**Sustainable hydrogen via catalytic steam reforming of model oxygenate compounds present in bio-oil**

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**Background and aim:** Currently, there is tremendous interest in the use of hydrogen as a clean fuel, especially for power generation with fuel cells. Sustainable sources for hydrogen, *e.g.*, biomass, is key for a CO\(_2\) neutral energy supply. Recent developments in flash pyrolysis technologies make it possible to convert lignocellulosic biomass efficiently to a bio-oil which is easier for handling and transport [1]. The bio-oil so generated contains a variety of aliphatic and aromatic oxygenates (aldehydes, ketones, acids, alcohols).

The most promising catalytic option to generate hydrogen from bio-oil is *via* catalytic steam reforming followed by water gas shift reaction, since these reaction steps maximise the hydrogen yield. Attempts to produce hydrogen from bio-oil have been hindered by severe deactivation of catalysts due to coke/oligomer deposition [2]. In this study, Pt/ZrO\(_2\) was investigated since earlier work [3] has shown excellent activity and stability for Pt/ZrO\(_2\) under conditions favourable for coke formation, *e.g.*, during CO\(_2\) reforming of natural gas.

Bio-oil is a complex mixture of oxygenates. Thus, establishment of structure activity correlations demands the use of model oxygenate components. Acetic acid (HAc) is one of the major components of bio-oil. This study pertains to the steam reforming of HAc over a Pt/ZrO\(_2\) catalyst. The purpose of this study is to elucidate the reaction and deactivation mechanisms and order to provide a knowledge base for the design of active and stable catalysts.

**Experimental:** The 0.5 wt% Pt/ZrO\(_2\) catalyst used in the study was made by wet impregnation [3]. The catalyst was reduced *in situ* in hydrogen at 925 K before use. Steam reforming of HAc, was carried out between 725-975 K in a fixed bed reactor, with a steam to carbon ratio of 5. Infrared spectra were recorded *in situ* in a vacuum IR cell (Bruker) at 725 K.

**Results and discussions :** Fig. 1 shows conversions and yields obtained during steam reforming of HAc over Pt/ZrO\(_2\) at conversion at GHSV = 40000 h\(^{-1}\)) for 3 hours. Products observed were H\(_2\), CO\(_2\) and CO and hydrogen yield was at equilibrium. The catalyst deactivated rapidly causing a sharp drop in conversion after 3 hours time on stream. H\(_2\) and CO\(_2\) yields decreased correspondingly, but the CO yield remained constant. Interestingly, acetone was observed as deactivation set in. The catalyst could be regenerated with oxygen at 925 K, indicating that the deactivation was caused by

Fig. 1. Time on stream of acetic acid steam reforming over Pt/ZrO\(_2\) at 873 K. Steam/Carbon = 5, GHSV = 40000 h\(^{-1}\).
carbonaceous deposits which blocked active sites.

Over ZrO₂, acetone and CO₂ were the main products. These are formed via the ketonization reaction (2CH₃COOH → CH₃COCH₃ + CO₂ + H₂O). H₂ was formed only in smaller amounts. Pt black (without support) showed negligible steam reforming activity. These results indicate that Pt and ZrO₂ both are essential for the steam reforming of HAc. This is in agreement with the bi-functional mechanism proposed for steam reforming of methane, where methane is activated on the metal and water on the support, the reaction occurring at the metal support boundary [3].

*In situ* IR spectra recorded over Pt/ZrO₂ are shown in Fig 2. In the presence of HAc and water (Fig. 2a) characteristic peaks for CO adsorbed on Pt (linear 2060 cm⁻¹, bridged 1873 cm⁻¹) were observed. This confirms the production of CO in the *in situ* experiment. Additionally bands due to oxygenates (acetate, carbonate) derived from acetic acid (1541, 1426 and 1405 cm⁻¹) were also seen. Acetic acid is known to undergo ketonisation to acetone [4], followed by condensation of acetone to diacetone alcohol, mesityl oxide and possibly further oligomerisation [5] (CH₃COOH → CH₃COCH₃ → (CH₃)₂C=CHCOCH₃ → coke/oligomers). Sorption of acetone as well as mesityl oxide at 725 K resulted in similar bands in the 1300 to 1600 cm⁻¹ region, suggesting such transformations might be occurring during steam reforming of HAc.

During kinetic experiments for the steam reforming of HAc at 725K, the catalyst deactivated rapidly (< 30 min). When acetone was used as reactant, the deactivation was even more rapid. As discussed earlier, acetone can yield products such as mesityl oxide or coke which can deactivate the catalyst. Thus, we contacted Pt/ZrO₂ with mesityl oxide during an *in situ* i.r experiment to simulate deactivation. After pre-exposure to mesityl oxide, *in situ* IR spectra were recorded with HAc and water (Fig. 2b). The spectra showed similar oxygenate peaks on the support but the CO peak was very weak. However, when CO was introduced in the gas phase, the intensity of the peak for CO significantly increased (Fig 2c). This indicates that the Pt surface is not blocked completely. Thus the formed oxygenates/oligomers might be blocking the support-metal boundary responsible for the reforming as expected from a bifunctional mechanism.

Ketonisation/condensation reactions are catalysed by the acid base properties of the support oxides. Thus the design of a stable catalyst has to take this into account, and at the same time enhance the steam reforming capacity to gasify the products of the condensation/oligomerisation reactions.

References