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Sol-derived AuNi/$MgAl_2O_4$ catalysts: Formation, structure and activity in dry reforming of methane

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ABSTRACT

Ni nanoparticles doped with different amount of gold were supported on $MgAl_2O_4$ by deposition from aqueous metal sol producing a series of catalysts with different Au content. The sol procedure was allowed to obtain dispersed metal particles with different composition. The particle size and the particle composition of the sol were maintained even after being deposited on the support. The catalysts, characterized by several techniques such as TPR, XPS, XRD, TEM, HRTEM and EELS at the different stages of their life exhibited significant structural modification. In particular, thermal treatments in reducing and oxidizing environment produced NiAu alloy phases and NiO surface segregation, respectively. When testing for methane dry reforming with CO_2 in temperature ramped reaction, the monometallic nickel catalyst was more active at lower temperature whereas the bimetallic catalysts were more active at higher temperature. The presence of gold slightly affected the CO/H_2 ratio due to the occurrence of parallel reactions such as the reverse water gas shift reaction (RWGS). Both types of catalysts, monometallic and bimetallic ones, deactivated a little with time but the degree of activity loss was not in straightforward relation with Au content due to the different effect of gold on the stability and on the amount of carbon formation.

1. Introduction

Reforming of methane with CO_2, known also as dry reforming (DRM), is a convenient and feasible process to produce synthesis gas and at the same time to remove two powerful greenhouse gases like CO_2 and CH_4, from the environment [1–3]. As compared to the steam reforming of methane, producing syngas with a H_2/CO ratio of 3, the DRM produces a synthesis gas with the H_2/CO molar ratio close to unity, making it useful feed for the Fisher Tropsch syntheses to liquid hydrocarbons and for the syntheses of oxygenates [4]. The DRM reaction (1) is endothermic and requires high temperatures to attain good conversion levels.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^{\circ}_{700\,^{\circ}C} = 258\,kJ/mol \tag{1}$$

At high temperatures the following endothermic reactions (2) and (3) referred as decomposition of methane and reverse water gas shift (RWGS), respectively, are also favored.

$$CH_4 \rightarrow C + 2H_2, \quad \Delta H^{\circ}_{700\,^{\circ}C} = 85\,kJ/mol \tag{2}$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H^{\circ}_{700\,^{\circ}C} = 38\,kJ/mol \tag{3}$$

For the dry reforming of methane, noble metals have been successfully used providing stable and active catalysts at the lowest as possible temperatures [5]. However, because of their high cost and low availability, most of the applications are based on the use of the group VIII transition metals [6]. Among these, Ni has been studied extensively, being the most active, cheap and available metal [7–9]. However, its main drawback is represented by the production of significant amount of carbon and by the sintering at the high temperatures of the reaction. Carbon deposits are formed when the rate of methane dissociation is faster than the oxidation of carbon, occurring with the surface oxygen species arising from CO_2 dissociation on the metal component or from carbonates formed at the metal support interface. Both, the amount and the type of carbon deposited from methane decomposition during the dry reforming, would affect the activity/stability of the Ni based catalysts [9,10]. Researchers, through the use of several surface techniques have shown different types of carbon deposits such as, polymeric, filamentous, graphitic carbon and bulk nickel carbide [10–14]. The strategies adopted to decrease the carbon poisoning include the support formulation, the support morphology and the doping of the nickel catalysts with other elements such as alkali metals, sulfur and also gold.

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The dry reforming of methane over nickel catalysts is generally considered structure sensitive, therefore Ni dispersion should be maintained as high as possible through the use of proper supports [15]. The $MgAl_2O_4$ spinel oxide is highly stable and thermally resistant, furthermore, it can ensure strong metal–support interaction favoring the higher metal dispersion. Additionally, in virtue of its basic nature this support will enhance the chemisorption of the CO_2 which is beneficial for the catalytic activity providing the oxygen to form CO and also favoring the elimination of the coke [16].

The addition of a noble metal such as Pt and Rh has been reported to increase the resistance of the nickel catalysts to the deactivation by carbon [5,11,17–19]. The effect of the addition of gold has been mainly studied in the steam reforming of hydrocarbons [14,20,21]. In such reaction the decrease of reactivity upon dilution of Ni sites with the less reactive Au metal, was counterbalanced by the positive effect of a lower deactivation by carbon in the presence of gold. This effect was attributed to the formation of a surface NiAu alloy with the Au preferentially located at the high-energy steps and edges sites where the carbon nucleation over nickel is supposed to initiate [14]. In contrast, in the case of the dry reforming of methane, the modification of the nickel catalysts by gold has received less attention and furthermore, with controversial results. The positive role of gold for a series of $Ni/MgAl_2O_4$ catalysts prepared by wet impregnation was described [13]. On the contrary a recent study on alumina supported nickel and gold-doped nickel catalyst did not provide any experimental evidence for the beneficial effect of gold [10]. Probably the influence of the gold and generally of a second metal, is mediated by other factors such as the catalyst preparation method, the relative amount of the active site components and the support formulation.

In order to verify the role of gold in nickel catalysts used for the CO_2 reforming of methane, bimetallic Ni–Au catalysts supported over commercial $MgAl_2O_4$ spinel were prepared by a non conventional sol method. Intending to selectively inhibit the carbon formation without affecting much the activity, different atomic Au/Ni ratios were considered. The choice of the sol procedure aimed to the formation of highly dispersed metal particles with well defined structure and the close proximity of generally immiscible Ni and Au phases.

2. Experimental

2.1. Sample preparation

Aqueous solutions of $HAuCl_4 \cdot 3H_2O$ (Aldrich), 20 wt% poly(diallyldimethylammonium) chloride (PDDA) in water (Aldrich), nickel(II) nitrate hexahydrate (Aldrich), tannic acid (Aldrich), sodium-citrate (Aldrich), freshly dissolved sodium borohydride, and commercial $MgAl_2O_4$ nanopowder (Aldrich) support were used in the preparations. In order to obtain the Ni core–Au shell structured nanoparticles, the Ni precursor was reduced first in the presence of stabilizing agents. The sol preparation method, that was successfully applied to get Au nanoparticles with size of the order of 6 nm [22] was modified for Ni, because tannin and citrate reducing agents at the slightly basic pH used for preparation of gold sols were not strong enough to reduce Ni(II) nitrate. Thus, Ni nitrate solution in the presence of tannin and citrate at pH ~ 5–6 was reduced with freshly prepared $NaBH_4$ solution at 60 °C. One min after the addition of the reducing agent a color change to deep brownish–greyish was observed, that turned a bit reddish when adding Au^{3+} ions after 9 min. Then fast fading of the liquid occurred with time and, after 1.5–2 h, the monometallic Ni-containing sol became green, the bimetallic sol paled as well, meaning that oxidation and dissolution of Ni must have occurred. In order to avoid losing much of the nickel in solution the sol immobilization step was done within 1 h after the reduction step. After 15 min at 60 °C sol adsorption onto the $MgAl_2O_4$ support was carried out with the aid of PDDA polycation as before in a previous study [22]. Samples were filtered, washed with water and dried at 80 °C for 48 h. The notation and the exact concentrations of the final materials as determined by XRF and by Prompt Gamma Activation Analysis (PGAA) [23] are given in Table 1.

Table 1

List of catalysts prepared on $MgAl_2O_4$ support, corresponding metal content,[a] molar ratio and metal particle sizes as determined by TEM after the catalytic reaction.

Catalyst	Metal content		Ni/Au (molar ratio)	d_{Me} (nm)
	Ni wt%	Au wt%		
Ni	4.1			6.7 ± 4.6
Ni–0.5Au	4.2	0.5	28	8.6 ± 5.1
Ni–1.4Au	4.3	1.4	10	9.6 ± 5.8
Ni–3Au	4.1	3.0	5	–

[a] Ni content was measured by XRF, Au content was measured by PGAA.

2.2. Sample characterization

The phase composition of crystalline components of fresh and calcined/reduced samples was investigated by X-ray diffraction (XRD) analyses. XRD patterns were recorded in Bragg-Brentano para-focusing geometry using a Bruker D5000 diffractometer, equipped with a Cu Kα anode and a graphite monochromator. The XRD data were collected in the angular range 10–70° in 2θ using 0.05° step size and counting time of 5 s per step. The assignment of the various crystalline phases was based on the JPDS powder diffraction file cards [24]. Mean crystallite sizes are calculated from the line broadening of the most intense reflection using the Scherrer equation [25].

The distribution of Ni (and Au) and the size of metal particles were studied by a conventional Philips CM20 transmission electron microscope (TEM) operating at 200 kV equipped with energy dispersive spectrometer (EDS) for electron probe microanalysis. The TEM samples were prepared by drop drying either the aqueous suspensions of the $Au–Ni/MgAl_2O_4$ samples or simply the sol on carbon-coated micro grids. The particle size distribution was obtained by measuring the diameter of equiaxial metal particles. High resolution transmission electron microscopy investigations (HRTEM) and electron energy loss spectroscopy (EELS) elemental mapping were carried out by a JEOL 3010 microscope operating at 300 kV with point resolving power of 0.17 nm and a GATAN Tridiem Electron Energy Loss Spectrometer in the image filtering mode, respectively. Temperature programmed reduction (TPR) experiments were carried out with a Micromeritics Autochem 2910 apparatus equipped with a thermal conductivity detector (TCD). The gas mixture with composition 5% H_2 in Ar (50 ml/min) is used to reduce the samples (30 mg), heating from room temperature to 800 °C at the rate of 10 °C/min. Before starting the TPR analyses, the catalysts were pretreated with a flowing gas mixture of 5% O_2 in He (50 ml/min) at 550 °C for 30 min, then cooling down under Ar. The amount of carbon on the sample surface after catalytic run was estimated from the amount of CO_2 evolved in temperature programmed oxidation (TPO) experiments carried out in 10 vol.% O_2 and 1 vol.% Ar in He. Mass spectrometer was employed to detect CO_2 formation.

The X-ray photoelectron spectroscopy (XPS) analyses of the fresh and calcined/reduced catalysts were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al Kα source (1486.6 eV) run at 14 kV and 15 mA. The analyzer operated in the constant analyzer energy (CAE) mode. Survey spectra were