HYDROTERMALLY STABLE CATALYSTS FOR THE REMOVAL OF EMISSIONS FROM SMALL-SCALE BIOFUEL COMBUSTION SYSTEMS

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Abstract
Catalytic oxidation of model pollutants, simulating the emissions from small-scale biofuel combustion systems, was studied over different fresh, aged and sulfur poisoned Pd-MeO\textsubscript{y}-alumina (Me = Ni, Ce and La) catalysts. Release of chlorine and restructuring of PdO particles was believed to cause activation of the Pd-MeO supported catalysts.

Keywords Catalytic combustion, palladium, hydrothermal ageing, sulfur

INTRODUCTION
In Europe and particularly in the Nordic countries biofuels are readily available from forestry and agro products and are used both for energy generation and leisure. The use of biofuels is also attractive both due to economical as well as environmental considerations since its combustion does not affect the CO\textsubscript{2} balance [1]. However, high emissions of CO, light hydrocarbons such as methane and ethene as well as poly-aromatic hydrocarbons are associated with combustion systems operating with biofuels. The Comité Européen de Normalisation has suggested an emission standard of 2500, 100 and 150 mg/Nm\textsuperscript{3} for CO, hydrocarbons and particulates from boilers and wood stoves, for fuel supplies of 50-150 kW [2]. The present study is focused on catalytic removal of common emissions from small-scale (30-35 kW) combustion of biofuels.
EXPERIMENTAL

A series of Pd- and Pd-MeO/alumina catalysts (Me = Ni, Ce and La) with varying metal loading was prepared. The Pd-, Pd-Ce- and Pd-La-catalysts were prepared by consecutive impregnation and intermediate calcination of γ-alumina (LaRoche, Versal GL-25), with solutions of Pd-chloride, Ce-nitrate and La-nitrate of high purity. Nickel was deposited on pre-calcined γ-alumina by controlled precipitation. A Pd/Al₂O₃ reference catalyst was prepared by the incipient wetness method of a pre-calcined support using Pd-nitrate salt. Both fresh and pre-calcined (8 h at 900 °C) γ-alumina supports were used.

The impregnated catalysts were dried at 80°C in air for 12 h and calcined at 550°C for 3 h. The Pd-Ce/Al₂O₃ catalyst was also applied on a 400 cpsi cordierite (NGK) monolith by washcoating technique.

The catalysts were tested both as powders (250 – 500 μm) and monoliths in conversion of gas mixtures simulating the emissions from wood burning stoves at GHSV = 20 000 h⁻¹ (total flow = 2100 mL/min). The gas mixture contained 200 ppm CH₄, 50 ppm naphthalene (model polyaromatic hydrocarbon), 2500 ppm CO, 10 vol% O₂, 12 vol% CO₂, 12 vol% water vapor and balance nitrogen was used. The catalytic activity of the different materials was tested in four test cycles including fresh tests and tests following ageing with reactant flow (800°C, 6 h), hydrothermal treatment (850°C, 12 vol.% H₂O, 16 h) and sulfur poisoning (5 ppm in the feed). Flue gas concentrations were measured by a HP-5890 GC equipped with FID and 30 m DB1 column and an NDIR gas analyzer. The catalysts were characterized by XRF, XRD, XPS, N₂- physisorption, H₂-chemisorption and O₂ and SO₂ TPD.

RESULTS AND DISCUSSION

The results from the catalyst testing for some of the catalysts are given in Table 1. As shown in the table, the catalysts exhibited high activities in conversion of model pollutants. The ageing of the fresh Pd-MeO/Al₂O₃ catalysts prepared from the Pd-chloride precursor resulted mostly in improved catalytic activities in terms of light-off temperatures, especially in CH₄ oxidation. The Pd-Ce/Al₂O₃ catalysts prepared from the non-precalcined support, as fresh, exhibited similar activities to their corresponding catalysts prepared from the pre-calcined support. However, when hydrothermally aged, decreased low-temperature activities in methane oxidation was observed.

The hydrothermal ageing of the alumina supported catalysts was found to result in decreased BET surface area (Table 2) as well as decreased dispersion and increased mean Pd-particle size. The XRD pattern of both pre-calcined and hydrothermally aged catalyst indicates beside the γ-phase the presence of δ- and to a lesser extent α-phase of alumina.