Challenges and recent developments for emission control on stationary biomass combustion devices for energy production

René Bindig^{1*}, Saad Butt¹, Daniel Dvoracek², Dirk Enke², Ingo Hartmann¹

DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH, Leipzig, Saxony 04347

Germany

²Universität Leipzig, Institut für Technische Chemie, Leipzig, Saxony 04103 Germany *corresponding author: rene.bindig@dbfz.de

Introduction

The energetic use of biomass becomes more and more important. Typically it is coupled to a burning process, which has to be adapted depending on the type of biomass. Often, primary measures are not sufficient to meet emission limits; especially those which will be tightened in 2015 in USA as well as in Germany. Catalytic treatment is considered to be economically feasible to satisfy the emission limits. The catalytic treatment has to be adapted to the corresponding burning process. The focus of this presentation is set on the following two cases.

For the heat production using wood log stoves with an integrated catalyst, a system is needed with a high thermal stability and sufficient high activity towards total oxidation of hydrocarbons and carbon monoxide at temperatures above 770 K. These requirements are met by mixed metal oxide catalysts synthesized through a new route called Reactive Surface Solid Activation (RSSA-Synthesis). Spinel-type oxides based on Nickel, Manganese, Iron, Chromium and Cobalt showed promising results for total oxidation of Methane and Propane.

For the catalytic after treatment of flue gases from biogas driven CHP units for power and heat production, catalysts with high activity towards total oxidation of hydrocarbons (formaldehyde/methane) at low temperatures, i.e. < 720 K, are required. This leads to the use of catalysts based on noble metals.

The challenges regarding catalyst development and application for both cases are presented.

Materials and Methods

For the development of catalysts for application in novel wood log stoves, various spinel-type mixed metal oxides, e.g. $MnFe_2O_4$ and $NiFe_2O_4$, were synthesized by different methods and tested for their ability to oxidize propane in concentrations similar to that in corresponding exhaust gases [1, 2, 3]. The experiments were run in a fixed bed continuous-flow reactor. They were conducted at a propane concentration of 1500 ppm, 370 - 870 K, and a $GHSV = 100,000 \ h^{-1}$. On a suitable substrate, these catalysts were incorporated into a novel wood log stove with down-draught combustion.

The approach to the second application, i.e. biogas driven CHP units, was the development of catalysts for total oxidation of methane below 720 K. The development was assisted by a high throughput technology. Preliminary investigations with commercially available standard catalysts were conducted to gain knowledge, concerning the reasons for the deactivation.

Results and Discussion

The synthesized $MnFe_2O_4$ and $NiFe_2O_4$ spinels showed high activities towards the total oxidation of propane and thus, make them promising for the use under temperature conditions within wood log stoves as shown in the **Table 1**.

The next step was to integrate them in a wood log stove. In this regard, the relevant approaches are going to be discussed.

Table 1	Propage	conversions of	selected	samples in	1500 nnmy	in a	ir (GHSV =	: 100 000 h	1)·

Mixed metal oxide	T _{cat} [K]	C ₃ H ₈ conversion [%]	Synthesis route
MnFe ₂ O ₄	834	98.4	Solid reaction
NiFe ₂ O ₄	836	78.4	Co precipitation
$MgFe_2O_4$	846	77.8	Sol-gel
MnMn ₂ O ₄	577	99.0	Co precipitation

Standard catalysts for the oxidation of methane lose their activity quite fast when used in CHP units. Usual methods to regenerate catalysts were not effective in this case, as can be seen in the **Figure 1**. This has to be considered for the development of new catalysts.

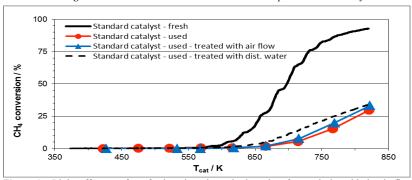


Figure 1. Light-off curves for a fresh and used standard catalyst for catalytic oxidation in flue gases tested at GHSV = $100,000 \ h^{-1}$ (gas composition for testing: $12 \ Vol.-\% \ CO_2$; $12 \ Vol.-\% \ H_2O$; $9 \ Vol.-\% \ O_2$; $2500 \ ppmv \ CH_4$; $600 \ ppmv \ CO$; $120 \ ppmv \ NO$; $N_2 = balance$)

Significance

With respect to the aforementioned results, it can be concluded that the thermal stability, promising oxidation activity and cost effectiveness make mixed metal oxide catalysts a potential candidate to replace the existing dominant trend of noble metals in catalytic converters for domestic fireplaces.

Moreover, as methane is considered to be a harmful greenhouse gas, necessary steps should be taken to reduce the methane emissions in CHP units.

References

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