher hydrogen mobility, it has high affinity with graphene-based structures, and tends to inhibit the encapsulation of Ni active sites by polyaromatic carbons [13].

3.3. Nanofilament features

Because of their very low yield, we have not examined the carbon products formed using the high Cu content catalysts, but only those obtained with Ni_{0.8}Cu_{0.2}MgAl and Ni_{0.9}Cu_{0.1}. MgAl synthesized with both methods. In agreement with the previous observations, the size of the catalyst particle and, in consequence, the diameters of the nanofilaments are smaller when a lower Cu content catalyst is used and this effect increases for the catalysts prepared with the colloid mill method. The filaments generally show a diameter in the range 60–100 nm (with some thicker ones up to 400 nm) for Ni_{0.9}Cu_{0.1}MgAl (traditional preparation methods, 30–50 nm for Ni_{0.9}Cu_{0.1}MgAl (from colloid mill).

The graphene-based structure of the nanofilaments observed in XRD patterns is confirmed by the Raman spectra (not shown here). The frequency and intensity of the D- and G-Raman bands provide information about the crystallinity of CNFs [14]. Table 1

Structural parameters of carbon nanofilaments: interlayer distance d_{002} , average size of coherently scattering domains along the normal to graphene layers (L_c) and in the graphene plane (L_a) from XRD

x	0.2	0.1	0.1
Preparation method	Regular	Regular	Colloid mill
$d_{002} (nm)$	0.331	0.334	0.338
$L_{\rm c}$ (XRD) (nm)	8.3	5.9	5.6
$L_{\rm a}$ (XRD) (nm)	7.3	6.2	4.2
$I_{\rm D}/I_{\rm G}$ (Raman)	2.4	1.3	1.7
$L_{\rm a}$ (Raman) (nm)	1.8	3.4	2.6

 $L_{\rm a}$ from Raman spectra is calculated with $I_{\rm D}/I_{\rm G} = 4.4/L_{\rm a}$ [15].

In particular, the ratio I_D/I_G is inversely proportional to the dimension L_a , i.e. the average planar size of the perfect graphenes [15]. The values reported in Table 1 indicate that the CNFs produced with Ni_{0.8}Cu_{0.2}MgAl have a higher disordered structure (smaller L_a) than those obtained with Ni_{0.9}Cu_{0.1}-MgAl. The discrepancy between L_a values obtained from XRD and Raman spectroscopy comes from the underestimation of values obtained with Raman due to the dominant effect of the smallest coherent domains [14]. The larger difference between the results of the two techniques for CNFs from Ni_{0.8}Cu_{0.2}-MgAl indicates that they present a higher dispersion of crystallite sizes although the average polyaromatic coherent domains are larger (following both dimensions L_a and L_c).

Fig. 2a shows typical TEM images of the CNFs formed over either Ni_{0.8}Cu_{0.2}MgAl or Ni_{0.9}Cu_{0.1}MgAl. Nanofilaments actually nanofibers (i.e. not hollowed) are frequently attached to the catalyst particle where they have grown from (Fig. 2a). The metallic Ni-Cu particle is detached from the support possibly because it is pushed up by the fiber during its growth [4]. Octahedral or cubo-octahedral catalyst particles of relatively large size (100-400 nm) were found well crystallized, giving rise to sharp and bright dots in electron diffraction patterns (Fig. 2b, arrows), and to lattice fringes in highresolution TEM images (Fig. 2e). The sample appeared quite homogeneous (a very large majority of the filaments are from the same type) with only a scarce occurrence of other filament types (herringbone type, not illustrated). Fig. 2d indicates that the graphene layers are oriented parallel to the particle surface, making them perpendicular to the filament axis ('platelet' texture). Actually, arrows in Fig. 1a indicate the very location where the nanofilament was about to split, due to easy gliding resulting from the weak van der Waals forces between stacked graphenes. Square-like particles that make up most of the specimen after the TEM preparation procedure (grinding) are therefore merely platelet-CNF fragments (not illustrated), most of them exhibiting the same graphene display. Interestingly, such a graphene display implies that the fiber surface is actually made of free-graphene edges, meaning that high surface reactivity and surface energy are expected. As stated by numerous Bragg fringes (dark contrasts), the carbon nanofilaments decorated with the nanotexture are quite high. Electron diffraction patterns (Fig. 2b) exhibit rather sharp and dotted reflections together with multiple order reflections (e.g. 002, 004, 006) which both indicate large coherent domains, which is



Fig. 2. TEM images of carbon nanofiber formed over $Ni_{0.8}Cu_{0.2}MgAl$. (a) Low magnification. Arrows indicate steps at the CNF surface which result from a slight gliding; (b) electron diffraction pattern giving rise to the labeled rings, with a very limited contribution of catalyst particles (arrowed spots); (c) enlargement of the area framed in (b); (d) high magnification image; (e) high magnification image of catalyst particle.

consistent with the high nanotexture quality. The most outstanding feature is, however, that nanofibers exhibit at least a partially graphitic structure, i.e. many of the graphene layers are stacked according to the ABAB stacking sequence typical of graphite. Such a structural feature is ascertained by the occurrence of three-indice reflections such as 110 and 112 (Fig. 2c), as opposed to two-indice asymmetric bands (such as 10 and 11) that are found in turbostratic, polyaromatic carbon materials such as regular multi-wall carbon nanotubes (MWNTs). All these results are in full agreement with the previous data, particularly the interplanar distance d_{002} measured at 0.333 nm in Fig. 2d which matches well the 0.331 nm measured from XRD (Table 1) and is very close to that of pure graphite (0.335 nm).

Fig. 3a gives a typical TEM image of the products obtained over the catalyst $Ni_{0.9}Cu_{0.1}MgAl$ (colloid mill). $Ni_{0.9}Cu_{0.1}$ -MgAl catalyst prepared following the common co-precipitation method produces CNFs with similar features. As in the case of



Fig. 3. TEM images of typical carbon nanotubes formed over $Ni_{0.9}Cu_{0.1}MgAl$; (b) high magnification of a nanotube from catalysts obtained from colloid mill method; (c) high magnification of nanotube from catalysts obtained from the conventional co-precipitation method.

x=0.2, TEM images show a filament growing from single octahedral or cubo-octahedral crystallites. As already mentioned, the particle sizes (20-60 nm) and the resulting CNF diameters (the majority in the range of 25–35 nm) are much smaller than for the Ni_{0.8}Cu_{0.2}MgAl catalysts. All the CNFs are herringbone-type nanotubes (i.e. hollowed). The double angle between the graphene layers and the fiber axis ranges between $\sim 30^{\circ}$ and $\sim 150^{\circ}$, and most often between 30° and 80° (two examples are shown in Fig. 3b and c). This agrees with the previous experimental observations [16] and theoretical calculations [17]. Statistics, however, show that the conventional co-precipitation method tends clearly to provide larger angle values than the colloid mill method (not shown). As in the case of platelet nanofibers, a gentle grinding can dismantle the herringbone-nanotubes, which thereby show mechanic brittleness to shearing stresses. This agrees with a texture that may be sketched by a stacking of cones rather than by a helical display of a single graphene layer superimposing to itself at each turn. The formation of curved graphene on the top of the cone and the angle between the basal plane (constituted of hexagonal rings) and the growth axis depends on the number n of pentagonal carbon rings [18]. However, it is worth noting that as opposed to nanofibers, the pentagon occurrence is virtual in the case of nanotubes (as in Fig. 3) due to the hollow core. According to Zhu et al. [17], in the example of Fig. 3, this number could be 1 (corresponding to an angle equal to 56.5°) for the CNFs produced over the catalyst Ni_{0.9}Cu_{0.1}MgAl obtained from the traditional co-precipitation method, and 2

(angle of 42.3°) in the case of catalyst obtained from the colloid mill method.

4. Conclusion

In this work, we have studied a series of catalysts $(Ni_{1-x}Cu_xMgAl \text{ with } 0 \le x \le 1)$ obtained by calcination of lamellar double hydroxides. The physicochemical characteristics (reducibility, particle size) of these catalysts depend on their composition. It appears that the reduced catalysts are formed of particles of Cu^0 and Ni^0 (with maybe Ni–Cu alloy) on MgO, NiAl₂O₄ and MgAl₂O₄ support. The size of the octahedral and cubo-octahedral particles decreases with decreasing Cu amount.

The kinetic study of carbon growth from the catalytic decomposition of methane indicates a high activity of the catalysts at low Cu contents ($x \le 0.2$) and a high stability in time of the catalysts Ni_{1-x}Cu_xMgAl compared to that of NiMgAl homologue.

The carbon products are typically polyaromatic carbon nanofibers or nanotubes, with either a graphitic or a turbostratic structure depending on the texture (either 'platelet' or 'herringbone'). The latter depends on the size of the catalyst particles, which is related to their composition. For x=0.2, there is a wide distribution of catalyst particle sizes, hence a wide distribution of filament diameters (between 60 and 400 nm). For x=0.1, the filament diameters range between 20 and 50 nm. The thickest filaments are

nanofibers with a 'platelet' texture (graphene layers perpendicular to the fiber axis) with large domains of high nanotexture quality. On the other hand, filaments with a diameter smaller than 50 nm are nanotubes with a 'herringbone' texture, where the graphene layers are oriented obliquely, with the angle between the graphene planes and the fiber axis ranging from 30° to 60° .

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