

Hydrogen from sustainable feedstocks – Design of stable catalysts for the steam reforming of model oxygenates

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Introduction

Hydrogen as an energy carrier attracts tremendous interest for the future. Biomass has recently drawn attention as a renewable hydrogen source from the context of CO₂ emissions.

Flash pyrolysis of lignocellulosic biomass results in liquid bio-oil, a convenient feedstock for further processing, including H₂ production. Catalytic steam reforming of bio-oil followed by water gas-shift maximizes hydrogen yield. Bio oil is a complex mixture of aliphatic and aromatic oxygenates. Therefore, catalyst design principles are established based on kinetic and mechanistic studies on specific oxygenates.

In earlier studies [1] we have shown that Pt/ZrO₂ shows excellent activity for steam reforming of acetic acid, a typical oxygenate present in bio oil, but suffers from rapid deactivation due to coking. Both Pt and ZrO₂ have been shown by us [1, 2] to have catalytic functions, Pt for the activation of acetic acid and ZrO₂ for water. Thus, the catalyst is bifunctional and catalysis occurs at metal support interphase. Therefore, the oxide support is also key in the design of stable catalysts by minimizing coke accumulation. In this manuscript, minimization of coke by using oxide support (ceria) with redox properties and using water and/or traces of oxygen as oxidant for coke removal is discussed.

Materials and Methods

Catalysts were prepared by wet impregnation of H₂PtCl₆ on commercial grade ZrO₂ and CeO₂. Final catalysts were characterized by: H₂ chemisorption, X-ray fluorescence spectroscopy (XRF) and temperature programmed reduction (TPR). Catalytic tests were carried out in a fixed bed reactor. The extent of coking was determined by temperature program oxidation (TPO). MALDI-TOF characterization of deactivated catalysts was employed to establish the nature of coke.

Results and Discussion

Fig 1 shows that the steam reforming activity of Pt/ZrO₂ was rapidly lost. We have shown that acetone formed during reaction is the precursor for carbonaceous deposits [3]. Condensation/oligomerization reaction of acetone leads to most of the coke observed. The catalyst lifetime could be extended, but only to a limited extent, by adding traces of O₂ in the reaction feed. Stability was achieved by *in situ* coke combustion; and interestingly, product H₂ combustion was minimal. Temperature programmed oxidation (TPO) of the spent catalysts reveals lower amounts of coke deposits on Pt/ZrO₂ in the presence of oxygen, in agreement with the catalytic results.

Steam reforming of AcOH over Pt/CeO₂ resulted in longer catalyst lifetime as compared to Pt/ZrO₂. TPO results show that lower extent of coke deposits were accumulated on the former. The stability of Pt/CeO₂ was excellent with the addition of O₂ to AcOH/H₂O mixture and no acetone neither deactivation were observed during the whole experiment (>10 h)

Superior steam reforming performance of Pt/CeO₂ in combination with the presence of oxygen and the redox characteristics of CeO₂ makes it possible to (i) combust/ reform coke or coke precursors to a much better extent than on Pt/ZrO₂ and (ii) extend catalyst life.

MALDI-TOF spectra for coke formed in the presence and absence of oxygen are shown in Fig 2. These spectra indicate that in the presence of oxygen, lower molecular weight (MW) carbonaceous species are present. This suggests that oxygen limits the extent of coke growth. Such smaller MW coke species (precursors) can be expected to be more reactive. Therefore we propose that the combination of oxygen addition and the redox potential of CeO₂ is key to justify the excellent catalytic stability of Pt/CeO₂.

Significance

Pt/CeO₂ catalyst shows promise for the steam gasification of more complex biomass-derived oxygenates. Selective, *in situ*, combustion of coke/coke precursors (high H₂ yields maintained) makes it possible to apply it for gasification of bio oil to hydrogen.

Figure 1. H₂ and acetone yields vs. time on stream for the steam reforming of AcOH over Pt/ZrO₂ (left) and Pt/CeO₂ (right) in the presence (closed symbols) and absence (empty symbols) of oxygen. (■,□) H₂ yield, (●,○) acetone yield,

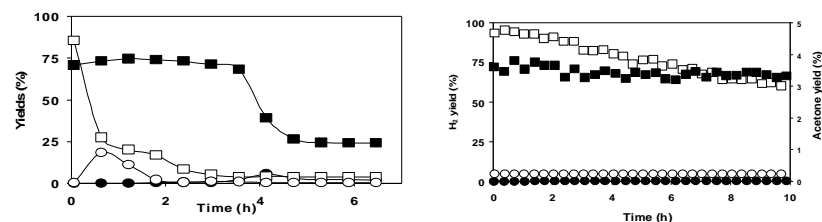
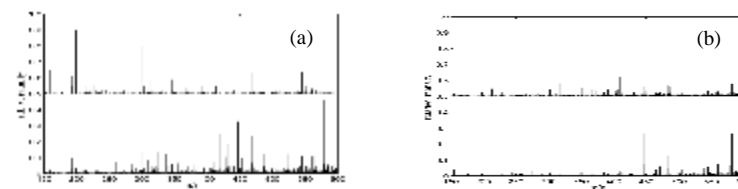


Figure 2. MALDI-TOF mass spectra of carbon deposited on (a) Pt/ZrO₂ and (b) Pt/CeO₂ during the steam reforming of AcOH in the presence (above) and absence (below) of oxygen.



References

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