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Hydrogen production by methane steam reforming over Ru supported on Ni–Mg–Al mixed oxides prepared via hydrotalcite route

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ABSTRACT

Catalytic performance of Ru/Ni_xMg_{6-x}Al₂ 800 mixed oxides, with $x = 2, 4$ and 6 , x being the molar ratio, towards Methane Steam Reforming, was studied. Ni_xMg_{6-x}Al₂ 800 oxide, used as support, was prepared via hydrotalcite route. It was thermally stabilized at 800 °C, impregnated with 0.5 wt.% ruthenium using ruthenium (III) nitrosyl nitrate Ru(NO)(NO₃)₃ precursor and then calcined again at 800 °C under an air flow. Ruthenium impregnation significantly enhanced the reactivity of the oxides in Methane Steam Reforming. In fact, it was found, that even with a low ruthenium content (0.5 wt.%), ruthenium oxide particles are formed but are well dispersed over the surface of the oxide Ni_xMg_{6-x}Al₂ 800.

Ru/Ni₆Al₂ 800 800 showed better catalytic performances, towards Methane Steam Reforming, than ruthenium impregnated on the two other supports. Indeed, nickel content is higher in Ni₆Al₂ 800 than in the other studied supports and therefore the probability of Ni–Ru interaction should be greater and consequently catalytic performances could be improved.

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Introduction

Hydrogen is considered as a promising energy vector. Its combustion does not emit carbon dioxide but water. One application of this vector is its injection into the fuel cell which acts as a direct converter of chemical energy of

hydrogen into electrical energy [1,2]. A fuel cell unit generates electrical energy from an electrochemical reaction of hydrogen with oxygen, yielding an environmentally benign by product, water. However, hydrogen must be made before use. Its use is involved in many industrial processes [3]. Given the importance of hydrogen in the chemical industry, multiple ways of producing this reagent in large quantities have been

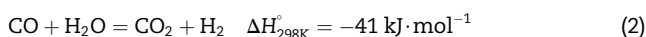
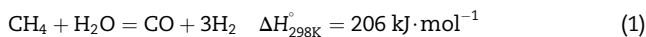
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developed. Among them, there is the method of Methane Steam Reforming (MSR) [4–6]. The catalytic steam reforming of light hydrocarbons to produce hydrogen is of significant industrial importance and is of increasing interest in the context of hydrogen economy. Industrial hydrogen production is generally conducted by steam reforming of methane over supported nickel catalysts and is performed around 850 °C with steam to carbon molar ratio in the range of 2–5, in order to preserve a stable catalyst activity. Two major reactions are considered in the MSR process: The MSR itself Eq. (1) and the Water Gas Shift reaction (WGS) Eq. (2).



Combining these two reactions gives Eq. (3):



To be feasible at relatively low pressure and temperature ($T < 1000$ °C, $P < 5$ bars), these reactions are carried out in the presence of a catalyst.

However, coke formation is a major problem. It destroys the catalysts structure and deteriorates its activity. It is thermodynamically favored at high temperature, under atmospheric pressure and steam to carbon ratio less than 1. At reaction temperatures between 500 °C and 800 °C, carbon formation occurs at the interface between the nickel crystal and the metal-support, creating large amount of fibrous carbon that destroys the catalyst. Additional problem of the Ni catalysts supported on Al_2O_3 is the severe deactivation of the catalyst due to the formation of spinel, NiAl_2O_4 [7]. Numerous studies have been conducted on strategies for processing conditions and catalyst formulations to minimize carbon formation during steam reforming [8–11]. One approach to minimizing carbon formation on the catalyst is using noble metals, such as Rh and Ru, which do not produce carbon filaments due to poor carbon oxidation [12].

The main objective of this work is to develop new formulations of catalysts which present high activity and selectivity towards MSR test. For this, two families of catalysts are being developed: Systems based on noble metal (Ru), which are very active and selective in MSR [13] and systems based on metals (Ni, Mg, Al), which are less expensive than noble metals, and show good catalytic activity, basic properties and thermal stability [14–18].

Many methods are used to prepare a catalyst. It is known that the preparation method influences the catalytic performances of the solid. Mixed oxides prepared by hydrotalcite route have interesting properties in heterogeneous catalysis [19].

Hydrotalcite-like compounds, also known as layered double hydroxides (LDH) or anionic clays, have a layered structure derived from that of brucite, i.e. magnesium hydrotalcite. To understand the structure of these compounds, it is necessary to start from the structure of brucite, $\text{Mg}(\text{OH})_2$, where octahedral of Mg^{2+} (6-fold coordinated to OH^-) share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding. When Mg^{2+} ions are substituted by a trivalent ion having not too different a

radius (such as Fe^{3+} for pyroaurite and Al^{3+} for hydrotalcite, respectively), a positive charge is generated in the hydroxyl sheet. This net positive charge is compensated for by CO_3^{2-} anions, which lie in the interlayer region between the two brucite-like sheets. In the free space of this interlayer the water of crystallization also find a place. The most interesting properties of the oxides obtained by calcination are the following [19]:

- High surface area,
- Basic properties,
- Formation of homogeneous mixtures of oxides with very small crystal size, stable to thermal treatments, which by reduction form small and thermally stable metallic crystallites.

The calcination of hydrotalcite can lead foremost to the formation of amorphous compounds followed by pre-spinel oxides which can contribute to increase significantly the specific surface area. It is known that hydrotalcite have basic properties significantly lower than those of their mixed oxides obtained by the thermal decomposition. The basic properties of the decomposed phase depend of the report $M^{\text{II}}/M^{\text{III}}$ and of the temperature of calcination. In general, the carbonates affect the effective basicity of catalyst covering the most basic sites which are no longer available for a possible interaction with an acid reactant [19].

Thus, in our work, a series of solids based on Ni, Mg and Al was prepared via hydrotalcite route and calcined to give the corresponding metal oxides. These oxides are impregnated with 0.5 wt% of ruthenium. The oxides, before and after ruthenium addition, have been catalytically tested in MSR reaction and characterized by different physico-chemical techniques.

Materials and methods

Preparation of catalysts

Ni, Mg and Al based mixed oxides were synthesized by hydrotalcite route: A solution containing appropriate quantities of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (SIGMA-ALDRICH), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (FLUKA) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (FLUKA) was added slowly under vigorous stirring into NaOH (FLUKA) 2 M and Na_2CO_3 (FLUKA) 1 M aqueous solution. The pH was maintained at 9 by dropwise addition of 2 M NaOH solution and the resulting slurry was heated at 60 °C for 24 h. Then, the precipitate was filtered, washed several times with hot deionized water (60 °C) and dried at 60 °C for 48 h. Three samples were synthesized with different Ni and Mg contents: $\text{Ni}_x\text{Mg}_{6-x}\text{Al}_2\text{HT}$ with $x = 2, 4$ and 6, where x designs the atomic ratio. The calcination treatment was performed under flow of air (4 L h^{-1} , $1 \text{ }^\circ\text{C min}^{-1}$, 4 h at 800 °C). The as-obtained mixed oxides were named $\text{Ni}_x\text{Mg}_{6-x}\text{Al}_2 800$. The chemical formula of these oxides is $\text{Ni}_x\text{Mg}_{6-x}\text{Al}_2\text{O}_9$.

Ruthenium impregnation was carried on $\text{Ni}_x\text{Mg}_{6-x}\text{Al}_2 800$. An appropriate volume of the solution of $\text{Ru}(\text{NO}) (\text{NO}_3)_3$ (ACROS organics, 1.65% wt Ru) was diluted in 50 mL of deionized water. The total volume of solution was then added to the support and mixed for 2 h. Then, water is slowly

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