**Kinetic analysis of the steam reforming of biomass derived oxygenates over Ni and Rh catalysts: Investigation of support effects**

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**Highlights**

* Steam independent kinetic pathways over oxide supports for ethanol reforming
* Sepiolite’s structure memory-effects revealed to influence rate determining step
* Rh shows an optimal performance in the steam reforming of phenolic compounds

**1. Introduction**

The steam reforming of oxygenates originating from biomass pyrolysis has received wide research attention in relation to the sustainable production of H2. Bio-oil produced from biomass pyrolysis comprises of a complex mixture of organic compounds. Research to date has focused on reforming of model compounds of the aqueous phase of bio-oil, such as acetic acid, however much less work has been carried out in relation to lignin-derived aromatic compounds. In the current work, an extensive kinetic study of ethanol, phenol and hydroquinone reforming is presented over single metal (Ni and Rh) and bimetallic (Ni-Co) catalysts. Various supports, ranging from SiO2 and γ-Al2O3, to mixed oxides of CeO2, ZrO2 and La2O3, to natural sepiolite, are utilized to probe support effects on the kinetic mechanism in combination with the active metal chosen.

**2. Methods**

The kinetic analysis was carried out using a fully automated reaction system by PID Eng & Tech (Micro Activity-effy unit). An HPLC pump (Gilson 307) was used to feed the water/organics mixture, the latter evaporated and mixed with N2 prior reaching the catalyst bed. A stainless steel (SS316) fixed bed reactor (9.1 mm i.d, total length 304.8 mm) was used heated by a single-zone furnace. The gases were analyzed in an HP5890 GC equipped with a TCD detector and MS-5A and HS-T columns, while the liquids were analyzed in a Thermo Scientific TRACE 1300 GC using an FID detector and a WAXMS A column. Catalysts were prepared via wet impregnation.

**3. Results and discussion**

Concerning ethanol steam reforming, the effect of temperature for both Ni and Rh revealed dehydrogenation and decomposition reactions to be dominant at lower temperatures whereas higher temperatures promoted reforming and water gas shift reactions. Ni catalysts supported on SiO2 and sepiolite showed a high methane selectivity at lower temperatures suggesting a metal-depended reaction pathway due to Ni’s known methanation activity at these conditions [1]. On Rh no methane was detected, with the metal effectively promoting the dehydrogenation pathways of CHx groups [2]. Identification of primary and secondary products on Ni catalysts revealed at lower temperatures acetaldehyde as a primary product, originating from ethanol dehydrogenation, with CH4 and CO being secondary products, emerging from acetaldehyde’s decomposition, and CO2 from the water gas shift reaction primarily and acetate species decomposition to a smaller degree.

Strong support effects were observed in terms of the reaction pathway for ethanol reforming. A particularly low methane selectivity was observed over the CeO2-ZrO2-La2O3 mixed oxide supported catalysts, attributed to known activity of CeO2 to form surface and bulk oxygen vacancies than can be replenished by water from the feed, hindering the development of CHx to CH4 and contributing to the elimination of the deposited carbon [3]. Interestingly, the catalyst supported on natural sepiolite exhibited a positive reaction order to water and negative to ethanol, in contrast to the rest of the supports. The calcination temperature of this catalyst was further revealed to have a critical impact on the reaction network, attributed to the memory-effect the structure of sepiolite exhibits when the mineral has not been exposed to temperatures higher than 530oC. Water preferentially adsorbs in sepiolite’s structural channels, replacing the absent water and unfolding its structure, but also restricting the transfer of water from the support to the metal [4], resulting in steam activation being the rate determine step at low temperatures (Figure 1a). The lack of water derived species on the metal potentially further leads to a surface saturation by ethanol derived species explaining the negative order observed on ethanol (Figure 1b). Increasing the calcination temperature to 550oC (Figure 1c) or the reaction temperature to 500oC (Figure 1d) leads to the permanent collapse of sepiolite’s structure, inhibiting water from entering its channels and facilitating the transfer of water to the metal for the promotion of the reforming reactions [5].



**Figure 1.** Partial reaction orders of ethanol steam reforming over Ni/SiO2 and Ni/Sepiolite at 400oC (P = 0.9 bar, Vtot = 160 cm3 min-1) for (a) water and (b) ethanol. Partial reaction orders of ethanol steam reforming for water and ethanol at (c) 400oC on pre-treated Ni/Sepiolite catalyst at 550oC and (d) 500oC over untreated Ni/Sepiolite.

Reforming of phenol and hydroquinone, over Rh and Ni-Co catalysts supported on γ-Al2O3, revealed the effective conversion of the aromatic compounds to H2 and COx at high temperatures (>500oC) and H2O/C ratios (>8). Ongoing work at low temperatures focuses on liquid products analysis to elucidate the mechanistic pathways of these compounds.

**4. Conclusions**

The steam reforming reaction pathways of different classes of biomass derived oxygenates over a wide range of conditions and catalysts were investigated. For ethanol, the production of acetaldehyde is strongly related to the operating temperature. Ni promotes methanation reactions while Rh favors dehydrogenation reactions. On all oxide supports a steam-independent pathway is observed. Unique support effects are observed with sepiolite related to the interaction of water with the internal channels of the clay, restricting water from transferring to the metal and resulting on a steam-dependent kinetic mechanism. Current work extends the study to aromatic compounds.

**References**

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