Catalytic cracking of tar with perovskite catalysts

E. Grieco, C. Gervasio, A. Barresi, G. Baldi

Chemical Engineering Department, Politecnico di Torino - ITALY

1. Abstract

One of the most promising techniques to clean the gas produced by gasification is catalytic tar cracking. The performances of some oxide catalysts based on nickel were investigated. Some pollutants were tested (naphthalene, phenol, exadecane) with concentrations ranging between 5 and 15 g/Nm$^3$. The most critical compound is naphthalene. The investigation was concentrated on perovskites, composed by La, Ni and Fe or Cr. Perovskites based on Fe and Ni were not able to get stable operating conditions, and a continuous decrease of activity was observed, in particular with naphthalene. Much more promising are the LaCr$_{x}$Ni$_{1-x}$O$_{3}$ perovskites. The tests were performed with LaCr$_{0.5}$Ni$_{0.5}$O$_{3}$. The crystalline structure of the perovskite is stable in reducing working atmosphere, and the catalyst activity was stable also after long test (500 h) performed with exadecane or phenol. Naphthalene caused an initial loss of activity, followed by a stable conversion that was maintained for more than 500 h.

2. Introduction

Solid combustibles will increase their importance in global energy supplies. In particular renewable combustibles like biomass, are expected to provide the greatest contribution. Solid combustibles are normally treated in stationary plants, to produce electricity by means of combustion and Rankine cycles. This common technology leads to quite low yields of electricity (15-20 %). On the other hand it could be much interesting to transform biomass in gaseous or liquid fuels that could be used in other than stationary plants.

Gasification is considered one of the most important techniques. Gasification produces syngas (H$_2$, CO, CO$_2$) that can be used either for direct energy production (gas turbines, engines, combined cycles) and for liquid fuels synthesis.

One of the major problems in the application of this technology is the gas cleanup from tar. Tar is a complex mixture of organic compounds with a molecular weight higher than benzene. The composition of tar depends on pyrolysis conditions [1]. Tar can be dangerous for the process equipment such as gasifier, engine or turbine system because of its deposits [2]. Tar can be eliminated downstream the gasifier by means of scrubbing with H$_2$O or organic liquids. These methods give good performances but they are very expensive due to the big amount of liquid effluents that are produced. Hot gas clean-up is much more attractive, in particular cracking allows to convert tar in valuable gaseous products [3]. Thermal cracking occurs at higher temperatures than those normally employed for catalytic cracking. Catalytic cracking of tar is a more promising way to eliminate tar. Our goal is to find a catalyst sufficiently active, resistant to deactivation and not much expensive.

Many types of catalysts were tested for this application: minerals like calcined rocks, olivine, clay minerals and iron ores or synthetic catalysts like zeolites, activated alumina, alkali metal-based or transition metal based catalysts. In particular Ni-based catalyst seem to be the most active in tar cracking. The problem is their rapid deactivation due to sulphur and high tar
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content in the feed [4]. As suggested by S. Rapagnà et al. [5] in order to limit the problem of rapid deactivation, nickel should be dispersed in a well defined structure with high metallic dispersion and a strong interaction between the elements included in the structure. These conditions can limit the sintering of the active species and carbon build-up. To inhibit the coking is necessary that the clusters of the active metal remain of a dimension smaller than a certain critical size [6]. Ni-Fe and Ni-Cr perovskites were tested in this work.

3. Experimental

3.1. Catalyst preparation and characterization
Two different catalysts were tested with respective composition: LaFe$_{0.7}$Ni$_{0.3}$O$_{x}$ and LaCr$_{0.7}$Ni$_{0.3}$O$_{x}$. In both cases, catalysts were prepared as powders by means of thermal decompositon of nitrates of La, Fe, Cr, Ni. The right amounts of La(NO$_3$)$_3$•6H$_2$O, Ni(NO$_3$)$_2$•6H$_2$O and Fe(NO$_3$)$_3$•9H$_2$O and Cr(NO$_3$)$_3$•9H$_2$O were dissolved in a double weight of distilled water and then added of 10% in weight (with respect to the nitrates weight) of glycerol. Then the solution was put in a porcelain crucible and heated at 200°C for 1 hour in order to allow the decomposition of metal nitrates assisted by the organic reducing agent (glycerol). The resulting solid was then heated to 700-850 °C in order to allow the formation of the perovskite structure. In most cases crystallization was performed at 700 °C for 4 h, leading to a perovskite structure in the case of LaFe$_{0.7}$Ni$_{0.3}$O$_{x}$ catalyst.

On the other hand it was verified that when iron is replaced by chromium at lower temperature the formation of La$_2$CrO$_6$ is promoted with respect to perovskite. For this reason some catalysts were prepared at 850 °C in order to allow the formation of the perovskite phase.

The catalysts have been characterized by powder X-Ray Diffraction (XRD) on a X’Pert Philips diffractometer using the Bragg Brentano camera geometry and the Cu-K$\alpha$ incident radiation.

XRD analysis have been carried out before the cracking tests to assess the formation of the desired phase and also after the cracking tests to evaluate the stability of the catalyst or the formation under the reaction conditions of other phases different from the original one.

BET surface areas have been determined by nitrogen adsorption at 77 K in a Micrometrics ASAP 2010 M instrument.

3.2. Catalyst preparation and characterization
The cracking tests have been performed in a laboratory plant (figure 1). During the tests a nitrogen flow of 50 ml/min is used as carrier gas. It passes through a tar evaporator to achieve the saturation. Water is added through a syringe pump and then vaporized, on order to get a molar fraction of water of 5%. The flow passes through a damping tank and then in a reactor placed in an oven.

The effects of naphthalene, phenol and exadecane were studied. For naphthalene and exadecane a concentration of 5 g/Nm$^3$ was used, phenol was tested at 15 g/Nm$^3$.

3.3. Catalyst preparation and characterization
Reaction products are analyzed with two different gas chromatographs by sampling online. The first one (Varian 3400) is connected to the reactor by a heated line and analyzes the concentration of residual tar. The connection line is maintained at a temperature higher than the condensation one. The second one (Micro-GC 2 channel system Varian CP-4900)
analyzes the concentration of light gases produced by cracking reaction such as H₂, O₂, CO, CO₂, CH₄, etc.

Fig. 1  Draft of the experimental plant

4. results

4.1. Catalyst based on Fe an Ni
The perovskite LaFe₀.₇Ni₀.₃Oₓ was tested in the past both for methane steam reforming and tar cracking [5][6]. These previous studies demonstrate that such composition represent the best compromise between activity and stability. In this study this perovkite was tested for a quite long period in order check the resistance of the catalyst and to provide reliable data for comparison with the catalyst based on LaCrNi. Two basic tests were performed both with exadecane and naphthalene. According to Coll et al. [7] naphthalene is one of the most stable tar compounds. The high carbon to hydrogen ratio makes naphthalene one of the most dangerous product with respect to coking. Operating conditions were 600 °C and 500 °C respectively for naphthalene and exadecane with a GSHV of 3300 h⁻¹.

Fig. 2  Conversion of naphthalene on LaFe₀.₇Ni₀.₃O₃ catalyst.

As shown in the figure 3 the conversion of exadecane is generally stable with time, on the other hand, naphthalene lead to a rapid strong deactivation. In this case also a regeneration at 700 °C with steam was tested, with no appreciable results.
XRD analysis showed clearly both before and after tests a perovskite structure. The analysis of the light gases produced allowed to determine the amount of carbon escaping from the reactor, this was very close to that one produced by cracking. However with naphthalene a rapid deactivation of catalyst was observed.

4.2. Test on chromium – nickel catalysts
In order to improve catalyst stability and to promote coke oxidation some attending to replace iron with chromium were done. Chromium was chosen for two main reasons: according to many literature studies, LaCrO$_3$ perovskites are quite active with respect to soot oxidation [8], on the other hand chromium oxide is stable also in slowly reducing atmosphere.

**Fig. 3** Conversion of exadecane on LaFe$_{0.7}$Ni$_{0.3}$O$_3$ catalyst.

**Fig. 4** Conversion of naphthalene on LaCr$_{0.5}$Ni$_{0.5}$O$_3$ catalyst
The method used to prepare the catalyst was initially the same used for \( \text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_3 \). Preliminary tests allowed to identify the catalyst with atomic ratio \( \text{Cr/Ni} \) equal to 1 as the most promising. The catalyst was then tested in the usual conditions (3300 h\(^{-1}\) GSHV) with exadecane and naphthalene. In both cases a temperature of 600 °C was adopted. The results are presented in figures 4 and 5. The same catalyst was also tested with phenol, with a concentration of 15 g/Nm\(^3\) (fig. 6).

Fig. 5  Conversion of exadecane on \( \text{LaCr}_{0.5}\text{Ni}_{0.5}\text{O}_3 \) catalyst

The behaviour of catalyst with exadecane and phenol was very good, but the most important results is that, in presence of naphthalene, the catalyst reaches stable working conditions that can be hold for at least 500 hours.
Fig. 5 Conversion of phenol on LaCr$_{0.5}$Ni$_{0.5}$O$_3$ catalyst

XRD analysis showed that the catalyst used for the tests was initially contained mainly by La$_2$CrO$_6$ and nickel oxide. After the tests instead XRD analysis showed that the structure is clearly perovskite. Some attempts to produce the perovskite by crystallization in air showed that a temperature higher than 800 °C is required.

In order to analyze the effect of the formation of the perovskite structure, two other tests were performed with naphthalene using respectively catalysts formed at 700 °C and at 850°C. A lower amount of catalyst (0.25g) was used leading to a GSHV close to 13000 h$^{-1}$. In this case it was possible to observe (Fig 6) that the perovskite produced at 850°C is much more rapid to reach the stationary behavior (with a lower conversion). The initial reduction of activity is probably due to the formation of the perovskite, that can form also at lower temperature because of the reducing atmosphere of the reactor. After the initial phase, the behavior of the catalysts produced at 700 and 850°C is quite close, and the lower activity of the perovskite can be explained by much lower specific area (table 1).

Fig. 6 Conversion of naphthalene on LaCr$_{0.5}$Ni$_{0.5}$O$_3$ catalyst, reactor with 0.25 g of catalyst

<table>
<thead>
<tr>
<th>Catalyst Formulation</th>
<th>Before Test</th>
<th>After Test</th>
</tr>
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<tbody>
<tr>
<td>LaFe$<em>{0.7}$Ni$</em>{0.3}$O$_3$ cryst. 700 °C</td>
<td>BET area 8.6 m$^2$/g</td>
<td>BET area 8.6 m$^2$/g</td>
</tr>
<tr>
<td>LaCr$<em>{0.5}$Ni$</em>{0.5}$O$_3$ cryst. 700 °C</td>
<td>BET area 19.7 m$^2$/g</td>
<td>BET area 19.4 m$^2$/g</td>
</tr>
<tr>
<td>LaCr$<em>{0.5}$Ni$</em>{0.5}$O$_3$ cryst. 850 °C</td>
<td>BET area 7.8 m$^2$/g</td>
<td>BET area 7.5 m$^2$/g</td>
</tr>
</tbody>
</table>

The analysis were performed on the catalyst both before and after tests, in all cases no appreciable reduction of the specific area was observed.

5. Conclusion
The activity of two different perovskite catalysts with respect to tar cracking was tested. Some organic compounds representative of tar were used: naphthalene, which is the most critical, exadecane, phenol. Some preliminary tests were performed on LaFe\textsubscript{0.7}Ni\textsubscript{0.3}O\textsubscript{3} perovskite; this catalyst showed a continuous decrease of activity when naphthalene is treated. Most of the efforts were concentrated on LaCr\textsubscript{0.5}Ni\textsubscript{0.5}O\textsubscript{3} catalyst. This catalyst seems much stable in presence of naphthalene, and the tests were continued till 500 h with stable conversion. The catalyst crystallized at 700°C is composed mainly by La\textsubscript{2}CrO\textsubscript{6} and nickel oxide, after tests the structure instead is mainly perovskite. In order to investigate the effect of such transformation, other tests were performed with catalyst produced ad 850 °C. Such high crystallization temperature allowed for a complete formation of perovskite phase. In this case it was observed a more rapid stabilization, and a lower activity, that can be explained by the lower specific area of the catalyst produced at 850 °C.

7. References


