

Development of a Honeycomb Catalyst Based on Rh-LaCoO₃ For Conversion of Tar into Syngas

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Honeycomb catalysts have been developed for conversion of tar from biomass pyrolysis on the basis of the very promising results obtained on Rh-LaCoO₃ based powder catalysts in order to propose them as secondary catalysts in biomass gasification processes, reducing the pressure drops across the reactor and blocking due to solid particulate.

The structured catalysts have been tested in a suitably designed plant consisting in a double reactor system where products of biomass pyrolyzed in the first reactor pass through a second reactor containing the catalyst. Honeycomb catalysts have been fully characterized by ICP-MS, BET, SEM and H₂-TPR techniques. The effect of active phase loading, of honeycomb cell density and of the gas flow rate on the performances have been investigated in order to find operating conditions approaching results obtained on the powder system.

1. Introduction

A clean syngas can be produced by biomass gasification for energy purpose or for production of fine chemicals provided that a suitable conditioning of the biomass derived products is operated. In fact, the biomass gasification, in addition to a gas phase (H₂, CO, CO₂ and light hydrocarbons), produces a solid residue (char) and a mixture of condensable hydrocarbons (tar) (Yung et al., 2009).

The formation of tar represents a severe limitation due to its condensation in downstream pipes and filters and a loss of energetic efficiency due to the incomplete carbon conversion. Catalytic tar conversion into valuable permanent gases at low temperatures (650-850°C) has been proposed (Devi et al., 2003). Catalysts proposed for tar reforming range from natural materials as dolomite or olivine (Kuhn et al., 2008) to synthetic catalysts as noble metals (Colby et al., 2010) or transition metals (Vivanpatarakij et al. 2014). Recently, a new catalytic system based on rhodium ($\leq 1\%$) dispersed in a LaCoO₃ matrix supported on stabilized γ -Al₂O₃ has been developed in order to overcome the typical drawbacks (low activity, coke deactivation) of conventional catalysts (Ammendola et al., 2010a). The Rh-LaCoO₃ catalyst was found to completely convert tar as well as light hydrocarbons into syngas even at 600 °C showing, in addition, a high stability to thermal and redox cycles, a good sulfur tolerance and a low coke formation (Ammendola et al., 2012b). The excellent performance of this catalyst, tested also in the presence of O₂ (Ammendola et al., 2014), was definitely better than that of natural or synthetic Ni-based catalysts under the same conditions (Ammendola et al., 2010b).

The use of structured catalysts as secondary systems, i. e. located downstream the gasifier, represent a promising technology in a biomass gasification process, reducing the pressure drops across the reactor and blocking due to solid particulate. Indeed, hot gases from the gasifier contain a lot of fly ash which would require a prior filtration in order to avoid catalyst deactivation (Toledo et al., 2006). Nevertheless, only few studies report the use of structured catalysts for tar conversion, generally Ni-based mainly affected by the typical coke formation (Qiu et al., 2012).

In this work, cordierite honeycomb monoliths were firstly washcoated with γ -Al₂O₃ and then Rh and LaCoO₃ were dispersed on the alumina layer to reproduce as much as possible formulation and properties of powder catalyst which provided the best performance. Physico-chemical characterization was aimed at verifying that typical features of powder sample were preserved in the structured catalyst. Therefore, parameters as active

phase loading, honeycomb cell density and gas flow rate were investigated evaluating the catalytic performances in order to find operating conditions approaching results obtained on the powder system.

2. Experimental

In order to evaluate and compare the performance of structured catalysts to that of powder samples previously tested (Ammendola et al., 2009) active monoliths were prepared with a loading of Rh and LaCoO₃ on the alumina washcoat similar to the powders.

Commercial honeycombs with straight, parallel channels of extruded cordierite (2MgO·2Al₂O₃·5SiO₂), provided by Corning (400 cpsi) and NGK (600 and 900 cpsi), were cut in the shape of disks of 17 mm diameter and 20 mm long. The monoliths were washcoated with alumina by repeated dipping in a slurry of finely grounded La-stabilized γ -Al₂O₃ powder (Puralox SCF-L3, SASOL), diluted nitric acid solution and pseudoboehmite up to reach a target average thickness of the washcoat layer of 50 μ m. LaCoO₃ and Rh precursor salts, La(NO₃)₃·6H₂O (Aldrich, > 99 %), Co(NO₃)₂·4H₂O (Aldrich, > 99 %) and Rh(NO₃)₂·xH₂O (Riedel-de-Haën), were deposited by several cycles of incipient wetness impregnation to reach a target loading of active phase in the washcoat layer (monolithic substrate excluded) of 20% (wt/wt) LaCoO₃ and 1 % (wt/wt) Rh, respectively. After each impregnation cycle the catalysts were calcined in air at 800 °C for 3 h.

In the following Rh-LaCoO₃ catalysts are labelled as 400, 600 and 900, corresponding to the different cell density of the honeycomb substrates. An additional sample was prepared (400-II), using the 400 cpsi cordierite substrate with an about half thick washcoat layer (nominal average thickness of 25 μ m), in order to evaluate the effect of active phase loading on the catalytic performance of tar conversion.

The actual metal content was quantitatively determined on catalysts by inductively coupled plasma spectrometry (ICP) on an Agilent 7500 ICP-MS instrument, after microwave-assisted digestion of samples in HNO₃/H₂O₂ acid solution. BET specific surface area of monolith samples, evaluated by N₂ adsorption at 77 K using a Quantachrom Autosorb 1-C after degassing under vacuum at 150 °C, was assigned only to the active washcoat layer (SSA of honeycomb substrate \leq 1m²/g). SEM analysis was performed using an Inspect S (FEI) microscope equipped with an EDAX detector for EDS microanalysis. H₂-TPR experiments were carried out with Micrometrics Auto-Chem II apparatus equipped with a TCD. Samples were pre-treated at 800 °C under air flow for 1 h before the experiment, and then reduced with a 2 % H₂/Ar mixture (50 cm³/s) heating at 10 °C/min from room temperature up to 800 °C.

An experimental setup consisting of two fixed bed quartz reactors (i.d. = 1 or 2 cm, length = 60 cm) independently heated in two different electric furnaces was used to test the catalysts (Ammendola et al., 2010b). The biomass sample (W = 0.5-1 g) of maple wood chips (800-900 μ m) was heated up to 800 °C (5 °C/min) in the first reactor (i.d. = 1 cm) under pure N₂ constant flow rate (Q = 6, 12, 24 NL/h). The gaseous and condensable species formed during biomass pyrolysis passed through the second reactor (i.d. = 2 cm) containing the catalytic monolith kept at 700 °C. Then the stream was sent to a two stage-condenser, following the CEN/TS 15439 (2006) procedure for sampling and analysis of tars. Permanent gases were analysed with a micro-gas-chromatograph (Agilent 3000A), equipped with four different independent channels and a TCD. All the connection lines upstream the first condensation stage were heated (300-400 °C) to avoid the condensation of tarry compounds. The sampling train was weighted before and after each experiment for the quantitative evaluation of the condensable tars yield. The analysis of the condensed tars was performed off line in a gas chromatograph (Agilent 7890A), equipped with a FID and a MS detector. The char yield was estimated by weighing the biomass residue in the first reactor after pyrolysis. At the end of each experiment the amount of coke deposited on the catalyst was determined by quantitative evaluation of CO₂ produced by its oxidation (5 °C/min to 800 °C; 0.5%O₂/N₂ mixture at 17 NL/h) after cooling down under inert atmosphere. Catalytic activity was thus estimated as the difference between the yields and type of gas, liquid, and solid products obtained with the different catalysts. For all experiments the mass balance was closed with a maximum error of \pm 10% wt.

3. Results and discussion

3.1 Catalyst characterization

In Figure 1 pictures of the sample 400 coated only with the alumina washcoat (a), and covered also with the active phase (b), are represented, while in Table 1 the main geometrical characteristics of the different catalytic monoliths are reported. The dark colour of the monolith in Figure 1b clearly shows the formation of a perovskite-like compound on alumina. The SEM analysis carried out on both longitudinal and cross section of the catalysts highlights that the washcoat is uniformly distributed and well anchored to the cordierite. The characteristic rounding of the channel cross section, originally square, due to an accumulation of washcoat in

the corners is also evident. The EDAX analysis, performed on both longitudinal and cross section, evidences that the Rh, Co and La are uniformly distributed throughout the thickness of the washcoat layer.

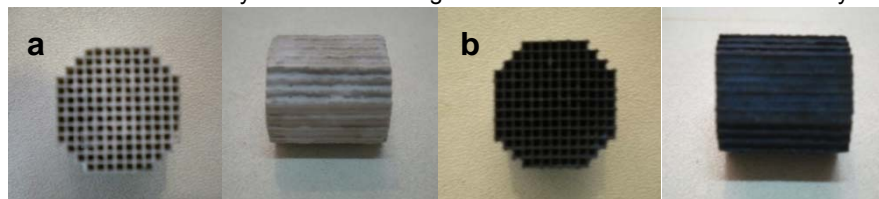


Figure 1: 400 cpsi monolith coated only with Al_2O_3 washcoat (a) and covered also with active phase (b)

The metal contents, determined by ICP analysis and reported in Table 1, are very close to the nominal ones calculated on the basis of 20%wt LaCoO_3 load and 1wt% Rh load.

Table 1: Physico-chemical properties of structured catalysts and quantitative results of TPR experiments (H_2 uptake/(Rh+Co))

Catalyst	BET area (m^2/g)	surfaceRh (%wt)	Co (%wt)	La (%wt)	H_2 uptake/(Rh+Co) (-)
400	83.1	0.34	1.1	3.5	0.28
400-II	87.0	0.15	0.9	2.0	0.19
600	89.0	0.41	1.7	5.3	0.14
900	84.2	0.52	2.7	7.6	0.19

Values of BET specific surface area are also reported in Table 1. The stabilized alumina used as catalyst support has a specific surface area of roughly $140 \text{ m}^2/\text{g}$ (Ammendola et al., 2010a) after calcination in air at 800°C . Addition of 21 %wt of active phase entails reduction of the specific surface down to $80\text{-}90 \text{ m}^2/\text{g}$ for all the samples.

The reducibility of Rh and Co is evaluated through H_2 -TPR experiments. All TPR profiles (not reported) show a signal at $370\text{-}400^\circ\text{C}$, assigned to the reduction of surface RhO_x , a small peak at intermediate temperature, associated to the reduction of a fraction of cobalt and a large peak mostly under the isothermal step at 800°C related to both RhAl_2O_4 and CoAl_2O_4 (Ammendola et al., 2010a). The redox behavior of monolithic catalysts is in same way different from that of the corresponding powder sample (Ammendola et al., 2012a). The value of $\text{H}_2/(\text{Rh}+\text{Co})$ ratio, calculated from the integration of the TPR profiles and reported in Table 1, is far from the theoretical ratio of 1.5 obtained assuming the complete reduction from the oxidation state of +3 to 0 for both metal cations. This is indicative of a strong interaction with alumina, especially for cobalt, favoured by the repeated impregnation-calcination cycles required for the preparation of the monoliths compared to powder samples which undergo only one calcination step. This leads to the formation of an increasing fraction of cobalt aluminate, as also observed for powders calcined at higher temperature (Ammendola et al., 2009) or subjected to several redox cycles (Ammendola et al., 2012a). On the other hand the formation of CoAl_2O_4 spinel partially inhibits the diffusion of rhodium in the alumina structure preserving its reducibility and in turn its ability to convert tar, assigned to dispersed Rh (Ammendola et al., 2009). Therefore, it can be generally concluded that this specific feature of powder catalysts is kept in the monolith samples.

3.2 Catalytic activity

Three preliminary blank tests were carried out. In the first one the second reactor was excluded and the decomposition of biomass occurring in the first reactor was monitored in order to obtain qualitative and quantitative analysis of the pyrolysis products. In the second blank test a bare cordierite monolith (400 cpsi) was loaded in the second furnace at 700°C in order to verify and evaluate the occurrence of thermal cracking reactions. In the last one an alumina-washcoated monolith (400 cpsi) (without active phase) was loaded in the second furnace at 700°C , in order to assess the possible contribution of stabilized Al_2O_3 to catalytic reactions. The results obtained in this preliminary experimental campaign are reported in Table 2 in terms of solid, liquid and gas yields and in Figure 2 in terms of yields of different permanent gaseous products (CO , CO_2 , H_2 , CH_4

and traces of light HC, like acetylene, ethylene, ethane, propane, propene, C4 and C5). In the absence of the second reactor, the product yields are in good agreement with the results of the biomass proximate analysis (Ammendola et al. 2009). The presence of the cordierite in the second reactor strongly affects the distribution of the liquid and gas products promoting homogeneous cracking reaction of condensable products with consequent increase of the gas yield, due to a strong increase of CO, H₂ and light HC. Tarry compounds are further converted in permanent gas when the Al₂O₃-washcoated monolith is present in the second reactor due to the acid character of alumina. The condensed tars in the first blank test correspond to phenols, PAHs and guaiacols; in the presence of the second reactor oxygenated compounds, such as guaiacols and phenols, reduce or disappear, in agreement with the increase in CO_x and light hydrocarbon productions before described for the gas phase. The char yield is the same in all the tests, as expected.

Table 2: Operative conditions and results of catalytic tests (St= standard conditions: W = 0.5 g - Q = 12 NL/h)

Catalyst	Operative conditions	Solid yield (wt%)		Liquid yield (wt%)	Gas yield (wt%)
		char	coke		
-	St	16.6	-	74.6	7.8
Cordierite	St	16.2	-	45.9	40.0
Cord/washcoat	St	16.7	8.7	26.8	51.4
	Q = 6 NL/h	18.2	0.4	15.6	63.0
	St	17.7	1.6	6.6	69.5
400	Q = 24 NL/h	17.9	2.7	3.2	74.9
	W = 1 g - Q = 24 NL/h	18.4	3.2	-	79.5
400-II	St	18.6	1.1	6.1	70.1
600	St	18.1	0.8	4.7	72.9
900	St	19.0	0.2	-	81.2
powder	St	17.0	1.3	-	77.0

For the proper catalytic tests a catalytic bed height similar to that previously adopted for tests on powder catalysts (Ammendola et al, 2009) was chosen. Standard conditions, reported in the caption to Table 2, were used in order to assess the effect of both cell density and active phase loading. The results are reported in Table 2 and Figure 2, compared with those provided by a powder sample, calcined at 800 °C, under the same standard conditions, i.e. using the same amount of Rh-LaCoO₃/Al₂O₃ of the washcoat layer of monolith (Ammendola et al., 2014). Some parameters were changed for monoliths 400 in order to highlight the effect of both N₂ flow rate and biomass amount on the performance of structured catalysts. It must be reminded that changing in flow rate also involves modifications of the concentration of compounds produced by the biomass pyrolyzed in the first reactor, then modification of the feed to the catalytic reactor. For all experiments the mass balance was closed with a maximum error of ±10%wt.

Preliminary fluid dynamic calculations show that a laminar flow regime (Reynolds ≤1.40 in all cases) and negligible entrance effects (hydrodynamic entry length always lower than 3.5 % of the total length of the channel) can be assumed. Remarkably, in the axial direction, the characteristic convection time is always sufficiently smaller than the dispersion time (5.1 ≤ axial Peclet number ≤25), with the consequence that back-diffusion is negligible. On the other hand the radial Peclet varies in the range 0.013–0.217, increasing with channel dimension, thus suggesting that, even if the organic compounds can always reach the catalytic surface during their residence time in the channel, significant radial gradients should be expected particularly for monoliths with low cell density. As a matter of fact, the mass transfer coefficient (evaluated for both short and long chain hydrocarbons) strongly increases for monoliths with higher cell density, due to the increase of both the specific geometrical surface and the radial Peclet. The external mass transfer is also positively affected by an increase of N₂ flow rate at a fixed monolith cell density.

In all catalytic tests, the effectiveness of the structured catalysts in tar conversion is highlighted by a considerable reduction of tar, even absent in some cases, and a significant increase in the yield of gaseous products with respect to blank tests. The gas composition is strongly influenced by the presence of the catalyst: the main gaseous products are H₂ and CO, with a ratio H₂/CO ranging from 1.22 to 1.35, methane production is negligible and no light hydrocarbons are produced. All these results are very similar to those obtained for the powder system. These evidences confirm that the catalytic properties of the active layer on the monoliths closely reproduce the properties of the active phase on the powder system. Moreover, the performance of Rh-LaCoO₃, also when dispersed on a structured substrate, in tar reforming are very high with

respect to Ni-based monoliths (Simell et al., 1996), due to a complete tar conversion, a large syngas production and a very low coke formation at temperature as low as 700 °C.

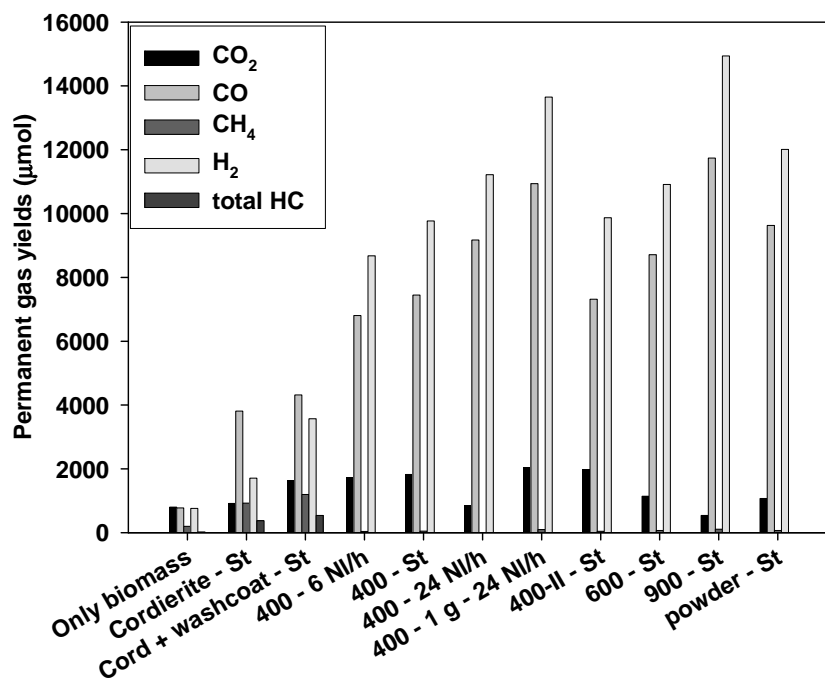


Figure 2: Yields of permanent gaseous products obtained with different catalytic systems under different operating conditions

The negligible role played by internal diffusive mass transfer is proved by comparing the results obtained for 400 catalyst with those of 400-II sample, characterized by a half of active phase loading. They show comparable performances in terms of product yields and gas composition, thus indicating that catalytic reactions are mainly affected by the external surface of the active layer. On the other hand, the experimental results also demonstrate the important role played by the external diffusive resistances to the mass transfer, as expected for structured systems. Indeed, an increase of cell density involves better performances in terms of increased gas yields and quality, and decreased tar and coke production (up to their disappearance), in line with the lower external diffusion limitations and, in turn, with higher mass transfer coefficient, evaluated for the monoliths with higher cell density. In particular, the 900 catalyst shows the best performances even with respect to the powder system. Even the results obtained for the sample 400 at different N₂ flow rates confirm the role of external mass transfer on the performance in tar conversion. In particular, an increase of gas yield to the detriment of liquid phase and a better gas quality are found at higher flow rate approaching the performance of the reference powder catalyst obtained otherwise under the less favourable conditions (lower flow rate). On the other hand, it should be underlined that an increase of the flow rate involves both a positive effect (i.e. the increase of the mass transfer coefficient) and two negative ones (i.e. the decrease of gas residence time in the channel and the dilution of organic species coming from biomass, which, in turn, can negatively affect the reaction kinetics of tar reforming in the case of a global order ≥ 1). The experimental evidence related to enhanced performances at higher flow rates demonstrate that the positive effect of the reduction of external diffusive limitations to the mass transfer prevails on the other effects. The hypothesis of a kinetics order ≥ 1 is confirmed by comparing two tests performed at a fixed N₂ flow rate (24 NL/h), i.e. at fixed mass transfer coefficient, but at different biomass loading (0.5 and 1 g), i.e. at different partial pressures of organic compounds. The better performances obtained in the case of higher partial pressures of tar species (1g biomass) are associated to an enhanced kinetics of conversion of tarry compounds.

4. Conclusions

In this work honeycomb monoliths with the same chemical formulation of a very performing γ -Al₂O₃-supported Rh/LaCoO₃ powder catalyst were proposed as secondary systems for tar conversion in hot gas cleaning of biomass pyrolysis. Physico-chemical characterization of structured catalysts showed that the same features of

the powder sample were basically reproduced for the monoliths although the different and more complex preparation technique. Comparison of catalytic activity under similar conditions showed that tar reforming can be effectively carried out on monolith catalysts which provide performance very close to that of the powder system, thus reducing pressure drops across the reactor and blocking due to solid particulate. The study of the effect of different operative parameters (cell density of the monolith, amount of active phase, flow rate of the carrier gas and amount of biomass) allowed the definition of the conditions reducing the external diffusive mass transfer limitations which represent the main barrier to the achievement of the best performance of the monolithic catalyst, even in comparison with the powder system. In particular, an effective way to achieve high conversion of tar is the use of honeycomb substrates with a high cell density.

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