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The effect of copper content on the reactivity of Cu/Co₆Al₂ solids in the catalytic steam reforming of methane reactionDoris Homsi^{a,b,c}, Samer Aouad^{a,*}, Cédric Gennequin^{b,c}, John El Nakat^a, Antoine Aboukais^{b,c}, Edmond Abi-Aad^{b,c}^a Department of Chemistry, Faculty of Sciences, University of Balamand, P.O. Box 100, Tripoli, Lebanon^b Université Lille-Nord-de-France, 59000 Lille, France^c Unité de chimie environnementale et interactions sur le vivant (UCEIV), université du Littoral-Côte-d'Opale, 145, avenue Maurice-Schumann, 59140 Dunkerque, France

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ABSTRACT

The steam reforming of methane over Cu/Co₆Al₂ mixed oxides with different copper contents was studied. The Co₆Al₂ support was prepared via the hydrotalcite route. It was thermally stabilized at 500 °C, impregnated with 5 wt.%, 15 wt.% or 25 wt.% copper using copper (II) nitrate Cu(NO₃)₂·3H₂O precursor and then calcined again at 500 °C under an air flow. The impregnation of copper enhanced significantly the reactivity of the solids in the considered reaction. The 5Cu/Co₆Al₂ solid was the most reactive one, with a methane conversion of 96% at 650 °C. The selectivities of H₂ and CO₂ were also better for the catalyst containing 5 wt.% copper compared to higher copper loadings. The decrease in the catalytic reactivity with increasing the copper content was attributed to the formation of agglomerated and less reactive CuO species, which were detected by XRD and TPR analyses.

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R É S U M É

La réaction de vaporeformage catalytique du méthane sur des solides à base de cuivre, Cu/Co₆Al₂, est étudiée. Le support Co₆Al₂ est préparé par voie hydrotalcite. Après calcination à 500 °C, le support est imprégné par différentes teneurs de cuivre (5, 15 et 25 % en masse), et le solide obtenu est calciné de nouveau à 500 °C à l'air. L'imprégnation du cuivre améliore considérablement la réactivité dans la réaction considérée. La conversion du méthane atteint 96 % à 650 °C en présence du solide le plus performant, 5Cu/Co₆Al₂. Les sélectivités en H₂ et CO₂ sont également meilleures en présence du même catalyseur. Les analyses en réduction en température programmée ainsi qu'en diffraction des rayons X ont montré que la performance catalytique diminue quand la teneur en cuivre augmente ; cela est dû à la formation d'agglomérats d'espèces CuO.

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1. Introduction

Hydrogen is increasingly regarded as an ideal clean and alternative energy source and vector for the near future [1,2]. Methane is one of several fuel candidates that can be used for the production of hydrogen and synthesis gas via the catalytic steam reforming reaction [3].

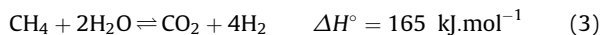
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Two major reactions are considered in the methane steam reforming (MSR) process. The methane steam reforming Eq. (1) and the water gas shift reaction WGS Eq. (2).



Combining these two reactions gives Eq. (3):



Catalysts for hydrogen production processes are mainly based on noble metals and nickel. Rh-based catalysts are highly active, but their elevated cost makes them unsuitable for use on the industrial scale, unless it is possible to reduce the quantities used without impairing catalytic performances. The advantage of using Ni-based catalysts is that they are cost-effective, but they are prone to form carbon [4]. However, studies have proven that catalysts obtained via hydrotalcite-type precursors are resistant to carbon deposition, and therefore could be applied to the MSR process [5]. These compounds gain increasing importance as catalyst precursors for MSR due to their high specific surface area, basic character, and memory effect [6,5].

Several authors showed that the presence of copper as an active metal can suppress carbon formation in the syngas production step and can improve water gas shift activity in MSR [7–10]. They claimed that Cu played a role in promoting the gasification of deposited carbon, and its addition to Ni led to the enhancement of the WGS reaction activity in the overall MSR process and decreased the coke deposit [7–10].

In this study, the $x \text{ Cu}/\text{Co}_6\text{Al}_2$ catalysts were prepared via the hydrotalcite route, were characterized using several physicochemical techniques, and their reactivity was tested in the MSR reaction.

2. Experimental

The Co–Al layered double hydroxides were prepared by precipitating ions in an aqueous solution with appropriate quantities of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 98%) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (FLUKA, 98%) into a 1 M sodium carbonate Na_2CO_3 (HIMEDIA, 98%) aqueous solution at 60 °C. The pH of the solution was maintained constant (pH \sim 10). The resulting slurry was heated at 60 °C for 2 h and then placed in a drying oven for 24 h. The precipitate was filtered, washed with hot deionized water (until its pH reached 6–7), dried for 48 h at 60 °C and then grinded to obtain fine powders. Thermal stabilization was performed under an air flow (2 L·h⁻¹) up to 500 °C (1 °C·min⁻¹), with a dwell of 4 h at the final temperature. The latter temperature was chosen since thermo-gravimetric analysis (TGA) revealed that at this temperature, stable oxides are obtained with no further weight loss.

$x \text{ Cu}/\text{Co}_6\text{Al}_2$ catalysts (x represents the Cu weight percentage) were prepared by adding an adequate quantity of copper (II) nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Prolabo,

99%) solution to the calcined support and mixing for 2 h. The excess of water is then slowly eliminated in a rotary evaporator. The obtained solid was then dried at 100 °C overnight and then thermally stabilized under the same conditions as those used for the support.

X-ray diffraction (XRD) experiments were performed at ambient temperature on a Bruker D8 Advance diffractometer using the Cu K α radiation (1.5405 Å). The diffraction patterns were indexed by comparison with the JCPDS files. Temperature-programmed reduction experiments (TPR) were carried out on a Zeton Altamira apparatus with a hydrogen flow of 30 mL·min⁻¹ (5 vol.% H₂ in Ar). The sample was heated (5 °C·min⁻¹) at atmospheric pressure, and the amount of H₂ consumed was monitored with a thermal conductivity detector (TCD).

The MSR test was carried out under atmospheric pressure in a catalytic reactor (internal diameter = 6.6 mm) coupled with a micro GC (Varian CP-4900) equipped with a TCD. Two hundred milligrams of the catalyst were introduced into the reactor and reduced in situ under an H₂ flow (15 mL·min⁻¹) at 400 °C for 1 h to activate the catalyst. Next, the catalyst was purged with an Ar flow to assure that the reaction started in a hydrogen-free feed. The catalytic reactivity was studied in the 600–800 °C temperature range, in which the MSR reaction is thermodynamically possible under the test conditions. The reactant gas flow consisted of a stoichiometric ratio of steam to methane (3:1) and the total flow was 50 mL·min⁻¹ (GHSV = 1,5000 mL·g⁻¹·h⁻¹).

3. Results and discussion

Fig. 1a shows the XRD patterns obtained for freshly calcined solids. The obtained patterns present diffraction lines corresponding to the three cobalt oxide spinel phases, which are difficult to differentiate by this technique – Co_3O_4 (JCPDS No. 42-1467), CoAl_2O_4 (JCPDS No. 44-0160) and Co_2AlO_4 (JCPDS No. 38-0814). The diffraction lines of CuO in the tenorite phase (JCPDS No. 45-0937) are observed for impregnated catalysts. These lines became more intense when the copper content was increased to 15 wt.% and 25 wt.%, respectively. This indicates that a copper quantity exceeding 5 wt.% leads to the formation of agglomerated CuO species at the surface of the solid. However, the formation of Cu–Co mixed oxides phase with diffraction lines at 31.2°, 36.7° and 44.7° (JCPDS N°37-0878) cannot be excluded, as these latter may be present but masked by the more intense diffraction lines of the mixed cobalt oxides spinel phase.

Fig. 1b presents the TPR profiles of different freshly calcined solids. The Co_6Al_2 TPR profile showed two reduction peaks. Peak I is attributed to the reduction of the Co_3O_4 species and peak II is due to the reduction of a cobalt aluminate $\text{Co}^{3+}\text{--Al}^{3+}$ or $\text{Co}^{2+}\text{--Al}^{3+}$ species [11]. The TPR profiles corresponding to copper-impregnated catalysts present reduction peaks in the 150–230 °C temperature range (peak I'). These latter are associated with the reduction of different copper oxide species. In fact, CuO is reduced into Cu_2O and then into metallic Cu. Moreover, different Cu (II) species may exist in the freshly calcined catalyst: isolated Cu^{2+} ions, Cu^{2+} clusters, small well

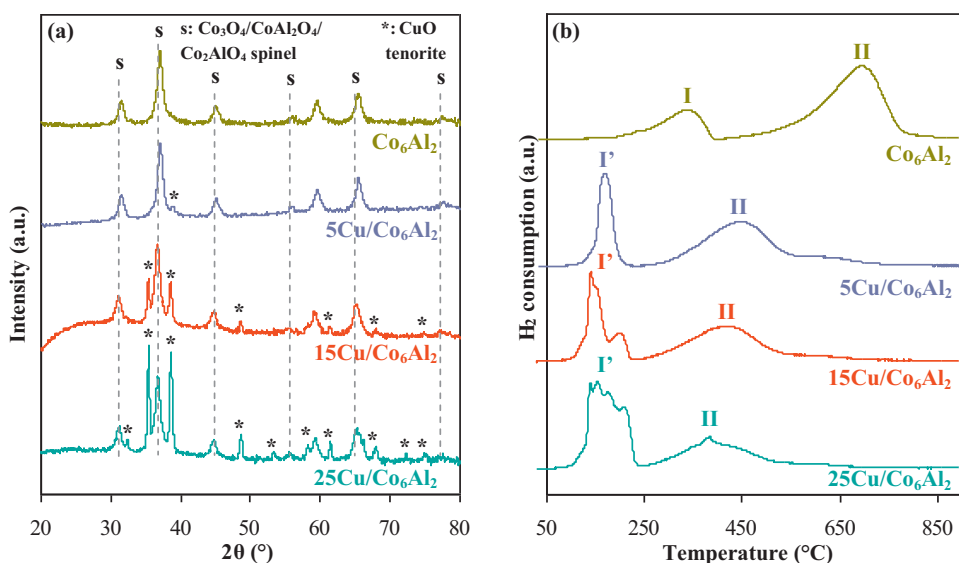


Fig. 1. (a) XRD patterns and (b) H₂ consumption profiles of the freshly calcined x Cu/Co₆Al₂ solids.

dispersed CuO particles, CuO agglomerates and even bulk CuO [12]. The presence of these different species is demonstrated by the different reduction peaks obtained at low temperatures, especially for the 25Cu/Co₆Al₂ solid. Differentiation is impossible using the TPR technique; however, the peak at the lowest temperature probably corresponds to the reduction of a well-dispersed small CuO species, while the one at the highest temperature is most probably due to the reduction of bulk CuO.

Table 1 presents experimental (peaks I, I' and II) and theoretical (CuO → Cu) hydrogen consumption values for the different solids. While consumption corresponding to peak I' was attributed to the reduction of the copper oxide species, it is clear that there is a hydrogen over-consumption compared to theoretical predictions. Therefore, it is suggested that the presence of copper facilitates the reduction of some cobalt oxide species by the hydrogen “spill-over” phenomenon. This is confirmed by the lowering of peaks I, I' and II at the maximum temperature with the increase of copper content. It seems that the two metals, cobalt and copper, react synergistically with hydrogen, making the reduction of their corresponding oxide species (CuO, Co₃O₄, Cu–O–Co...) possible at lower temperatures compared to that of those obtained for the non-impregnated support.

Table 1
Theoretical hydrogen consumption values for the different calcined solids.

	H ₂ consumption [$\mu\text{mol H}_2\text{g}^{-1}$ catalyst]		
	Experimental		Theoretical
	Peak I or I'	Peak II	CuO → Cu
Co ₆ Al ₂	2568	9132	–
5Cu/Co ₆ Al ₂	3302	8378	787
15Cu/Co ₆ Al ₂	4831	7500	2360
25Cu/Co ₆ Al ₂	6035	5940	3934

Fig. 2 displays methane conversion in the MSR reaction in the presence of the calcined solids. It is observed that once 5 wt.% of copper are impregnated on calcined Co₆Al₂, methane conversion reached 100% at 700 °C, whereas it did not exceed 3% for Co₆Al₂ at the same temperature [13].

When copper loading was increased, the conversion of methane was negatively affected. In fact, 15Cu/Co₆Al₂ and 25Cu/Co₆Al₂ exhibited comparable catalytic performances in the considered temperature range. However, they presented lower methane conversions compared to the 5Cu/Co₆Al₂ catalyst (82% and 79% methane conversion at 650 °C for 15Cu/Co₆Al₂ and 25Cu/Co₆Al₂ respectively

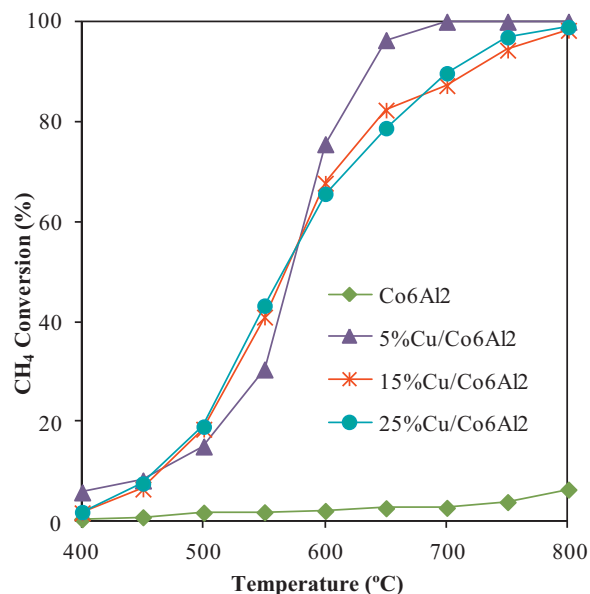


Fig. 2. Methane conversion in the MSR reaction over the different calcined solids.

Table 2
Molar flow rates ($\text{mol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}_{\text{cata}}$) of H_2 , CO and CO_2 as a function of temperature over the different calcined solids.

	400	450	500	550	600	650	700	750	800
Co_6Al_2									
H_2	–	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.1
CO	–	–	–	–	–	–	–	0.01	0.01
CO_2	–	–	–	–	–	–	0.01	0.02	0.03
$5\text{Cu}/\text{Co}_6\text{Al}_2$									
H_2	0.05	0.08	0.28	0.73	2.02	2.60	2.82	2.84	2.81
CO	–	–	–	–	0.19	0.26	0.34	0.43	0.47
CO_2	0.01	0.02	0.07	0.23	0.66	0.82	0.54	0.73	0.67
$15\text{Cu}/\text{Co}_6\text{Al}_2$									
H_2	0.08	0.17	0.52	1.17	1.89	2.23	2.34	2.49	2.56
CO	–	–	0.01	0.04	0.19	0.33	0.38	0.46	0.46
CO_2	0.01	0.05	0.15	0.36	0.42	0.39	0.37	0.35	0.40
$25\text{Cu}/\text{Co}_6\text{Al}_2$									
H_2	0.07	0.21	0.54	1.27	1.88	2.16	2.39	2.56	2.60
CO	–	–	–	–	0.23	0.44	0.60	0.67	0.74
CO_2	0.01	0.06	0.16	0.36	0.49	0.42	0.36	0.15	0.09

compared to 96% for $5\text{Cu}/\text{Co}_6\text{Al}_2$). As shown from the XRD and TPR results, an increase in metal loading resulted in copper oxide species agglomeration and therefore in a decrease of its dispersion. Consequently, this would decrease catalytic reactivity. In addition, the hydrothermal atmosphere at high temperature resulted in sintering of copper clusters dispersed on the surface of the catalyst with high copper loadings. This reduces the dispersion of the active metal, leading to a decrease in the catalytic reactivity. In addition, the presence of both Cu^0 and Cu^+ species in Cu/ZnO catalysts during the water-gas shift reaction was reported in the literature [14]. It was concluded that Cu^+ was the actual active species under the reaction conditions, and this might influence the catalytic activity via a reduction–oxidation mechanism between Cu^0 and Cu^+ , in which the Cu^+ sites oxidize chemisorbed CO to CO_2 to form Cu^0 , whereas the reduced Cu^0 sites were reoxidized by H_2O to form Cu^+ and H_2 .

Molar flow rates of the produced gas as a function of the reaction temperature for the different calcined solids are reported in Table 2. As the temperature is raised from 600 to 800 °C, H_2 concentration increases. And the significant increase in the CO concentration should be expected as a result of the thermodynamic equilibrium of the water gas shift (WGS) reaction and the reverse carbon gasification reactions where a temperature rise would not favor them, thus causing more CO formation. The CO_2 concentration showed a gradual decrease with a temperature increase. This is probably due to the contribution of the reversed water gas shift (RWGS) reaction favored at higher temperatures. The $25\text{Cu}/\text{Co}_6\text{Al}_2$ catalyst showed the highest CO molar flow rate with the lowest CO_2 production, indicating the greater importance of the RWGS reaction over this catalyst. As the surface of this catalyst is covered with copper oxide clusters, it can be assumed that these types of species favor the RWGS reaction. On the other hand, the $5\text{Cu}/\text{Co}_6\text{Al}_2$ catalyst produced the highest quantities of H_2 and CO_2 , emphasizing that this solid favors the WGS reaction. An intermediate behavior is observed for the $15\text{Cu}/\text{Co}_6\text{Al}_2$ catalyst.

In order to check the oxidation state of the different species and the possible formation of coke after catalytic testing, the XRD pattern of the used $5\text{Cu}/\text{Co}_6\text{Al}_2$ was recorded (Fig. 3).

The XRD pattern corresponding to the $5\text{Cu}/\text{Co}_6\text{Al}_2$ catalyst after its use in the MSR reaction presents diffraction lines attributed to Cu^0 , marked with the symbol “ δ ” (JCPDS No. 04-0836) in Fig. 3. The CuO diffraction lines were absent, indicating an advanced reduction of copper oxide species during the catalytic test. The cobalt oxide spinel phase diffraction lines were still present after the test, but their intensities were decreased. Intense diffraction lines attributed to Co^0 , marked with the symbol “ θ ” (JCPDS No. 15-0806), were identified, indicating that a part of the cobalt oxide species were reduced during the

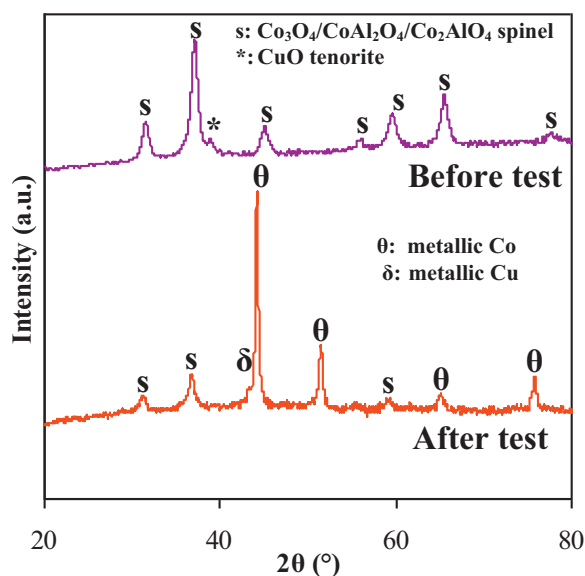


Fig. 3. XRD patterns recorded before and after MSR reaction over the $5\text{Cu}/\text{ethane}$ conversion in the MSR reaction over the different calcined solids.

catalytic test. It is worth mentioning that DSC/TG analyses done on catalysts after the tests showed that no carbon species or coke were deposited on them, which can be promising for the development of stable catalysts for the SRM reaction.

4. Conclusion

In this study, the catalytic behavior of Co_6Al_2 , $5\text{Cu}/\text{Co}_6\text{Al}_2$, $15\text{Cu}/\text{Co}_6\text{Al}_2$ and $25\text{Cu}/\text{Co}_6\text{Al}_2$ was studied in the MSR reaction. It was demonstrated that, depending on the copper content, different types of copper oxide species were present in the impregnated solids after calcination at 500°C . The addition of a small amount of copper (5 wt.%) increased dramatically the catalytic reactivity of the Co_6Al_2 support. Increasing the copper loading did not enhance the catalytic performance of the solids. The addition of copper did not contribute to the enhancement of the reactivity of the different solids. A higher copper loading led to the formation of clusters of copper oxide species that are less reactive in the MSR reaction. Compound $5\text{Cu}/\text{Co}_6\text{Al}_2$ exhibited the best catalytic performance, with no coke deposition after the catalytic test. It appeared that this catalyst favors the WGS reaction, leading to the transformation of CO into CO_2 .

Acknowledgments

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References

- [1] Y. Li, Y. Wang, X. Zhang, Z. Mi, *Int. J. Hydrogen Energ.* 33 (2008) 2507.
- [2] J.N. Armor, *Appl. Catal. A* 176 (1999) 159.
- [3] K. Hou, R. Hughes, *Chem. Eng. J.* 82 (2001) 311.
- [4] F. Basile, P. Benito, G. Fornasari, A. Vaccari, *Appl. Clay. Sci.* 48 (2009) 250.
- [5] A.F. Lucrédio, E.M. Assaf, *J. Power Sources* 159 (2006) 667.
- [6] K.O. Christensen, D. Chen, R. Lodeng, A. Holmen, *Appl. Catal. A* 314 (2006) 9.
- [7] K.S. Cha, H.S. Kim, B.K. Yoo, Y.S. Lee, K.S. Kang, C.S. Park, Y.H. Kim, *Int. J. Hydrogen Energ.* 34 (2009) 1801.
- [8] T.J. Huang, S.Y. Jhao, *Appl. Catal. A* 302 (2006) 325.
- [9] T.J. Huang, T.C. Yu, S.Y. Jhao, *Ind. Eng. Chem. Res.* 45 (2006) 150.
- [10] A. Djaidja, A. Kiennemann, A. Barama, *Stud. Surf. Sci. Catal.* 162 (2006) 945.
- [11] A. Aoun, S. Aouad, J. El Nakat, B. El Khoury, E. Abi Aad, A. Aboukaïs, *Phys. Procedia* 21 (2011) 1.
- [12] M. Labaki, J.F. Lamonier, S. Siffert, A. Aboukaïs, *Thermochim. Acta* 427 (2005) 193.
- [13] D. Homsı, S. Aouad, C. Gennequin, A. Aboukaïs, E. Abi-Aad, *Adv. Mat. Res.* 324 (2011) 453.
- [14] S.S. Maluf, P.A.P. Nascente, E.M. Assaf, *Fuel Process. Technol.* 91 (2010) 1438.