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Nickel catalyst with outstanding activity in the DRM reaction prepared by high temperature calcination treatment

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ABSTRACT

The catalytic performance of some Ni–Ce/Al₂O₃ catalytic systems (11 wt.% Ni and 3 wt.% Ce) were checked after being submitted to different calcination and reduction treatments. It was found that, the reduced Ni–Ce/Al₂O₃ catalysts were more active and stable in the dry reforming reaction of methane than the corresponding not-reduced catalysts. This high activity was initially connected with the smaller size of pre-reduced Ni species, which at the same time leads on to the formation of filamentous carbon. The best overall performance was obtained for the reduced catalyst after being calcined at 1000 °C. This catalyst presents a very high stability, a low level of carbon formation, maintaining the nickel particle size constant during reaction. Surprisingly, although its reduction degree is only 12% at 750 °C, its catalytic activity is similar to the full reduced catalysts. So, the small number of reduced metallic particles of this catalyst shows a very high activity, much higher than the other catalysts.

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Introduction

Synthesis gas (mixture of hydrogen and carbon monoxide) can be obtained in e.g. steam reforming of methane [1], partial oxidation of methane [2] or dry reforming of methane (DRM) [2]. Steam reforming of methane is currently the most used

process for hydrogen production although, as obtained, the synthesis gas mixture is inappropriate for Fischer-Tropsch synthesis or methanol preparation due to high H₂:CO ratio [1,2]. Partial oxidation of methane generates large amount of heat, which makes it hazardous or difficult to control [3]. From economical point of view it is not suitable due to the consumption of pure oxygen [2].

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The dry reforming of methane provides synthesis gas with H₂:CO ratio (1) more suitable for the Fischer-Tropsch synthesis or methanol production [4]. Ni-based catalysts play an important role in the reaction due to its low cost, easy availability and good catalytic performance. On the other hand, nickel based catalysts suffer from sintering and coking. Formation of coke is given by two side reactions: the CO disproportionation (2) and the methane decomposition (3).



There have been published a lot of articles dealing with the improvements of resistance of Ni-based catalysts against coking and sintering. A critical role is played by the size of nickel particles, which is strongly affected by the preparation methodology and pre-treatment (temperature of calcination, reduction, etc.). Wang et al. [5] compared nickel precursors in the impregnated Al₂O₃ catalysts and found out that the nickel nitrate precursor led to the formation of the smallest nickel particles in Ni/γ-Al₂O₃ with the highest activity and stability in DRM. Kim et al. [6] reported that aerogel Ni/Al₂O₃ catalysts contain smaller nickel particles than the impregnated one, which also led to higher activity in the DRM and higher coke resistance. Rostrup-Nielsen [7] published that the partly sulphur-passivated nickel catalysts in the steam reforming of methane inhibits carbon formation much more than the activity in the methane reforming reaction. Because the size of ensembles for carbon nucleation is larger than for the steam reforming reaction, they conclude that the effect of sulphur mainly consists in the reduction of the ensemble size of active nickel sites. Chen et al. [8] published that Ni/Al₂O₃ catalyst with strong interaction between metal and support suppressed carbon deposition, which was attributed to the formation of nickel aluminate after calcination. Moreover, nickel aluminates exhibited high activity at high reaction temperatures at or above 750 °C [8] and decrease the sintering process [9]. On the other hand, the formation of filamentous carbon associated with Ni particles, do not significantly decrease the catalytic activity [10–12]. A lot of interest was given to the doping of Ni/Al₂O₃ catalysts with different types of metal e.g. alkali metals [10], alkaline earth metals [13–15] or rare earth elements [15–18]. A very special attention has been devoted to the role of cerium as a promoter, attract attention due to: increase of the catalytic performance [19], increase of the nickel dispersion over alumina surface [18,20], reduction of coke deposits [21], decrease of NiO particle size in as-prepared catalysts [22], led to the partial incorporation of Ni cation into ceria lattice [23], can affect strong metal-support interaction under reaction conditions [24]. There were also studied different types of Ni–Ce and Ni-perovskite catalysts. For example, Wang et al. [18] studied the effect of Al₂O₃, CeO₂ and CeO₂–Al₂O₃ supports. They found, that Ni supported on the CeO₂ showed lower activity in the dry reforming of methane. On the other hand, CeO₂ as a promoter enhanced catalytic activity and stability and the formation of carbon deposits was suppressed. Other promising

type of catalysts is perovskite-type catalyst such as LaNiO₃ with or without Ce [25,26].

As it has been mentioned above, several authors focused on the possibility to improve the catalytic behaviour of Ni based catalysts by decreasing of size of nickel particles resulted from the decreasing value of calcination temperature. In this article, we focused on the supported Ni/Al₂O₃ catalysts promoted by cerium in the dry reforming of methane. In order to improve the activity and stability of Ni–Ce/Al₂O₃, we focused not only on the process of calcination of catalyst, but moreover on the process of pre-reduction (none or 750 °C) after the calcination treatment of catalyst (500–1000 °C). Based on our previous study of Ni–Ce/Al₂O₃ catalysts in the oxidative dehydrogenation of ethane [27], the composition of catalysts were kept constant at 11 wt.% Ni and 3 wt.% Ce supported on alumina.

Experimental

Catalyst preparation

Ni–Ce/Al₂O₃ catalyst with 11 wt.% Ni and 3 wt.% Ce was prepared by co-impregnation of the mixture of Ni(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O aqueous solutions (0.25 M both) on Al₂O₃ (Eurosupport, S_{BET} = 323 m² g^{−1}). After impregnation, the material was dried at room temperature overnight and portions of samples were calcined in dry air (100 ml min^{−1}) at 500, 600, 750, 900 and 1000 °C for 5 h.

Catalyst characterization

X-ray diffractograms were recorded in a Siemens D-501 equipment, with a Bragg-Brentano configuration, using Cu Kα radiation (λ = 1.5406 Å). Diffractograms of calcined, reduced materials and of materials after reaction were collected in the range 2θ = 10°–80° with a step of 0.05° and an acquisition time of 1 s for each point.

The UV–Vis diffuse reflectance spectra of calcined materials (0.25–0.50 mm diameter) were measured using a Cintra 303 spectrometer (GBC Scientific Equipment, Australia) equipped with a Spectralon-coated integrating sphere using a Spectralon coated discs as a standard. The spectra were recorded in the wavenumber range of 11 111 cm^{−1} (900 nm) to 50 000 cm^{−1} (200 nm); lamps switched at 350 nm. The reflectance was recalculated to absorption using the Schuster-Kubelka-Munk (F(R_∞)) function, $F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$, in which R_∞ is the diffuse reflectance from a semi-infinite layer.

The H₂-TPR profiles were monitored by the AutoChem II 2920 (Micromeritics, USA). The experimental conditions were chosen to fulfil the resolution conditions, as described in Ref. [28]. A quartz microreactor was charged with 40 mg of catalysts. Two types of experimental conditions were used. Firstly, the reduction was carried out from room temperature up to 1050 °C, with a heating rate of 10 °C min^{−1} in flow of 5% H₂/Ar gas (50 cm³ min^{−1}). At this temperature, all the reduction processes were finished. A second type of TPR experiments were done only from room temperature up to 750 °C, holding the temperature isothermal at 750 °C during 2 h. The changes

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