C. R. Chimie 17 (2014) 454–458

Contents lists available at SciVerse ScienceDirect

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The effect of copper content on the reactivity of Cu/Co_6Al_2 solids in the catalytic steam reforming of methane reaction

Doris Homsi [a,b,c], Samer Aouad [a,*], Cédric Gennequin [b,c], John El Nakat [a], Antoine Aboukaïs [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

ARTICLE INFO

Article history:
Received 18 April 2013
Accepted after revision 15 July 2013
Available online 22 August 2013

Keywords:
Copper
Hydrotalcites
Methane steam reforming
TPR
XRD

Mots clés:
Cuivre
DRX
Hydrotalcites
RTP
Vaporeformage du méthane

ABSTRACT

The steam reforming of methane over Cu/Co_6Al_2 mixed oxides with different copper contents was studied. The Co_6Al_2 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 $Cu(NO_3)_2{\cdot}3H_2O$ 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 $5Cu/Co_6Al_2$ solid was the most reactive one, with a methane conversion of 96% at 650 °C. The selectivities of H_2 and CO_2 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.

RÉSUMÉ

La réaction de vaporeformage catalytique du méthane sur des solides à base de cuivre, Cu/Co_6Al_2, est étudiée. Le support Co_6Al_2 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, $5Cu/Co_6Al_2$. Les sélectivités en H_2 et CO_2 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.

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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[*] Corresponding author.
E-mail addresses: doris.homsi@std.balamand.edu.lb (D. Homsi), samer.aouad@balamand.edu.lb (S. Aouad), cedric.gennequin@univ-littoral.fr (C. Gennequin), john.nakat@balamand.edu.lb (J.E. Nakat), aboukais@univ-littoral.fr (A. Aboukaïs), abiaad@univ-littoral.fr (E. Abi-Aad).

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http://dx.doi.org/10.1016/j.crci.2013.07.004

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).

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H^\circ = 206 \ \text{kJ.mol}^{-1} \tag{1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^\circ = -41 \ \text{kJ.mol}^{-1} \tag{2}$$

Combining these two reactions gives Eq. (3):

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \Delta H^\circ = 165 \ \text{kJ.mol}^{-1} \tag{3}$$

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 Cu/Co_6Al_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 $Co(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich, 98%) and $Al(NO_3)_3{\cdot}9H_2O$ (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}) −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 Cu/Co_6Al_2 catalysts (x represents the Cu weight percentage) were prepared by adding an adequate quantity of copper (II) nitrate $Cu(NO_3)_2{\cdot}3H_2O$ (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 Kα 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.% H_2 in Ar). The sample was heated (5 °C·min^{-1}) at atmospheric pressure, and the amount of H_2 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 H_2 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 Co^{3+}–Al^{3+} or Co^{2+}–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