Highly conductive Ni steam reforming catalysts prepared by electrodeposition

Francesco Basile,[a] Patricia Benito,*[a] Pascal Del Gallo,[b] Giuseppe Fornasari,[a] Daniel Gary,*[b] Valentina Rosetti,[a] Erika Scavetta,*[c] Domenica Tonelli[c] and Angelo Vaccari[a]

Received (in Cambridge, UK) 29th January 2008, Accepted 14th March 2008
First published as an Advance Article on the web 18th April 2008
DOI: 10.1039/b801645c

New highly conductive, active and stable Ni steam reforming catalysts were prepared through a method consisting of the calcination of a hydrotalcite-like compound electrodeposited in a single step on FeCrAlloy foams.

Hydrogen production by steam reforming (SR) of natural gas is a well-established technology.[1] In this process, because of the endothermicity of the reaction, a large amount of energy must be delivered, and although the thermal efficiency of the process is around 95%, only 50% is absorbed by the SR process. Furthermore, thermal gradients are generated along and radially inside the tubes, limiting the catalyst activity. For these reasons, new designs focus on improving heat transfer and reducing the heat supplied.[2] Alternatives to the conventional pelletized catalysts are structured catalysts (honeycombs, foams, plates),[3] especially those made of metallic supports. The advantages of these metallic supports include not only a decrease in the pressure drop and high mechanical strength, but also better heat transfer (by conduction), both axially and radially,[4,5] not available for random packing of catalyst pellets. However, despite of all the above-mentioned advantages, metallic supports show a poor adhesion of the catalyst to the metallic structure due to the lack of interaction between catalyst and support, which is even more problematic considering the large expansion coefficient of the metals, and it can lead to a cracking and loosening of the catalyst. In order to improve the catalyst-support interaction, a pretreatment of the support is usually performed before the coating step.[6,7]

In this work, an innovative method, based on electrochemical deposition (ECD) on highly conductive supports, was developed for the preparation of new Ni catalysts on FeCrAlloys. The electrochemical deposition was previously used in the analytical field for the preparation of electrodes covered with a very thin layer of hydrotalcite-like compounds.[8,9] Thus, in this work, the Ni-based SR catalysts were first deposited as a hydrotalcite-like support using metallic FeCrAlloy foams as electrodes.[10] Hydrotalcite-like compounds (HTlcs) are lamellar materials with the chemical formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2][A^{b-}]_{x/b}\cdot nH_2O$.[11] Those containing nickel and noble metals have been successfully applied as catalyst precursors in some natural gas conversion processes, such as steam- or dry-reforming and catalytic partial oxidation.[12] The synthesis reported consisted of the one-step electrosynthesis of Ni/Al–NO_3 HTlcs on the surface of a metallic foam within a short time (deposition time from 600 to 1800 s). The precursors were then calcined and reduced, leading to a catalyst active in the SR process.

The deposition of Ni/Al–NO_3 HTlc on metallic FeCrAlloy foams was carried out by cathodic reduction of a 0.03 M solution containing $Ni(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$ (molar ratio 3/1) and 0.3 M KNO_3 at room temperature using a single compartment three-electrode cell.[9]† The application of a cathodic potential for a fixed time (deposition time) led to an increase of the pH near the working electrode (W.E.) surface, and the precipitation of the hydrotalcite-like material Ni/Al–NO_3 occurred just on the surface of the support. After the ECD, the films were gently rinsed with twice-distilled water, dried in a dessicator over silica gel, and then promptly subjected to the characterization analysis. The electrosynthesis was carried out at two different deposition times and potentials. See Table 1.

Catalysts were obtained by calcination of the Ni/Al–NO_3 deposited on the foams at 900 °C for 12 h, and they were labeled by adding the prefix "ex" to the name, *e.g.* exHT-0.9-600. The thermal treatment led to the decomposition of the HTlc and segregation of the NiO and $NiAl_2O_4$ phases.[13] The morphology and chemical composition of Ni/Al–NO_3 HTlc and catalyst films were investigated by SEM/EDS analysis.‡

In order to select the optimum synthesis conditions, FeCrAlloy foams coated with Ni-based catalysts obtained at the different synthethic conditions were tested in the SR process. Catalytic tests were performed in a laboratory plant operating under severe, nearly industrial, conditions: $P = 20$ bar, S/C = 1.7, $T_{\text{oven}} = 900$ °C and $\tau = 4$ s ($T_{\text{catalyst}} \approx 840$–$850$ °C). Six supported metallic foams were loaded in the isothermal zone of the reactor for a height of 6 cm, the bottom and top sections of the tube were filled with inert materials (corundum beads or quartz pellets).§ Catalysts were activated by *in situ* reduction at 900 °C for

Table 1 Samples prepared by electrodeposition

Sample	Applied potential/V *vs.* SCE	Time/s
HT-0.9-600	−0.9	600
HT-0.9-1800	−0.9	1800
HT-1.2-600	−1.2	600
HT-1.2-1000	−1.2	1000

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[a] *Dip. Chimica Industriale e dei Materiali, Univ. di Bologna, V.le Risorgimento 4, 40136 BO, Italy. E-mail: pbenito@ms.fci.unibo.it; Fax: +390512093679; Tel: +390512093677*
[b] *Air Liquide, Centre de Recherche Claude Delorme, 1, Chemin de la Porte des Loges, BP 126, Les Loges-en-Josas-78354 Jouy-en-Josas Cedex, France. E-mail: daniel.gary@airliquide.com; Fax: +33 1 39 07 62 93; Tel: +33 1 39 07 62 62*
[c] *Dip. Chimica Fisica e Inorganica, Univ. di Bologna, V.le Risorgimento 4, 40136 BO, Italy. E-mail: scavetta@fci.unibo.it; Fax: +390512093690; Tel: +390512093667*

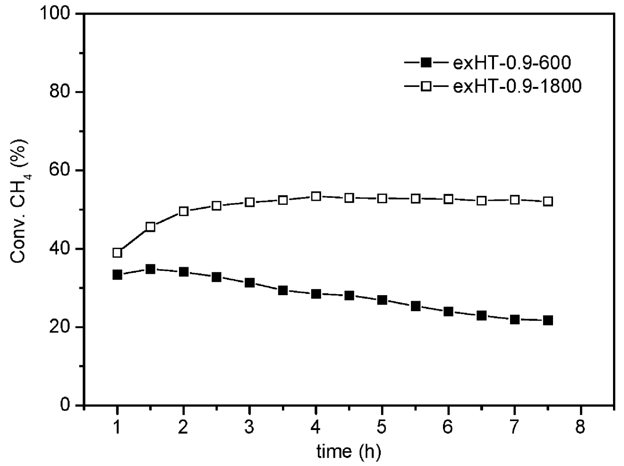

Fig. 1 CH_4 conversion of the samples prepared by ECD at −0.9 V for 600 and 1800 s.

3 h with an H_2/N_2 equimolar flow (7 l h^{-1}). For comparison purposes, a pelletized commercial Ni-based catalyst was also tested.

The activity trend of the catalysts prepared at −0.9 V in terms of methane conversion is shown in Fig. 1. Catalytic performances were strongly dependent on synthesis conditions, since they determined the amount and the thickness of the catalyst layer coating the metallic foams. Sample exHT-0.9-600 showed a rather low methane conversion, which steadily decreased with time-on-stream. The low amount of Ni due to the thin layer of deposited HT and the presence of uncovered supports were responsible for the low activity and the deactivation of the catalyst, also enhanced by the sintering phenomena that may occur during the first hours of operations under industrial conditions.

Consequently, in the next step of the work the deposition time was tripled (from 600 to 1800 s, sample exHT-0.9-1800), in order to increase the thickness and the stability of the layer of the HT precursor deposited, since an almost linear dependence of the film thickness with the deposition time was expected.[8] After an increase of the activity during the first hours, the steady-state condition was reached; although conversion and selectivity values increased, the methane conversion was still low and far from the equilibrium.

In a further attempt to improve the catalytic performances, the applied potential was also modified (Fig. 2). The catalyst prepared at −1.2 V for 600 s (exHT-1.2-600) also led to an improvement of the catalytic performance, but a deactivation process was observed.

It has been shown that an increase of the deposition potential increases the amount of deposited catalyst, but if the electrosynthesis time is low, a stable catalyst cannot be prepared. Furthermore, it can be seen that the deactivation was not related to the initial activity (*i.e.* to the Ni active in the reaction at the beginning) since this catalyst was more active than the exHT-0.9-1800 but significantly less stable. The deactivation was therefore due to the preparation procedure and time affecting the coverage of the support. For this reason, the deposition time was increased to 1000 s, working at −1.2 V. For the exHT-1.2-1000 catalyst, after an increase of the catalytic activity in the first hour, the activity neared the equilibrium value (64% instead of 67% for equilibrium). The catalyst was tested for two days; the starting activity in the 2nd day was slightly lower due to a partial oxidation of Ni^0 to Ni^{2+} in shut-down and start-up operations[14] affecting the low number of Ni active sites. Once the reaction started, the reducing atmosphere led to a slight activation and catalytic performances were constant, indicating that the coating was relatively stable under severe reaction conditions.

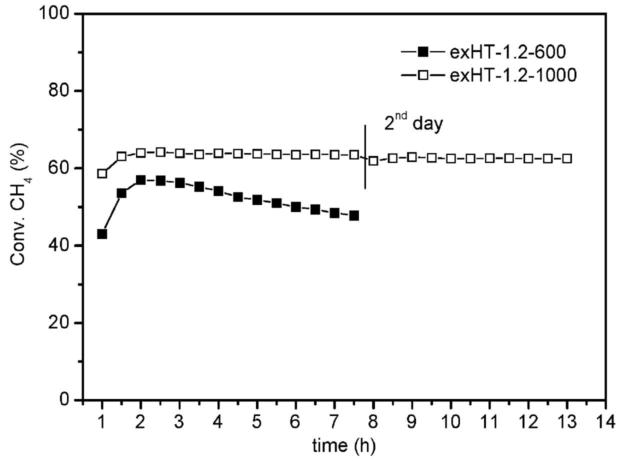

Fig. 2 CH_4 conversion of the samples prepared by ECD at −1.2 V for 600 and 1000 s.

Compared with a commercial Ni catalyst, with a higher catalyst volume, the foam prepared by ECD gave a higher methane conversion (Fig. 3). The highest conversion required lower oven temperature (910 °C commercial, 900 °C exHT) and it occurred despite a lower amount of active catalyst (gNi^{2+}(exHT-1.2-1000) = 0.012, gNi^{2+}(commercial) = 0.885). These observations indicated the enhanced performances of highly conductive materials, which improved the thermal transfer inside the bed. In this case, metallic monoliths could especially affect the radial thermal profile, and much less the axial profile, since the configuration used was of 6 pillared monoliths and not just a single monolith.

Lastly, the sample that gave the best catalytic performances, exHT-1.2-1000, and its precursor, HT-1.2-1000, were characterized by SEM coupled with EDS (Fig. 4). The metallic foam had pores with a mean pore size of about 200–300 μm (Fig. 4a,d). After the coating process, SEM images showed that the powder covered the surface of the support uniformly, without considerable cancellation of the pores (Fig. 4b). Although it was quite difficult to determine the film thickness exactly, a mean value of

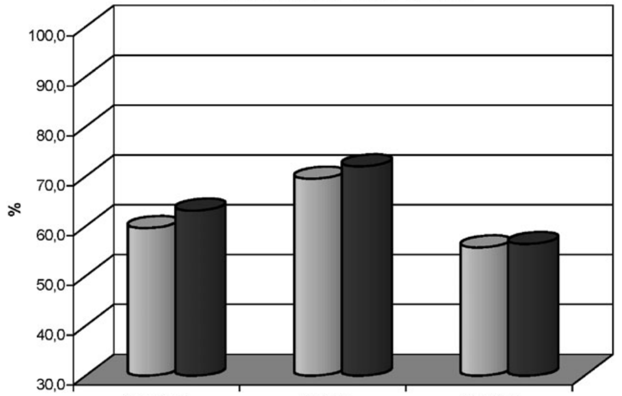

Fig. 3 Catalytic activity of commercial and exHT-1.2-1000 catalysts.

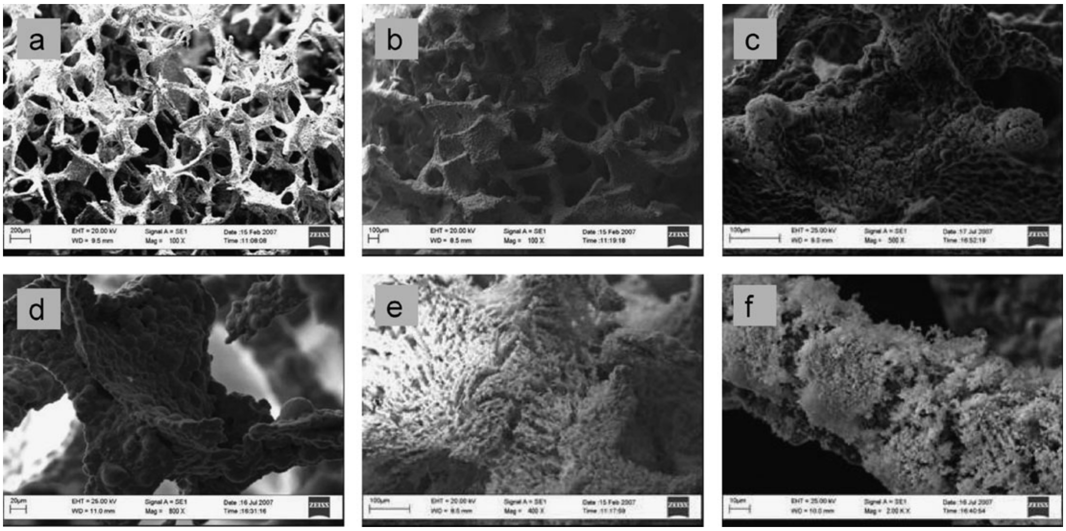

Fig. 4 SEM images of the bare metallic foam (a,d), HT-1.2-1000 (b,e) and exHT-1.2-1000 samples (c,f).

1–2 μm could be roughly estimated. A more detailed micrograph of the supported metallic foam (Fig. 4e) showed that small and uniform particles of HTlcs were deposited on the surface, forming a sponge-like structure. A Ni/Al molar ratio value of 3.4/1 was obtained by EDS analysis, confirming the formation of a pure HTlc.[15] After calcination, the film of the deposited solids was retained (Fig. 4c,f); moreover it seemed to be more compact and with an improved adherence, and no pores were clogged. The presence of small particles coating the foam surface may increase the adhesion on the substrate,[16] and the effectiveness factor for the supported particles was also enhanced, leading to a better utilization of the catalyst and resulting in an increase of catalytic activity.[17] The advantage of using ECD was that the increase of the pH took place in the closeness of the foam and it occurred rapidly and evenly, leading to a homogeneous precipitation of small, uniformly sized particles on the foam surface.

In conclusion, we reported for the first time a simple, fast, reproducible and effective method for preparing new catalysts from HTlcs supported on FeCrAlloy foams, which are active and stable in the SR process. This is a very innovative synthetic route for the preparation of structured catalysts on highly conductive metal supports. This method was shown to be controlled by two parameters (time and potential) that can be set during the synthesis of the precursor to obtain a thin, strongly adherent film and a suitable amount of active and stable catalysts in the SMR process.

Financial support from L'AirLiquide and Ministero dell' Istruzione, dell'Università e della Ricerca (PRIN, MIUR, Rome) is gratefully acknowledged

Notes and references

† Electrode potentials were measured with respect to an aqueous satured calomel electrode (SCE; *i.e.* reference electrode [R.E.]). A Pt wire was used as the counter electrode (C.E.) and the working electrode (W.E.) was the conductive material *i.e.* FeCrAlloy pellets. They were obtained by cutting a FeCrAlloy monolith made by stacking alternating flat corrugated strips. The electrochemical experiments were performed using a CH Instrument Mod. 660 C controlled by a PC *via* CHInstrument software.

‡ SEM/EDS analyses were performed using an EVO 50 Series Instrument (LEO ZEISS) equipped with an INCAEnergy 350 EDS microanalysis system and INCASmartMap for imaging the spatial variation of elements in a sample (Oxford Instruments Analytical). The accelerating voltage was 25 kV, the beam current 1.5 nA, and the spectra collection time 100 s.

§ Catalytic tests were performed in an Incoloy 800HT reactor, with a wall thickness of 9 mm and inner diameter of 12 mm, placed inside an electric oven. A thermocouple shell was inserted axially into the reactor, into which a chromel–alumel thermocouple can be slid to measure the axial thermal profile. The wet syngas passed through a water condenser that separated most of the unreacted water. The dry syngas was analyzed online using two gas chromatographs equipped with HWD: a Fisons Instruments 8000 Series and an AutoSystem XL from Perkin Elmer Instruments with Carbosieve S-II 100–120 mesh-packed columns: N_2 and He were used, respectively, as carrier gases in the analysis of H_2 and other products (CO, CO_2, and CH_4).

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