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Ni based catalysts promoted with cerium used in the steam reforming of toluene for hydrogen production

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ABSTRACT

$Ni_xMg_{6-x}Al_{1.8}Ce_{0.2}$ (with $0 \leq x \leq 6$) mixed oxides catalysts were prepared by hydrotalcite route. All the oxides were calcined at 800 °C and characterized by different physico-chemical methods. The catalysts are then reduced before their use in the steam reforming of toluene. The XRD and TG/DTA confirmed the formation of the hydrotalcite structure for the non-calcined samples. The N_2 adsorption/desorption results revealed that all catalysts correspond to mesoporous materials. The study by temperature programmed reduction (H_2-TPR) showed that the reducibility of the catalysts is influenced by the nickel content. The CO_2-TPD results showed that the catalyst with high magnesium content present the highest basicity. The $Ni_2Mg_4Al_{1.8}Ce_{0.2}$ shows the best toluene conversion among all the catalysts and it was then compared to a non-promoted catalyst. The spent catalysts were characterized by TPO, TG/DTA and XRD and they didn't reveal any coke formation.

Introduction

Owing to the growing concern about environmental degradation and the exhaustion of finite resources, there is a need to develop new means of power generation from renewable fuels [1]. Hydrogen has attracted attention as a clean secondary energy carrier [2]. Considered as other alternatives of clean energy source, tars -mainly heavy aromatic hydrocarbons such as benzene, toluene, and naphthalene- have many disadvantages because of their complexity and toxicity. They cause serious hazard to the equipment downstream due to

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their condensation at low temperatures. They result in a reduction in performance and an increment in maintenance requirements. Therefore, removal of biomass tars is highly desirable. Catalytic steam reforming is an interesting way to convert tar into syngas (especially hydrogen) during gasification [3,4]. Considered as an effective means for renewable hydrogen production, steam reforming of aromatic hydrocarbons has been studied as an on-board hydrogen feed for fuel cells [5].

Toluene has been chosen as a model compound tar because it is found in significant quantities, and it represents a stable aromatic structure especially at relatively low temperatures, being one of the major tar species surpassed only by benzene [6,7].

Eqs. (1) and (2) represent the Steam Reforming of Toluene (SRT) reactions according to toluene-to-steam ratio. Eqs. (3)–(12) show the different reaction routes which are involved and can be carried out during SRT:

- Steam Reforming of Toluene (SRT):

$$C_7H_8 + 7H_2O \Leftrightarrow 7CO + 11H_2 \ (S/C = 1) \tag{1}$$

$$C_7H_8 + 14H_2O \Leftrightarrow 7CO_2 + 18H_2 \ (S/C = 2) \tag{2}$$

- Water Gas Shift Reaction (WGSR):

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{3}$$

- Hydroalkylation:

$$C_7H_8 + H_2 \Leftrightarrow C_6H_6 + CH_4 \tag{4}$$

- Steam Reforming of Methane (SRM):

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \ (S/C = 1) \tag{5}$$

- Boudouard reaction:

$$2CO \Leftrightarrow CO_2 + C_{(s)} \tag{6}$$

- Thermal cracking:

$$C_7H_8 \Leftrightarrow mC_xH_y + zH_2 \tag{7}$$

$$C_6H_6 \Leftrightarrow mC_xH_y + zH_2 \tag{8}$$

- Steam Reforming of Benzene (SRB):

$$C_6H_6 + 12H_2O \Leftrightarrow 6CO_2 + 15H_2 \ (S/C = 2) \tag{9}$$

- Steam Reforming of Benzene (SRB):

$$C_6H_6 + 6H_2O \Leftrightarrow 6CO + 9H_2 \ (S/C = 1) \tag{10}$$

- Steam Reforming of Ethylene (SRE):

$$C_2H_4 + H_2O \Leftrightarrow 3/2CH_4 + ½CO_2 \tag{11}$$

- Vapodealkylation:

$$C_7H_8 + H_2O \Leftrightarrow C_6H_6 + 2H_2 + CO \tag{12}$$

The SRT reactions (Eqs. (1) and (2)) produce respectively CO and CO_2. In addition, in the water gas shift reaction, the produced CO, together with steam, yields H_2 and CO_2 (Eq. (3)). CH_4 is produced through the hydroalkylation (Eq. (4)) and SRE (Eq. (11)). The produced CH_4 is converted to CO and 3 moles of H_2 according to the methane steam reforming reaction (Eq. (5)). The Boudouard reaction (Eq. (6)) is an exothermic reaction in which 2 moles of CO are converted to CO_2 and $C_{(s)}$. The by-products benzene and ethylene are obtained by thermal cracking of the toluene (Eqs. (7) and (8)). Benzene is also produced by vapodealkylation (Eq. (12)). Both by-products undergo steam reforming reactions (Eqs. (9)–(11)). In toluene steam reforming, H_2 is mainly generated by the SRT and WGSR (Eqs. (2) and (3)) and its amount increases according to the SRT reactions (Eqs. (1) and (2)) [8].

Because of the high endothermicity of steam reforming of toluene, the use of a catalyst is essential to lower the activation energy of the reaction. In addition, a catalyst is needed to control the selectivity of reactions that occur thereby orienting the entire process to the desired products.

The use of calcined hydrotalcites (HTs) catalysts for steam reforming seems promising, given their basic properties (due to the presence of magnesium), high surface area and thermal stability. Moreover, after thermal treatment, the double-layered structure of hydrotalcites is known to form a homogenous dispersion of the active phase [9].

Nickel catalysts have been extensively applied for steam reforming reactions because of their high activity, low cost and high abundance [10]. However, the nickel based catalyst is prone to coke formation and/or sintering during steam reforming [11]. Therefore, it is necessary to improve the stability and the coke resistance of the Ni catalysts in order to reduce the use of steam and save energy. Many researchers focused on the following criteria: (1) the preparation method of the catalyst, (2) the nature of the support and (3) the addition of promoters. It is reported that high dispersion of Ni catalyst will allow a good resistance to coke formation. Another alternative to improve the stability of the catalyst is the addition of promoters such as cerium. The incorporation of cerium promotes the formation of smaller metallic nickel particles, which suppresses the carbon deposition and minimizes sintering of the metal species [12].

The goal of our work is to test the performance of Ni–Mg–Al–Ce oxides catalysts obtained through the hydrotalcite route in the steam reforming of toluene. A comparison