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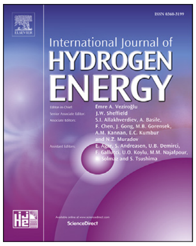

Partial oxidation of methane on co-precipitated Ni–Mg/Al catalysts modified with copper or iron

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ABSTRACT

Methane transformation to hydrogen and synthesis gas ($CO + H_2$) by heterogenous catalysts can play an important role to secure the supply of energy, chemicals and fuels in the future. Methane is the main constituent of natural gas and biogas and it is also found in crystalline hydrates at the continental slopes of many oceans. In view of this vast reserves and resources, the use of methane as chemical feedstock has to be intensified. In this present work, (NiMg)Al catalysts doped with Fe or Cu, prepared by co-precipitation method and characterized by different techniques, were studied in the partial oxidation of methane ($T_{reaction} = 750$ °C, CH_4/O_2 ratio $= 2$). The effect of catalyst composition and pretreatment conditions of these catalysts were investigated. Also, these catalysts show a very high activity and selectivity in the partial oxidation reaction, which depends on the conditions of catalysts preparation. The obtained results indicated increasing of activity and selectivity with decreasing calcination temperature and increasing nickel and aluminium contents in the catalysts composition. The solid doped with iron constituted the best catalyst for the total oxidation of methane and for the water–gas shift reaction. On the other hand, the addition of copper was remarkably improved the catalytic performances of the (NiMg)Al solid. So, the presence of this element supported the partial oxidation of methane with production of syngas ($CO + H_2$). With the addition of iron or copper for the catalyst composition, we were observed (in our previous work) the possibility of formation of NiM (M = Fe or Cu) alloy which increased nickel particles dispersion. In the case of copper, the reducibility of NiO was also assisted (TPR results) which increased catalytic activity in partial oxidation of methane.

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Introduction

Methane, the most simple hydrocarbon, exists in enormous source of our planet. It occurs as the principal component of natural gas with a concentration between 70 and 90% by volume. According to annually published BP Statistical Review of World Energy [1], proven world natural gas reserves were specified for the year 2013 to 187.3 × 10^{12} m^3. This number does not included natural gas found in crystalline hydrates at

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the continental slopes of many oceans and in permafrost areas, estimates of the amount of methane stored in hydrates differ widely ranging from 2500 × 10^{12} m^3 [2] to 15,000 × 10^{12} m^3 [3]. Reserves denote only that many researchers were interested to develop new processes for the transformation and the valorization of natural gas in synthesis gas primary product in the chemical and petrochemical industry. Examples include steam reforming (SRM) [4,5], CO_2 reforming [5,6], and the partial oxidation of methane (POM) [7–11]. Among these typical catalytic processes, the partial oxidation of methane has attracted considerable attention recently for the production of synthesis gas, because of its milder exothermic characteristics and more desirable $H_2/CO = 2$ ratio, which is suitable for a number of chemical processes [12–14].

Of course, for the non-catalytic homogeneous partial oxidation of methane, the synthesis gas production is well established. For example, in Malaysia, Shell has been successfully operating a highly selective process for production of synthesis gas at high temperatures, typically higher than 1200 °C, and pressures of around 50–70 bar as a part of the middle distillate synthesis process (SMDS) [15]. The operation temperature required for the reaction could be significantly reduced if a catalyst would be used, which would make the partial oxidation process even more economically attractive [16]. An estimated 10–15% reduction in the energy requirement and 25–30% lower capital investment are expected for catalytic partial oxidation compared to the typical steam reforming processes [17]. It was concluded that with renewed interest in inexpensive routes from natural gas to liquid fuels, catalytic partial oxidation is almost certainly the process of choice for future natural gas utilization.

Catalytic systems employed in the partial oxidation of methane to synthesis gas can be classified in two groups: noble metal-based catalysts [7,18–20] and transition metal-based catalysts [7,21–24]. Although precious metals such Pd, Pt, and Rh have been reported to be active and stable for transformation of methane [25–27], cost of these precious metals is still a major issue. It is clear that the development of cheaper and alternative metal-based catalysts such as Fe-, Co-, and Ni-based ones would be desirable [8–10]. In particular, Ni catalysts have been widely investigated because of their lower cost and relatively higher activity in the POM. However, Ni-based catalysts suffer from catalyst deactivation by sintering of Ni particles [28,29] and phase transformation of the supported solids [30] in the POM. The low cost and long-proven performance of Ni-based catalysts, therefore, warrant the efforts to optimize these catalysts in this process. It reported that the high dispersion of metal species in the catalyst limits the sintering and the formation of large aggregates of the active species, so that limit or prevent the deactivation [31]. Certain currents works were privileged the catalytic systems with great homogeneous distribution of metal in the define structure which leads, after an adapted reduction, to the formation of a stable and a well dispersed metal particles [32]. In this order, previous studies were proved the interest of these catalysts formed by a solid solution such as $NiAl_2O_4$ or NiO–MgO [33–38], revealed that the excellent performances in methane transformation and good sintering resistance ability were related to the formation of these solids solutions. Effectively, the insertion of the active species into define structure has several advantages:

- The active species is distributed homogeneously in the structure and is therefore well dispersed, which creates a dilution phenomenon.
- The active species is in strong interaction with the structure, therefore less mobile than on the surface of a conventional support.
- The structure serves as a reservoir for the active species, which can be activated progressively by in situ reduction leading to the production of well dispersed metallic sites. This good dispersion is the result of strong interactions between the different elements of the structure. These properties limited the formation of large aggregates of the active species and consequently to reduce the formation of coke.

The addition of promoters such as Fe or Cu is also used in this purpose, the possibility of formation of Ni–M alloy increased nickel species dispersion.

In this objective, in this article, we report the preparation, characterizations and catalytic performances of mixed catalysts (NiMg)Al and (NiMMg)Al (M = Fe or Cu) in partial oxidation of methane (POM), this completed our previous work reported in Ref. [39]. The catalytic activity and stability of these materials in this process were studied according to diverse parameters, such as: calcination temperature, nickel incorporation in the $MgAl_2O_4$ structure, doping by iron or copper (effect of Fe or Cu addition on the activity of catalysts in POM).

Experimental

Preparation of the catalysts

The catalysts, noted $(Ni_xMg_{1-x})Al_y$, $(Ni_xM_xMg_{1-2x})Al_y$ (M = Fe or Cu, x = 0.1 or 0.05 and y = 0.5 or 2), have been prepared at room temperature by co-precipitation method. Stoichiometric quantities of $Ni(NO_3)_2–6H_2O$, $Mg(NO_3)_2–6H_2O$, $Al(NO_3)_3–9H_2O$ and $Fe(NO_3)_2–6H_2O$ (or $Cu(NO_3)_2–6H_2O$) were each dissolved in distilled water. The resulting solution and an aqueous solution of ammonia (2 M) were dropped into a flask at the same time with constant stirring at a pH value about 9.5–10. The precipitate was ageing for 2 h. After the filtration, the resulting slurry was dried at 80 °C for 24 h and calcined at different temperatures (750 and 900 °C) for 12 h.

Characterizations

The BET surfaces areas were measured by N_2 adsorption at 77 K using a Coulter S.A 3100 apparatus. The crystal structure of catalysts was determined by X-ray powder diffraction (XRD) with a SIEMENS D5000 apparatus using a Cu $K\alpha$, ($\lambda = 1.5418$ Å) radiation. Diffraction peaks, obtained in a 2θ range between 20° and 80°, have been used to identify the structure of the samples. Temperature-programmed reduction (TPR) measurements were carried out in a conventional flow system with a moisture trap connected to a thermal conductivity

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