



## Influence of the Catalyst Support on the Steam Reforming Performance of Toluene as Tar Model Compound

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The large amount of tar produced along with the syngas during biomass gasification is one of the major obstacle for the diffusion of gasifiers at industrial scale. Catalytic cracking and reforming are the most suitable processes for the transformation of tar into lighter gases. The selection of suitable catalysts is a critical step. The catalysts must own high activity and high resistance to deactivation for coke deposition. In this work the effect of two different supports, mayenite and aluminium oxide, on the activity of the nickel was investigated in the steam reforming of toluene that was used as tar model compound. In particular, the performed experimentations aimed to test the mayenite in terms of improvement of resistance to carbon deposition in conditions similar to those of gasification reactors.

The obtained results indicate that Ni /mayenite catalyst needs higher temperature to activate and leads to lower value of toluene conversion with respect to Ni / alumina. However, mayenite, which is known from literature to have higher resistance to coke deposition due to the presence of free oxygens in the lattice which oxidize the coke deposited on the catalyst surface showed higher resistance to deactivation especially for low steam to carbon ratios.

### 1. Introduction

The concerns about the climate change made biomass one of the most attractive alternatives to fossil fuel. Biomass in fact have a neutral carbon dioxide balance allowing toward its exploitation lower CO<sub>2</sub> emissions, main responsible for greenhouse effect. Its use towards traditional combustion processes is however limited due to the low energy density of biomass with respect to that of fossil fuels and to its high water content which can reach up to 40 % of the biomass weight. These aspects can cause problems to the stability of the flame in the combustion reactors. Thus, in order to make this kind of fuel more valuable, an interesting solution is to transform the solid biomass into gaseous or liquid fuels, which are easier to handle and store. Gasification is an interesting option for the production of energy from biomass. During gasification the biomass is transformed into syngas, which can be used to produce energy or as raw material for the production of chemicals.

One of the main issue that limits the diffusion of this technology is the high amount of tar produced during the gasification along with the syngas (Peres et al., 2013). Tar is a complex mixture of condensable hydrocarbons comprising single-ring to 5-ring aromatic compounds plus other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs). Due to its value of condensation temperature, ranging between 150 and 400 °C, the presence of tar can cause operative problems to the colder part of gasification plants, such as pipes and filters obstruction and reduction of the heat exchangers efficiency due to its condensation on the downstream section (de Caprariis et al., 2015). Therefore to design an efficient process for biomass gasification it is of fundamental importance avoiding the presence of tar within the syngas. Tar contains a great part of the biomass energy, in fact its amount can reach up to 20 % of the biomass weight. For this reason, one of the most interesting option for the syngas purification consists in transforming it into lighter species such as CO, H<sub>2</sub> and CH<sub>4</sub> by means of thermal cracking and catalytic reforming (de Caprariis et al., 2017a). Thermal cracking and catalytic reforming are endothermic processes that require the use of a catalyst to be performed at relatively low temperatures (about 700 °C). Generally the catalysts used in reforming

processes consist of Ni as active specie supported on  $\text{Al}_2\text{O}_3$ . The main issue related to the use of this catalyst is its deactivation due to coke deposition. To overcome this problem the development of a different support could play a crucial role in the inhibition of the deactivation. An important property which the support should have is a good oxidation behaviour towards the coke deposited on the catalyst surface. Mayenite is considered a good candidate since it owns this feature having in its lattice free oxygen atoms, which can act as oxidizer. In literature few studies on the use of mayenite in the steam reforming of tar model compounds are present (D'Orazio et al., 2013; Martavaltzi and Lemonidou, 2010); Savuto et al. (2017) synthesized the mayenite with the citrate sol-gel method and obtained good results on the steam reforming of toluene and benzene. Li et al. (2009) tested Ni/Mayenite prepared by solid mixing in the steam reforming of toluene obtaining good stability of the catalyst and good activity even at low steam to carbon ratio.

In this work mayenite and alumina were used as support for nickel in the steam reforming of toluene. The Ni/mayenite was synthesized with a very simple newly one step method starting from  $\text{Al}(\text{OH})_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The  $\text{Ni}/\text{Al}_2\text{O}_3$  was prepared by wet impregnation. The tests were performed in a fixed bed reactor with steam to carbon ratio ranging from 5, typical for steam reforming of naphtha, and 1 in order to simulate the typical conditions of a pyrolysis reactor where usually water and tar have a 1:1 ratio.

## 2. Experimental section

### 2.1 Catalyst synthesis

Mayenite and Ni/mayenite were synthesized starting from a stable dispersion of boehmite (Valentini et al., 2001). The dispersion was prepared mixing commercial aluminium hydroxide powder (Sigma) in a 0.4 % (w/w)  $\text{HNO}_3$  aqueous solution.  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were added to the boehmite dispersion. The used amount of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was determined on the basis of the stoichiometric ratio in the mayenite ( $\text{Ca}/\text{Al}$  molar ratio = 12/14) while the amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was calculated in order to produce a catalyst with 10 % by weight of nickel. The two prepared dispersions were kept under stirring for 24 h till a gel was obtained. The gels were dried overnight at 100 °C and the resultant solids were grinded and calcined at 950 °C for 12 h. The calcination temperature was chosen on the basis of TGA-DSC analysis (TA instrument) performed on the precursor Ni/mayenite gel (Figure 1) where the exothermic peak of the phase transformation is recorded at 940 °C. The obtained solid was analysed by X-ray powder diffraction (XRPD) (Philips Analytical PW1830) and by Brunauer-Emmett-Teller (BET) analysis.

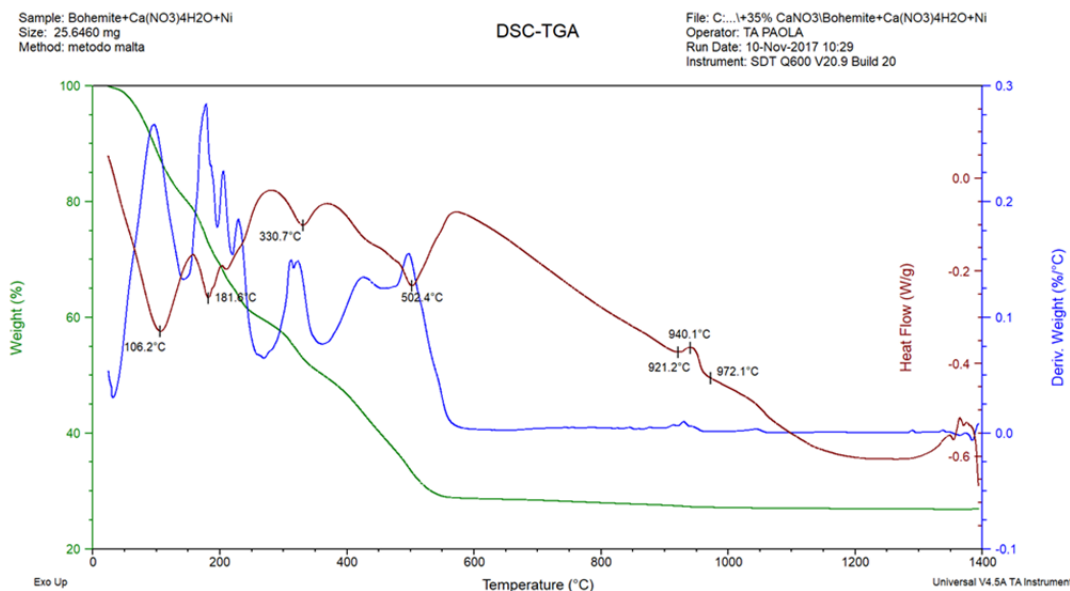


Figure 1: TG-DTG-DTA analysis of the dried gel Boehmite/ Calcium nitrate/Nichel nitrate.

The  $\text{Ni}/\text{Al}_2\text{O}_3$  catalysts was prepared by wet impregnation of commercial  $\gamma\text{-Al}_2\text{O}_3$  support ((SBET=230 m<sup>2</sup>/g, pore volume=0.66 cm<sup>3</sup>/g).  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used as precursor. The  $\text{Al}_2\text{O}_3$  was mixed with an aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , dried and then calcined at 700 °C for 6 hours. The amount of Ni was 10 % by weight of the support.

## 2.2 Experimental set-up

The laboratory set-up is composed by a stainless steel tube reactor, (id = 8 mm, h = 500 mm) equipped with an alumina frit for the formation of the catalyst bed composed by 0.1 g of catalyst diluted in 1.5 g of silicon dioxide. The reactor was heated by an external cable heater. Toluene and water were fed with two syringe pumps and passed through an evaporator before entering in the reactor. Nitrogen is used as carrier gas. The space velocity was about 25000 1/min in all the experimental tests, when the S/C ratio was decreased the total liquid flow rate was kept constant in order to have the same space velocity. The experimental set-up scheme is reported in de Caprariis et al. (2017b). The operative conditions are reported in Table 1. Time on stream tests were performed in order to investigate the resistance of the catalyst to deactivation for coke deposition for the experiments carried out with S/C 5 and 2.

Table 1: Experimental conditions used in the tests.

T (°C)	550-700
N2 flow rate (l/min)	0.25
Toluene flow rate (ml/min)	0.022-0.1
Water flow rate (ml/min)	0.12-0.13
Catalyst bed height (cm)	2
Catalyst amount (g)	0.1
S/C	1-5
GHSV (1/min)	24948

## 3. Results and discussion

### 3.1 Mayenite characterization

In Figure 2 the phases identified in mayenite and Ni-mayenite catalysts are shown. In both samples mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) was detected as the principal specie at  $2\theta$  angles of  $18.0^\circ$  and  $33.3^\circ$ , CaO ( $32.1^\circ$ ,  $53.8^\circ$ ) and  $\text{Ca}_5\text{Al}_6\text{O}_{14}$  present only in small amounts were detected at  $2\theta$  angles of  $30.5^\circ$  and  $30.9^\circ$ , respectively. The presence of CaO is probably due to segregation of the Ca during the preparation (Savuto et al., 2018), instead  $\text{Ca}_5\text{Al}_6\text{O}_{14}$ , a low temperature metastable phase in the Ca–Al–O system, is formed by CaO and  $\text{Al}_2\text{O}_3$  during calcination (Ruszek et al., 2011). The Ni-catalyst also shows the characteristic diffraction patterns of crystalline NiO ( $37.2^\circ$  and  $43.1^\circ$ ) and Ni ( $44.6^\circ$ ). The synthesized mayenite and Ni-mayenite have a body centered cubic crystal structure belonging to the I-43d (number 220) space group with  $a = 11.978 \text{ \AA}$  and  $a = 12.043 \text{ \AA}$ , respectively. The crystalline size of mayenite calculated using Scherrer's Formula on the (402) plane ( $33.3^\circ$ ) is 52.5 nm whereas the mayenite, Ni metal (111 plane at  $44.6^\circ$ ) and NiO (200 plane at  $43.1^\circ$ ) in Ni-mayenite catalyst are 125.6, 14.9 and 55.5 nm, respectively. The results obtained are in accordance with those reported in previous studies (Savuto et al., 2017).

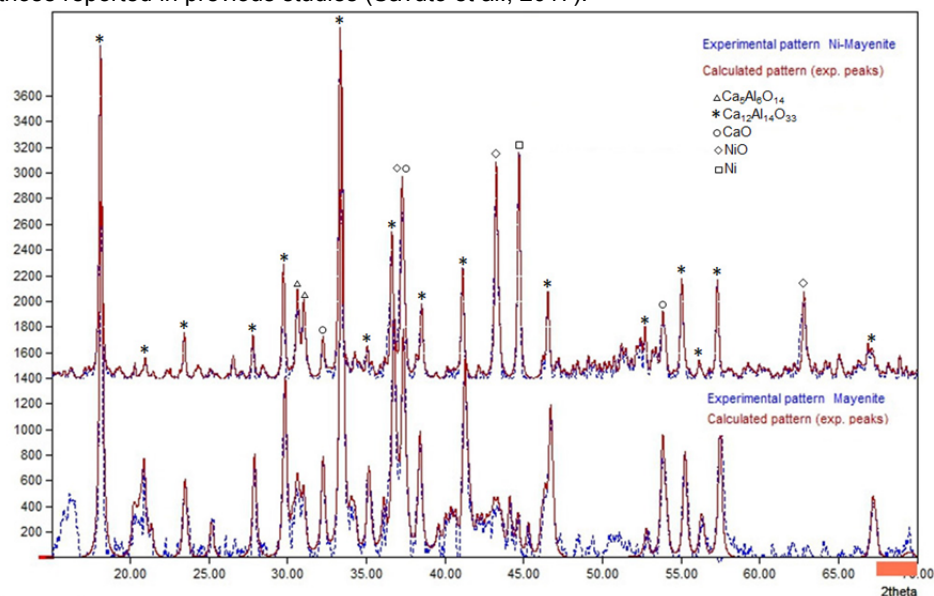


Figure 2: XRPD patterns of Mayenite and Ni-Mayenite.

The surface area of mayenite and Ni/Mayenite were measured to be 4.529 m<sup>2</sup>/g and 4.125 m<sup>2</sup>/g, respectively. As reported in literature mayenite has very low surface area especially if compared with the surface area of alumina (Martavaltzi and Lemonidou, 2010).

### 3.2 Toluene steam reforming results

In Figure 3 the results of the tests performed at different temperatures are reported. Ni/ Al<sub>2</sub>O<sub>3</sub> catalyst is more active at lower temperatures and reaches unitary conversion at 630 °C, while Ni/mayenite requires much higher temperatures to achieve the same performances of Ni/Al<sub>2</sub>O<sub>3</sub>. Unitary conversion is reached for temperatures of 750 °C.

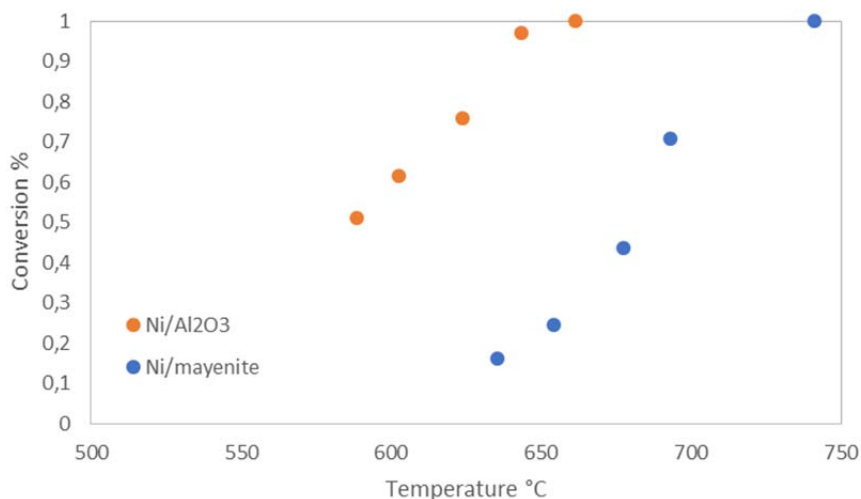


Figure 3: Toluene conversion at different temperatures for the two catalysts.

The long duration tests were performed for steam to carbon ratios 5 and 2 at a temperature of 680 °C. As shown in Figure 4, for steam to carbon ratio 5 the Ni/Al<sub>2</sub>O<sub>3</sub> begins to deactivate after the first 2 hours. At the end of the test it lost 18 % of its activity while the Ni supported on mayenite did not deactivate at all. This result confirms the higher resistance of mayenite to deactivation for coke deposition, due to the mobility of the oxygens present in its lattice which favors the oxidation of the carbon deposit on the catalyst surface.

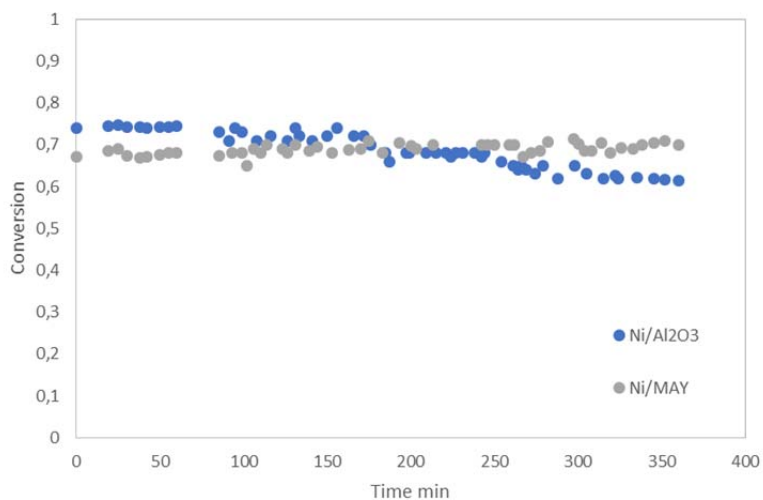


Figure 4: a) Long duration tests performed at 680 °C and S/C 5.

To investigate the catalysts performances at operative conditions similar to those achieved into real tar reforming reactors in gasification processes the steam to carbon ration was lowered, in fact in the gasifiers the S/C ratio when no steam is added is lower than 2.

The tests at different S/C ratio were performed for the Ni/Al<sub>2</sub>O<sub>3</sub> at a temperature of 630 °C and for the Ni/Mayenite at 680 °C, in order to avoid the unitary conversion of toluene when the Al<sub>2</sub>O<sub>3</sub> support was used. As expected, the catalyst activity decreases for lower steam to carbon since the reaction is less favorite (Table 2). The Ni/Al<sub>2</sub>O<sub>3</sub> shows a slightly higher activity but in accordance with the data obtained for S/C 5 during long duration tests performed at S/C 2 (Figure 5) after 2 hours a rapid deactivation occurs. Instead, the mayenite exhibits high resistance to carbon deposition even for the lower value of steam to carbon ratio.

Table 2: Results of the tests conducted at different steam to carbon.

	S/C (mol/mol)	Conversion	Gas flowrate (l/min)	vol%H <sub>2</sub>	vol%CO	vol%CO <sub>2</sub>
Ni/Al <sub>2</sub> O <sub>3</sub>	1	0.18	0.34	19.65	4.72	3.07
	2	0.35	0.34	19.11	4.55	3.51
	5	0.80	0.35	20.88	3.22	4.31
Ni/mayenite	1	0.16	0.33	16.82	4.04	2.92
	2	0.36	0.35	19.11	4.55	3.51
	5	0.77	0.35	20.92	3.87	3.36

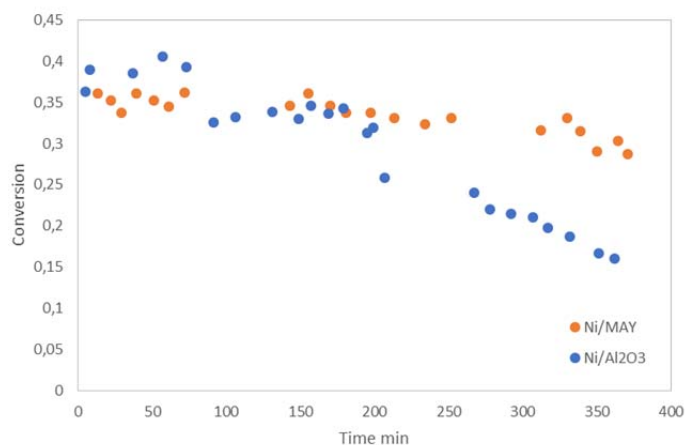


Figure 5: Long duration tests performed at 680 °C and S/C 2.

#### 4. Conclusions

In this work the effect of two different supports, mayenite and aluminium oxide, on the activity of the nickel was investigated in the steam reforming of toluene. The Ni/mayenite catalyst, synthesized with a newly and simple one step method, shows very interesting results. In fact, even if with the Ni/alumina higher toluene conversion are obtained for lower temperatures, the use of mayenite lead to higher resistance to deactivation. For S/C 5 after 6 h the loss of activity for the Ni/alumina is about 20 % and 50 % for S/C 2. In the case of Ni/mayenite for both the S/C tested the loss of activity was always less than 10 %. These features of the mayenite support could constitute very important element in the obtaining of cleaner syngas in biomass gasification plants. The mayenite was already tested for the steam reforming of tar model compounds but never with low steam to carbon ratio. In fact, when the value of the S/C is lowered below 2, the conditions of the experimental tests are similar to those obtained in the tar reforming reactors placed after the biomass gasifiers, so the resistance of the catalyst to carbon deposition in this case opens new perspectives for the solution of the presence of tar along with the syngas that is still a big challenge.

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