

Hydrogen and Syngas Generation (Hydrogen-storage properties of a Mg-based hydrotalcite prepared by Ni coprecipitation)

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Introduction

Steam reforming of hydrocarbons especially of CH₄, is the largest and generally the most economic way to produce hydrogen [1-3].

CH₄ autothermal reforming with H₂O and air is a good option for reforming fuel for cells feeds, as it avoids the necessity of large external supply of heat, and the cost of oxygen/nitrogen separation can be avoided for this application.

However in contrast to the large-scale use of reformers under the typical operating conditions, reaction temperatures are varied frequently at startup and shut down of the operation. These catalysts must be able to withstand multiple cycles under those conditions and must also tolerate operation under such unusual transient condition without deterioration. Additionally, it should be mentioned that natural gas is a regionally varying feedstock and may contain some light paraffins [1]. These are more reactive than CH₄ and tend to form coke rapidly. In large units, an additional step (prereforming) is being introduced serving mainly to remove the heavier hydrocarbons [4] and hence suitable catalyst also have to tolerate mixed feeds.

Highly dispersed metals show very high and stable activity for CH₄ reforming [5]. Vaccari [6] has been proposed the preparation of hydrotalcite like compounds containing noble metals as precursor for catalysts for the partial oxidation of CH₄ to synthesis gas.

In this contribution, we report therefore CH₄ autothermal reforming over Ni/Mg-Al catalysts prepared from hydrotalcites followed by calcinations and reduction. CH₄ autothermal reforming was carried out at constant temperature, 853 K.

Materials and Methods

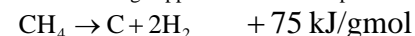
Ni-MgAl catalysts with various Ni contents were prepared by the method as follows: Mg-Al hydrotalcite precursors based on [Mg_{1-x}Al³⁺(OH)₂(CO₃)_xmH₂O] in which a part of Mg²⁺ was replaced by Ni²⁺. Compositions of catalyst are compiled in table 1. The Htlcs were prepared by coprecipitation at room temperature by adding simultaneously a solution containing the metal nitrates and a solution containing NaOH and Na₂CO₃(7). The pH was kept between 9.5 and 10 by adjusting the addition of the metal salts and a base solution. The precipitates were kept in suspension under stirring at room temperature during two hours, and then filtered, washed with distilled water and dried at 373 K during 10 h.

All samples prepared were calcined at 673 K for 4 h at a rate of 5 Kmin⁻¹ in a static air atmosphere by increasing the temperature from ambient, it causes an attach on the Htlcs

structure and in turn forms oxide (MgO) and spinel (MgAl₂O₄) phases. After that the samples were reduced in flow of Hydrogen at 773 K.

Results and Discussion

The catalytic behaviour of Ni/Mg supported Htlcs in the partial oxidation of CH₄



on the catalysts by changing the space velocity and compared with other catalysts. The experiments were obtained by using 100 mg of catalysts dispersed quartz in wool at high space velocity values.

Catalysts deactivation is a significant issue in methane reforming with high severity. It is caused by the decrease of catalytically active sites by coking, oxidation or sintering of metal. The influence of such factors markedly depends on the reaction temperature and the operation severity. Deposited coke originates mainly from two reactions, i.e., CH₄ decomposition and CO disproportionation. The former is endothermic and favoured at higher temperatures, while the latter is exothermic and favoured at lower temperatures.

Oxidation of metal may occur easily at lower temperatures at which methane can not be activated [7, 8].

Table 1. Physicochemical properties of the prepared compounds.

Catalysts	Loading % Ni	BET specific Area (m ² /g)	Pore Volume (cc/g)	Crystal Size of Ni (nm)
A	15	274.269	0.255	37.226
B	20	255.096	0.276	43.337
C	25	230.197	0.304	59.976
D	50	120.524	0.480	159.472

Significance

Methane reforming and hydrogen production from hydrotalcites precursors with Ni (Inv.).

References

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