Steam reforming of acetic acid – A major component in the volatiles formed during gasification of humin

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ABSTRACT

Acetic acid and phenols are the major components of the condensable by-products in the low temperature de-volatilisation stage of humin during gasification. Catalytic steam reforming of acetic acid using supported Ni on ceria-zirconia mixed oxide prepared via the hydrothermal route is discussed. The influence of steam reforming temperatures, steam/carbon ratios were studied. The catalyst showed high activity and good stability. Furthermore, activity improvement was achieved with multiple redox cycles as relevant to recycling the catalysts. Characterisation of the fresh and used catalyst by various techniques (e.g., LEIS, Raman spectroscopy, TPO/TPR) revealed the modification of metal-oxygen bond on the support under the steam reforming conditions. It in turn improved the oxygen mobility of the catalyst.

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1. Introduction

Lignocellulosic biomass is addressed as a sustainable alternative to fossil feedstock for transportation fuels and chemicals [1–4]. However, the bio based oils (derived via liquefaction) or chemical building blocks (synthesised via dehydration, fermentation etc.) usually have high oxygen contents. Therefore, to be green, sustainable hydrogen is mandatory in most of these biomass processes for upgrading these products. In our previous study [5], we have demonstrated the generation of hydrogen from humin, a major waste produced during the dehydration of carbohydrates for making bio-chemical platforms (viz. 2,5 hydroxy methyl furan and levulinic acid). Complete conversion of humin could be achieved with selectivity towards synthesis gas of 75% (on carbon basis). The rest of humin was mainly converted to organic volatiles during pre-heating to the gasification temperatures. In order to use the complete carbon content of humin for synthesis gas or hydrogen production, as well as cleaning the gaseous product stream, it is essential to steam reformed this volatile fraction which contains largely phenols, aromatics and acetic acid. Therefore, steam reforming of these molecules should be considered and integrated in the total gasification scheme. Supported Ni catalysts

with ceria–zirconia based support for steam reforming of phenolic fraction of the volatiles were developed and reported in our recent publication [6]. The catalyst using ceria–zirconia solid solution as support which was prepared from hydrothermal treatment preceded by co-precipitation showed most promise with the highest activity and stable selectivity to hydrogen (over 30 h time on stream). This catalyst also showed lowest amount of coke deposits. Acetic acid, on the other hand, is notorious for coke formation which is considered the main cause for catalyst deactivation in steam reforming of oxygenates. Thus, the catalyst for steam reforming of the whole volatile fraction should be active and stable for reforming of acetic, too.

Nickel based catalysts are the most widely used in petroleum industry for steam reforming of naphtha and methane. Basagiannis and Verykios reported that Ni showed the highest value of turnover frequency (TOF) among Al_2O_3 supported noble metal catalysts (e.g., Rh, Ru, Pt, Pd) [7]. In the same literature, the authors also noted that the carrier support had a strong influence on the apparent activation energies for the steam reforming reactions Acidic supports such as Al_2O_3 favour cracking and condensation reactions, thus causing the deposition of coke and deactivation of catalyst [7,8]. Addition of basic oxides (e.g., MgO, CeO_2, La_2O_3) to alumina support enhanced the coking resistance thus improving the catalytic activity, stability [7,9]. Other support materials such as ZrO_2, La_2O_3, and CeO_2 have also been used. However, despite the lower acidity in comparison with Al_2O_3, severe coke formation

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Nomenclature

AcOH	Acetic acid
LEIS	Low energy ion scattering
OSC	Oxygen storage capacity
S/C	Steam/Carbon ratio
S-CO/CO$_2$	Selectivity towards CO or CO$_2$, respectively
TOF	Turnover frequency
TPO/TPR/TPD	Temperature programmed oxidation/reduction/desorption
(R)WGS	(Reversed) Water gas shift
WHSV	Weight hourly space velocity
X-600/650/700	Conversion of acetic acid at 600 °C, 650 °C and 700 °C, respectively
XPS	X-ray photoemission spectroscopy
XRF	X-ray fluorescence
Y-Acetone/CO/CO$_2$/H$_2$	Yield of Acetone, CO, CO$_2$ or H$_2$, respectively
TOS	Time on stream

was also observed [10–13] with ZrO$_2$. Matas Güell et al. reported that the Pt catalyst using CeO$_2$ support is more stable than that using ZrO$_2$. This improvement was explained by the facile redox properties of CeO$_2$ which can help the oxidation of coke deposits with water. In addition, the oxygen storage capacity, one of the important variables for the redox properties of CeO$_2$, can be further increased by doping other elements such as Zr, Tb, Gd [14,15]. Catalytic activity, redox properties of ceria is enhanced when it is incorporated with Zr. Research about ceria–zirconia supports for hydrogen production from alkanes and oxygenates were recently reviewed by Nahar and Dupont which shows the strong influence of preparation methods on texture, OSC and redox properties of the catalyst thus catalytic activity for steam reforming [15]. Furthermore, reductive/oxidative pre-treatment can also modify the redox properties of ceria–zirconia [16–18] and steam reforming conditions also include reductive/oxidative conditions. In this paper, we studied the performance of Ni supported on ceria-zirconia prepared via hydrothermal route since it showed best activity and stability in steam reforming of m-cresol. In addition, influence of reductive/oxidative treatments (either during the steam reforming or recycling of the catalysts) on its catalytic properties was also investigated.

2. Experimental
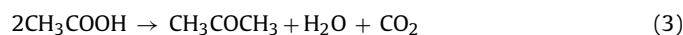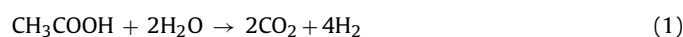
2.1. Catalyst preparation

All the chemicals used in this research are analytical grades purchased from Sigma–Aldrich. Ceria–zirconia oxide support was prepared *via* co-precipitation of Ce(NO$_3$)$_3$·6H$_2$O and ZrO(NO$_3$)$_2$·xH$_2$O with ammonia followed by hydrothermal treatment in 40 wt.% KOH for 24 h. The support was calcined in air at 800 °C for 6 h prior to deposition of Ni via homogeneous deposition precipitation of Ni(NO$_3$)$_2$·6H$_2$O with urea. The supported Ni catalyst was then calcined in air at 500 °C, reduced subsequently in 10 vol.% H$_2$/N$_2$ at 650 °C for 1 h. Hereby the catalyst is denoted as Ni/HT. In all thermal treatment steps, the total gas flow of 50 cm^3/min and ramping temperature rate of 5 °C/min was used. Details of catalyst synthesis were described elsewhere [6,19].

2.2. Catalytic performance

The catalytic experiments were carried out in an α-alumina fix bed reactor (internal diameter of 4 mm) at atmospheric pressure. The catalyst powder was pressed, crushed and sieved to sizes between 0.3–0.6 mm. The catalytic bed was held in place by two quartz wool plugs. Typically, the catalyst was reduced in situ with 50 cm^3/min flow of 10 vol.% H$_2$/Argon at 650 °C for 1 h, then purged under the flow of Ar for 30 min before the furnace was set to gasification temperatures (600–700 °C). Aqueous acetic acid solutions were delivered to an evaporator heated to 145 °C by a syringe pump (ISCO Model 500 D). Details are summarised in Table 1. In all cases, the weight hourly space velocities of acetic acid (WHSV) were similar i.e., 25.2 h^{-1}. In the case of using recycled catalyst, each steam reforming run was separated by regeneration step in which the catalyst (from the previous cycle, in the same reactor) was oxidised in 20 vol.% air/Ar (total flow-rate 30 cm^3/min) at 650 °C for 90 min then cooled down to room temperature before used in the next experiment according to the procedure mentioned above. A heating/cooling rate of 10 °C/min was used in all the ramping temperature steps. Ar was also used as internal standard gas for determination of total gas evolving during the steam reforming. Gas outlet stream from the reactor was cooled and separated using a flash condenser cooled by continuous water stream at 15 °C. Gas composition was analysed by an online Varian CP-3800 gas chromatograph. The liquid from the flash condenser was collected every 30 min intervals for the first 2 h TOS and then with the frequency of every 1–2 h. Composition of the condensed phase from the reactor was analysed using a Shimadzu HPLC system with an Animex HPX-87H column and a Refractive Index detector (RID-10D). Mobile phase of H$_2$SO$_4$ (0.005 M, 0.6 mL/min) was used for the separation. The column oven was maintained at 35 °C. It took typically 25 minutes for each analysis.

Reaction equations and calculations for conversion, selectivities and yields are given below.

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \tag{1}$$

$$CH_3COOH \rightarrow 2H_2 + 2CO \tag{2}$$

$$2CH_3COOH \rightarrow CH_3COCH_3 + H_2O + CO_2 \tag{3}$$

The yield and selectivity gas products were estimated on carbon basis (except for H$_2$) and from the equations, below:

$$Conversion(\%) = 100\% \times \frac{n_{AcOHc}}{n_{AcOHf}} = 100\% \times \frac{n_{AcOHf} - n_{AcOHu}}{n_{AcOHf}}$$

$$Yield\ of\ H_2(\%) = 100\% \times \frac{moles\ of\ hydrogen\ produced}{4 \times moles\ of\ acetic\ acid\ feed}$$

$$Yield\ of\ CO/CO_2/CH_4(\%) = 100\% \times \frac{moles\ of\ CO/CO_2/CH_4\ produced}{2 \times moles\ of\ acetic\ acid\ feed}$$

$$Yield\ of\ acetone(\%) = 100\% \times \frac{3 \times moles\ of\ acetone\ produced}{2 \times moles\ of\ acetic\ acid\ feed}$$

Selectivit to CO/CO$_2$/CH$_4$(%)

$$= 100\% \times \frac{moles\ of\ CO/CO_2/CH_4\ produced}{2 \times moles\ of\ acetic\ acid\ converted}$$

Where n_{AcOHf}, n_{AcOHc} and n_{AcOHu} are the moles of acetic acid that was fed to the reactor, converted and unconverted during the reforming, respectively. The amounts of unconverted acetic acid was calculated from HPLC data with the assumption that negligible amount of acetic acid vapour in the gas stream to GC. Thus, condensed liquid volume is theoretically calculated based on the feed concentration and water consumed in Eq. (1). Carbon balance of 97 ± 3% was achieved in all experiments if not specifically mentioned.