

CARBON DEPOSITION IN METHANE REFORMING WITH CARBON DIOXIDE

Dry reforming

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Abstract

Coke formation in the dry reforming of methane was studied using a thermobalance (TG) and with a catalytic microreactor in the temperature range 800–950 K. Silica-supported and lanthana-supported nickel catalysts were examined. The effects of process variables such as temperature and gas composition (He dilution, CH₄/CO₂ ratio) on the coke formation rate were determined. The reactivity of H₂ on several kinds of carbon was also investigated. The morphology of the coke was studied by scanning electron microscopy (SEM). The induction times for coke formation were significantly affected by temperature and by the CO content in the feed gas. The results of catalytic tests were consistent with the TG measurements. The behaviour of SiO₂ and La₂O₃ supported Ni catalysts agree with a mechanism in which the lanthana support plays an important role in the carbon deposition.

Keywords: carbon deposition, dry reforming, Ni catalysts

Introduction

The dry reforming of methane with carbon dioxide is more endothermic than steam reforming [1]. Carbon deposition is thermodynamically predicted and carbon formation over metal catalysts has been observed during the carbon dioxide reforming reaction [2]. An industrial process to produce CO-rich synthesis gas using a large excess of CO₂ has been developed [3].

A nickel based catalyst is indicated for this reaction, but carbon deposition is the critical problem which can be overcome only at high temperature. Efforts have been made to find a catalyst with low coke formation.

Both steam and dry reforming reactions proceed according to a very similar mechanism over noble metal catalysts with decreasing reactivity in the order Ru > Rh > Ni ≈ Ir > Pt > Pd [4]. High intrinsic reforming rates when combined with low carbon formation rates may cause a kinetic hindrance of coke formation.

It has been shown recently that Rh supported on alumina or on silica and lanthana [6] catalysed dry reforming also at low temperature and at low CO₂ content, with little or no coke formation.

We have previously studied [7] the role of lanthana on the surface of carbonaceous species; we report here the results obtained on nickel catalysts in a temperature range where coke formation is thermodynamically improved.

Experimental

Catalysts

Supported catalysts with variable percentage of Ni were prepared using wet impregnation starting from the pure nitrate. All freshly prepared catalysts were calcined and reduced with H₂ at 723 K before characterization. The total surface area was measured by the BET method (Quantasorb Q518) and the metal surface area was measured using standard hydrogen chemisorption techniques. XRD data of the catalysts were obtained using CuK α radiation (Philips diffractometer). SEM photographs were taken on fresh catalysts and after coke deposition (Zeiss DSM 940).

Reaction system

A typical microreactor flow system was used to study the activity and selectivity of the supported catalysts. The flow rates of the gases (CH₄, CO₂, N₂ for dilution) were controlled by mass flow meters (Brooks 5850). The quartz tube reactor (10 mm in diameter, 400 mm overall length) was filled with 200–500 mg of catalyst in the central zone between two layers of carborundum. The reactor was placed in a ventilated oven and the temperature was controlled using a thermocouple located inside the reactor. The catalytic activity was determined by monitoring the effluent concentration of reagents and products using a GC (Dani 3800) equipped with a Thermal Conductivity Detector and a column packed with Carbosieve S II. The deviation from a 100% mass balance was ascribed to coke and tar formation. A direct measurement of the amount of deposited coke was made by extensive hydrogenation after each experiment and by measuring the total methane production.

Thermogravimetry

Tests were performed on a Mettler TA2000 system; the reactant gases were premixed in appropriate ratios and successively fed to the TG–DTA instrument. All runs were performed at atmospheric pressure both at programmed increasing temperatures and at constant temperature. Every change in the reactive gas concentration (H₂, CH₄ and/or CO₂) was preceded by a purge with He for at least 60 min.

Gases

All gases used were purchased from commercial suppliers. They were ultra-high purity grade and were used directly from cylinders without any further purification.

Results and discussion

A typical TG curve at constant temperature (873 K) with a gas feed composition of $\text{CH}_4/\text{CO}_2 = 1:1$, is shown in Fig. 1. The catalyst sample was heated at a constant rate ($10^\circ\text{C min}^{-1}$) from ambient temperature up to 873 K in H_2 and stabilized in a He atmosphere for 1 h. After that the reactive gases were fed for 2 h, and after 2 h in He, H_2 was fed again. An induction time was observed before the carbon deposition started; then the rate of mass gain of the sample grows quickly and reaches a constant value. The rate of mass loss, during reduction with H_2 , appears nearly constant, but no induction time can be observed.

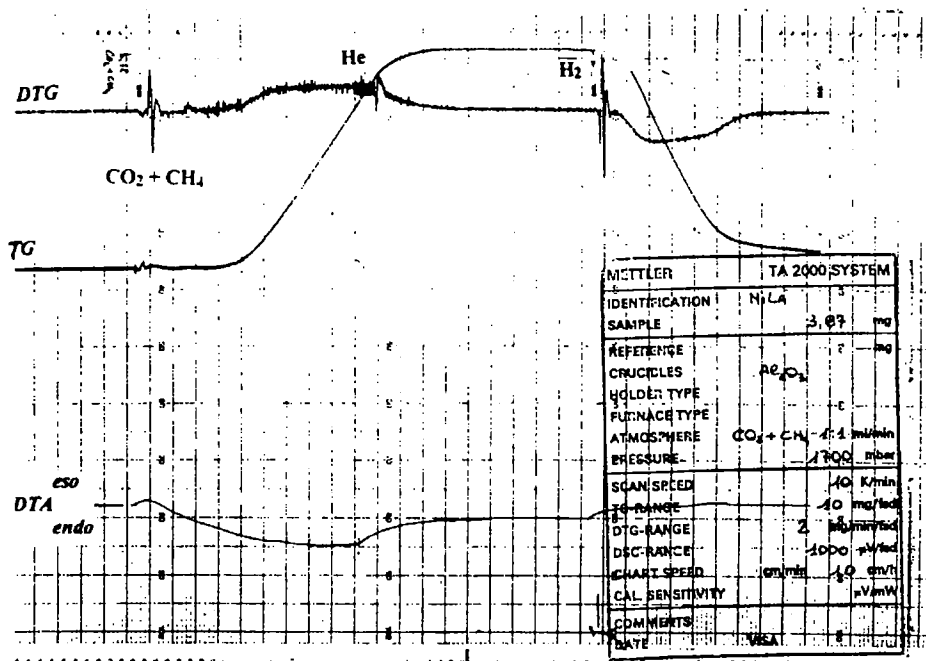


Fig. 1 A typical DTG-TG-DTA analysis using 3.87 mg of Ni(30)/ La_2O_3 catalyst at 823 K in a $\text{CO}_2/\text{CH}_4 = 50/50$ gas atmosphere (Crucibles: Al_2O_3 , Pressure 1700 mbar, Scan speed 10 K min^{-1} , TG-range 10 mg fsd, DTG-range $2 \text{ mg}/(\text{min fsd})^{-1}$, DSC-range $1000 \mu\text{V}/\text{fsd}$, chart speed 10 cm h^{-1})

TG experiments were performed at different temperatures and at different reactive gas compositions.

The curves of the initial mass gains at different gas compositions are plotted vs. time in Fig. 2 for the same temperature. A strong dependence may be observed of the induction times on the CO_2 concentration in the gas phase; this phenomenon is well known for the water/hydrocarbon ratio in steam reforming [8].

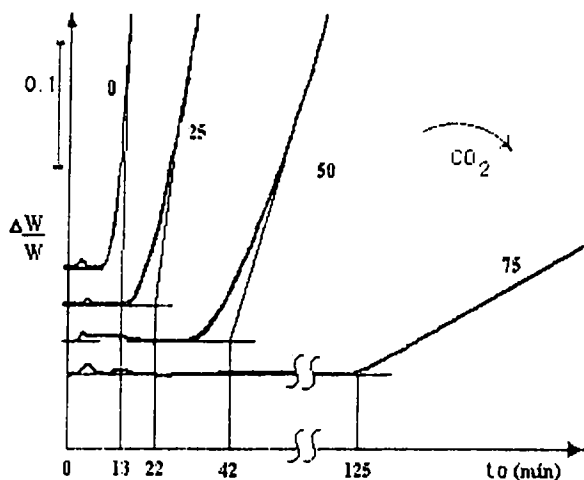


Fig. 2 Mass gain vs. time at different reactive gas compositions, at 873 K, for Ni(30)/SiO₂ in a CO₂/CH₄ gas mixture

For a CH₄ to CO₂ ratio of 1 the induction times, and the specific carbon deposition rates on Ni catalysts with different supports are given in Table 1. There is a strong dependence on the temperature and the support.

The induction times (t_0 for the Ni(30)/SiO₂ and Ni(5)/La₂O₃ catalysts are depicted in Fig. 3 as a function of the amount of CH₄ in the CO₂+CH₄ feed gas. Catalysts with a similar surface metal distribution are compared (1.0×10^{-3} and 2.1×10^{-3} g Ni/m² respectively for Ni(30)/SiO₂ and Ni(5)/La₂O₃), as the metal particle size affects the catalytic activity (Table 1). The rates of carbon deposition are presented also in terms of mgC/m²*min to check the surface effect.

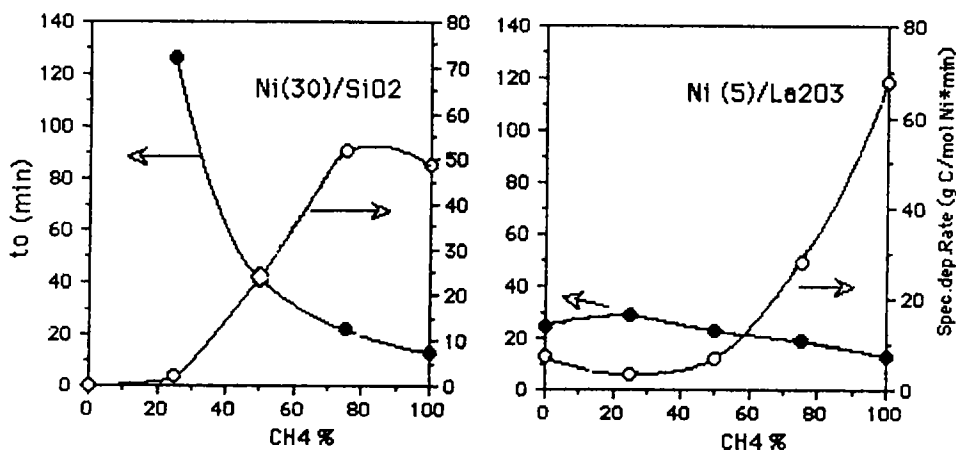


Fig. 3 Induction time and specific deposition rate vs. gas feed composition, for Ni(30)/SiO₂ and Ni(5)/La₂O₃; at 873 K in a CO₂/CH₄ gas mixture

Table 1 Results of TG analyses for several catalysts. The induction time t_0 (min) and the rate of the mass gain $\text{g}(\text{mol Ni} \cdot \text{min})^{-1}$ are given for the carbon deposition reaction. Furthermore, the hydrogenation rate $\text{g}(\text{mol Ni min})^{-1}$ is given in pure H_2 . The metal distribution is expressed in $\text{mg Ni} (\text{m}^2 \text{ catalyst})^{-1}$ +

Samples	Ni/ wt%	Metal distrib./ mg m^{-2}		Ind. time, ⁺ t_0/min		Rate _{carb.depos.} $\text{g}(\text{mol Ni} \cdot \text{min})^{-1}$			Rate _{carb.hydrog.} $\text{g}(\text{mol Ni min})^{-1}$			
		823 K	873 K	923 K	823 K	873 K	923 K	823 K	873 K	923 K	823 K	873 K
Ni(30)/SiO ₂	28.4	67	42	23	14.1	24	6.4	6.9	31.9	13		
					(0.2)	(0.4)	(0.1)					
Ni(5)L _a 2O ₃	3.5	26	23	22	8.2	7.2	2.6	n.d.	10.5	3.9		
					(0.3)	(0.3)	(0.2)					
Ni(30)L _a 2O ₃	30.5	60	24	13	2.7	3.1	3.9	2.5	3.5	6.2		
					(1.0)	(1.2)	(1.4)					

+ Feed gas $\text{CO}_2/\text{CH}_4 = 1/1$; italic number = $\text{mgC}/(\text{m}^2 \text{ min})$

For CH_4 percentages ≤ 60 , the induction time of carbon deposition on SiO_2 -supported catalyst is longer than for the lanthana-supported one, but the values are similar at CH_4 percentages greater than 60–70%.

The carbon deposition rate depends on the surface metal distribution as shown by the data in Table 1.

On La_2O_3 the mass gain has a shorter induction time than on SiO_2 , probably due to the faster adsorption of CO_2 on the basic sites.

Considering that under in the conditions of methane dry reforming (reaction 1),



the Boudouard (2) and methane decomposition (3) reactions are thermodynamically favourable,



it is justified to suppose that carbon deposition on La_2O may occur both by methane dissociation and by the Boudouard reaction while the coke on the SiO_2 catalyst is preferentially due to methane dissociation [7]. In this respect, some influence of the support must be considered.

SEM photomicrographs of both La- and Si-supported, used nickel catalysts with a high nickel loading clearly show whisker carbon. It can be seen from Fig. 4 that filaments of coke were formed.

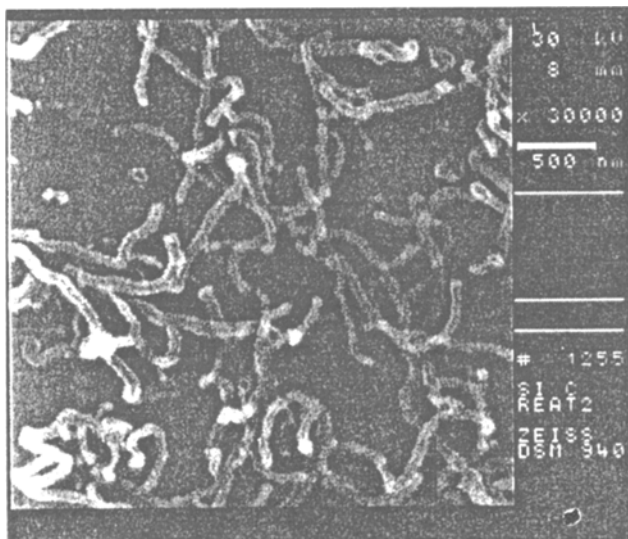


Fig. 4 SEM microphotograph of coke formed in the catalytic test at 873 K, $\text{CO}_2/\text{CH}_4 = 50/50$ on $\text{Ni}(30)/\text{La}_2\text{O}_3$

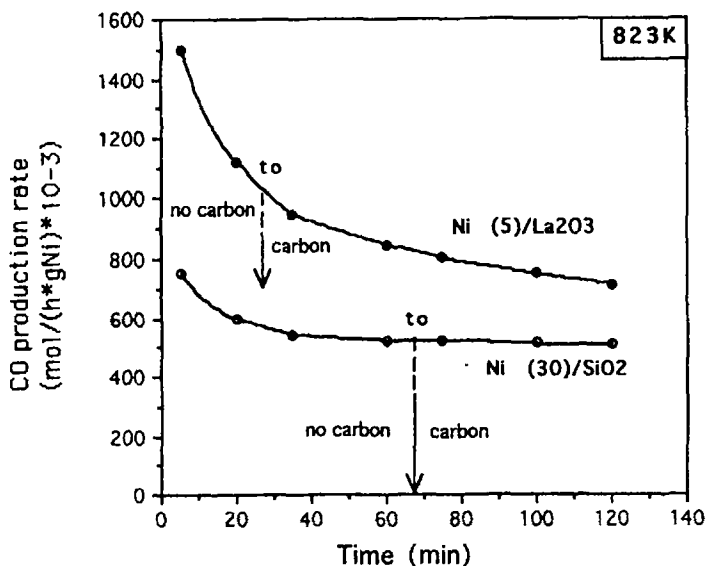


Fig. 5 CO production rate during the $\text{CO}_2 + \text{CH}_4$ reaction at 823 K for two catalysts. The induction time corresponding to the start of the carbon deposition is also indicated

Whisker carbon deposition does change the rate of synthesis gas production and deactivation appears only at very high carbon coverage of the surface. Catalytic tests performed at 800–900 K show that the CO production rate after an initial rapid reduction becomes quite constant, while at the same time coke deposition occurs. Comparison of TG results and catalytic tests led to the following conclusion: – on the Ni/SiO₂ catalyst, an asymptotic synthesis gas production is reached even in the induction period; – on Ni(5)/La₂O₃ a higher CO production than on the Ni/SiO₂ catalyst occurs but a continuous decrease in the activity can be observed (Fig. 5). Consequently we suppose that with lanthana different types of carbon deposits occur at some stage of the deposition. Moreover, the catalytic tests on lanthana-supported nickel show that the methane decomposition reaction is the principal route to the carbon formation at high temperature, while at low temperature the Boudouard reaction prevails [7]. In a previous work [6] we also reported a close correspondence between carbon deposition in TG tests and CH₄ obtained during the reduction after catalytic tests.

Conclusions

In the reforming catalyst, La₂O₃ is a very active support, because it promotes CO₂ adsorption, thus increasing the production of synthesis gas. CO may evolve

through carbonate decomposition *via* formate species whose formation by lattice anion vacancies could be relevant.

CO₂ on the catalyst surface probably opposes the Boudouard carbon deposition, and a rapid CO evolution from the surface acts in the same way. In the presence of too high CO₂ concentration on lanthana, great amounts of CO are produced. Consequently the fast CO₂ dissociation (direct Boudouard: 2CO → CO₂ + C) opposes the positive effect of CO₂ adsorbed on lanthana on the carbon removal.

To prevent carbon formation and to obtain high production of synthesis gas, powerful kinetic tools include the modification of the adsorption properties of the catalytic surface using low amounts of active lanthana as promoter.

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This work was supported by Ministero della Pubblica Istruzione (Italy).

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