



Steam reforming of phenol–ethanol mixture over 5% Ni/Al₂O₃

Gabriella Garbarino^a, Vicente Sanchez Escribano^b, Elisabetta Finocchio^a, Guido Busca^{a,*}

^a Dipartimento di Ingegneria Chimica e di Processo, Università di Genova, P.le J.F. Kennedy 1, I-16129, Genova, Italy

^b Dpto. de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Salamanca, Pl. de la Merced s/n, 37008 Salamanca, Spain

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ABSTRACT

The steam reforming of 1:2 phenol–ethanol mixture (ca. 80 g_{ph+eth}/N m³ in He) as a model of biomass gasification tar, has been investigated over Ni/Al₂O₃, Ni/MgO–Al₂O₃ and Ni/ZnO–Al₂O₃ catalysts. In this paper interest is focused over a 5% Ni–Al₂O₃ catalyst, that has been characterized in the unreduced and reduced states by IR of CO adsorbed at low temperature. The steam reforming reaction of ethanol and phenol has also been studied, separately, by IR spectroscopy. In spite of its low Ni content and the absence of alkali and alkali earth ions, this catalyst is actually active in the steam reforming of both ethanol and phenol. The reaction is, however, shifted to higher temperature than with catalysts containing higher Ni-loadings and also Mg and/or Zn ions. Ethanol steam reforming occurs at lower temperature than phenol steam reforming and does not seem to be much hindered by the presence of phenol. Phenol steam reforming in the presence of ethanol starts after, but is highly selective to CO_x and H₂. At low temperature, however, alkylation of phenol mainly occurs over the 5% Ni–Al₂O₃ catalyst to give mostly o-ethylphenol. Active ethoxide, acetate and phenate species are observed on the surface.

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1. Introduction

Hydrogen is mostly produced today through steam reforming of hydrocarbons, usually natural gas [1,2], performed at 1000–1200 K. The industrial catalysts are based on Ni supported on an alumina-based carrier, usually stabilized by the presence of alkali and/or alkali earth cations.

The production of “biohydrogen”, i.e. hydrogen arising from renewables, would result in the release of the energy production from fossil fuels and, simultaneously, in the reduction of greenhouse gases emissions. Several approaches can be applied to produce biohydrogen [3]. Among them, hydrogen and syngas may be produced by biomasses through a variety of pyrolysis and gasification processes [4]. Most of these processes are hampered by the coproduction of at least 10–50 g/N m³ of tars, a mixture of heavy compounds that may result in fouling of heat exchangers and reactors. Studies report that phenol is the main component of tar after low temperature gasification [4,5]. Lighter organics are usually also present together with tars, that also act as primary source for larger molecules in biomass derived syngases. Ethanol is cited among such syngas impurities [6].

A steam reforming step is frequently considered to remove such noxious compounds. However, well established catalytic systems for biomass tar steam reforming is still lacking. Among active catalysts for this step [7], commercial methane steam reforming catalysts based on alkali-or alkali earth containing Ni/Al₂O₃ have been reported to be quite performant [8–10] and are commercially proposed by, e.g. Nextec [11] for this application. These catalysts are prone to deactivation by sulphur poisoning, coking and sintering [12], but can also be regenerated by steaming [13,14]. Noble metal catalysts, in particular Rh-based catalysts may be more active at low temperature and resistant to sulphur poisoning [15,16] but are obviously more expensive.

The steam reforming of phenol was recently investigated by Efstathiou and co-workers over natural materials [17], usually added in the gasification reactor to limit tar in the effluent, and over Rh based catalysts [18,19]. In our laboratories, a systematic investigation of tar steam reforming has been undertaken. To model tar feed we decided to mix phenol with ethanol. The addition of ethanol allows both to test a mixture of lighter and heavier compounds and to use a single tri-component liquid phase fed through a single HPLC pump into the reactor. The presence of ethanol in ethanol–phenol–water solutions allows to increase phenol-to-water mole ratio in a single liquid phase. A number of catalysts have been tested in our preliminary investigation. Here we will report results using 5% Ni/Al₂O₃ catalyst. The composition of this material, with such a low amount of nickel and the absence of alkali and alkali metals, is far from that of best catalysts. However, the use of

* Corresponding author. Tel.: +39 010 353 6024; fax: +39 010 353 6028.
E-mail address: Guido.Busca@unige.it (G. Busca).

this catalyst allowed us to apply IR spectroscopy to study reactants adsorption, to investigate effect of loading and role of uncovered support surface, and to distinguish the effects of alkali and alkali earths on the reaction from those of the main catalysts components in the reaction.

2. Experimental

2.1. Catalyst preparation

5% Ni/Al₂O₃ catalyst (40 m²/g) has been prepared by conventional wet impregnation of Siralox 1.5/40 support (alumina with 1.5% SiO₂ from Sasol) using Ni nitrate hexahydrate water solution. After impregnation, drying 363 K for 8 h and calcination at 973 K for 5 h have been performed. In the same way has been prepared, with the appropriate Ni amount a sample with 50% NiO (w/w), corresponding to 39% Ni (w/w) prepared with higher surface area alumina (170 m²/g). The preparation of Ni/MgO-Al₂O₃ and Ni/ZnO-Al₂O₃ catalysts has been reported elsewhere [20].

2.2. Catalytic tests

The catalytic experiments were carried out in a fixed-bed tubular quartz flow reactor, operating isothermally, loaded with 44 mg of catalyst mixed with 440 mg of quartz particles (both of them 60–70 mesh sieved). The catalytic test were performed feeding 80 N ml/min containing 70% He (carrier gas), 27% water, 2% ethanol and 1% phenol mol/mol, corresponding to 84 g/N m³ of ethanol+phenol, 42.9 g/N m³ of phenol. The phenol–water–ethanol single phase liquid solution was pumped through a HPLC pump (Shimadzu Corp. LC-D10 AD) in an appropriate heating section at 673 K. After vaporization it is mixed to the carrier gas and fed to the reactor. The range of the temperatures of the reactor oven was varied from 773 K to 1073 K, and the results were reported in function of the measured temperature of the catalytic bed.

Products analysis was performed with a gas-chromatograph Agilent 4890 equipped with a Varian capillary column “Molsieve 5A/Porabond Q Tandem” and TCD and FID detectors in series. Between them a nickel catalyst tube was employed to reduce CO to CH₄. A six-port valve with a 0.5 cm³ loop was used for the gas sampling of the outlet gases. The sampling of the outlet vapors was also made by injection, using a gas-tight with a nominal volume of 0.25 ml. A sampling injection point at the end of the vaporization zone allowed to analyse the reagents and to determine that the feed composition was not modified in the vaporization zone. Products analysis was also performed with a GC/MS (HP GCD plus), in order to have a precise identification of the compounds. Hydrogen was detected as a negative peak in the TCD detector signal of GC and also calculated on the basis of the C-product yields. The two measures were confirmed to be in reasonable agreement.

No catalyst pretreatments were performed. The results reported are based on reactant conversions, selectivity to carbon-containing products vs. temperature, as measured at each temperature when

apparent steady state was reached, generally in 1 h. Reactant conversion is defined as follows:

$$X_{\text{react.}} = \frac{n_{\text{react.in}} - n_{\text{react.out}}}{n_{\text{react.in}}} \quad (1)$$

while selectivity to product *i* is defined as follows:

$$S_i = \frac{n_i}{\nu_i(n_{\text{react.in}} - n_{\text{react.out}})} \quad (2)$$

where *n_i* is the moles number of compound *i*, and *ν_i* is the ratio of stoichiometric reaction coefficients. When applied to the overall carbon feed, *n_i* is the carbon moles number of compound *i*, *n_{react.}* is the carbon moles number of reactants mixture as a whole and *ν_i* = 1.

2.3. IR studies

Pressed disks of the pure catalysts powders were activated “in situ” by using an infrared cell connected to a conventional gas manipulation/outgassing ramp. The catalyst disk was first submitted to a treatment in air for 30 min, followed by evacuation at 773 K before the adsorption experiments. In order to obtain the reduced catalyst, after the mentioned evacuation, it was put into contact with H₂ ~ 400 Torr at 773 K, for 30 min, and successively outgassed at the same temperature. CO adsorption was performed at 133 K by introducing a known dose of the gas (10 Torr) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were collected using a Nicolet Nexus FT instrument, during evacuation upon warming at increasing temperatures between 133 K and 273 K.

Steam reforming studies have been performed in the IR cell by admitting controlled low pressures of the reactants at room temperature (ethanol 7 Torr + H₂O vapor 14 Torr for ethanol steam reforming, phenol 1 Torr + H₂O vapor 7 Torr for phenol steam reforming) then increasing temperature. Spectra of the gas and of the catalyst were recorded alternatively upon increasing temperature.

3. Results and discussion

3.1. Catalytic steam reforming of ethanol/phenol mixture

In Table 1 data on catalytic experiments are reported for the studied Ni-based catalysts. The data shown here refer to experiments done using the same conditions and the same furnace temperature, 873 K. The real measured bed temperature is also reported in the table.

The results show that the 5% Ni/Al₂O₃ catalyst is the least active, as expected indeed due to the lowest Ni content. With the other catalysts, more loaded with Ni, conversion at this furnace temperature approaches to unit value, with CO₂ and CO largely being the main C-containing products, together with hydrogen. Only a small amount of methane is also found with the higher Ni-loading samples. Only with the 5% Ni/Al₂O₃ catalyst several incomplete conversion products are found, such as ethylene, ethane,

Table 1

Carbon conversions and selectivities for steam reforming of ethanol–phenol mixture over different catalysts at *T* furnace = 873 K.

Catalyst	<i>T</i> furnace [K]	<i>T</i> bed [K]	C conversion	S _{CH₄}	S _{CO}	S _{CO₂}	S _{CH₂CH₂}	S _{CH₃CH₃}	S _{HCHO}	S _{CH₃CHO}	S _{CH₃COCH₃}	S _{C₆H₆}	S _(C₈+C₁₀)
Ni5%/Al ₂ O ₃ *	873	810	0.30	0.02	0.05	0.18	0.29	0.02	0.01	0.38	0.01	0.01	0.04
Ni39%/Al ₂ O ₃ *	873	804	0.98	0.04	0.37	0.55	0.02	0.01	0.00	0.00	0.00	0.01	0.00
Ni60%-MgO-Al ₂ O ₃ **	873	823	0.99	0.08	0.28	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni47%-ZnO-Al ₂ O ₃ **	873	824	0.99	0.08	0.24	0.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00

* Ni% wt with respect to the support weight.

** Ni% wt with respect to the overall catalyst weight.

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