Influence of the preparation method on the hydrothermal stability and sulfur poisoning resistance of Mn-and Fe-based CO oxidation catalysts

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Introduction

Pt and Pd-based catalysts are presently used as the most active and thermally stable diesel oxidation catalyst (DOC) formulations. Apart from oxidation of hydrocarbons and carbon monoxide (CO) in a O_2 rich exhaust gas and they also contribute to the abatement of soot [1]. Nevertheless, due to their high and still increasing costs alternatives such as non-noble transition metal oxides are increasingly considered [2, 3, 4] .

Among a good performance, a crucial point in the design of catalysts is the understanding of potential deactivation behavior [5,]. Basically, a number of critical conditions were identified for deactivation, e.g. high temperature, presence of H_2O or low temperature SO_x adsorption[6]. We have recently reported the promising CO- and NO-oxidation activity of Fe- and especially Mn-based catalysts [7] prepared by flame spray pyrolysis (FSP) and incipient wetness impregnation (IWI). The objective of this study was to systematically investigate the effect of hydrothermal ageing and SO_2 poisoning of Al_2O_3-supported manganese catalysts. For this purpose the samples prepared by the two different methods (FSP and IWI) were coated on cordierite honeycomb monoliths. CO oxidation was taken as a test reaction relevant for automotive pollution control. Hydro-thermal deactivation and the resistance toward SO_2 poisoning were additionally studied on powder catalysts. For comparison, analogous studies have been performed on Fe-based catalysts.

Materials and Methods

The monoliths coated with the 20 wt.% as well as the pure Mn samples have been used for hydrothermal ageing at 750°C in 10 vol.% H_2O, 10 vol.% O_2 and N_2. The flow was kept at 1 l/min corresponds to a GHSV of 20,000 h^{-1}. This procedure was repeated for ageing of 2h, 4 h and 6 h.The SO_2 poisoning was performed for the 10 wt.% Mn/Al_2O_3 IWI and 20 wt.% Mn/Al_2O_3 FSP catalysts. For this purpose the coated honeycombs were exposed for 1.5 h at 150°C to a feed of 1L/min 10 ppm SO_2, 10 vol.% O_2, using N_2 as balance. The resulting poisoned catalysts have been tested before and after thermal regeneration by heating them at 400°C and 700°C in 10 vol.% O_2/N_2.

Table 1. BET surface area of of the fresh and hydrothermally aged 20 wt.% Me /Al_2O_3 catalyst. *after ageing at 750°C in 10 vol.% H_2O, 10 vol.% O_2 and N_2

Catalyst [wt.%]	method			
	IWI		FSP	
	S_{BET} [m^2/g]	S_{BET} [m^2/g]*	S_{BET} [m^2/g]	S_{BET} [m^2/g]*
20Mn/Al_2O_3	139	95	161	141

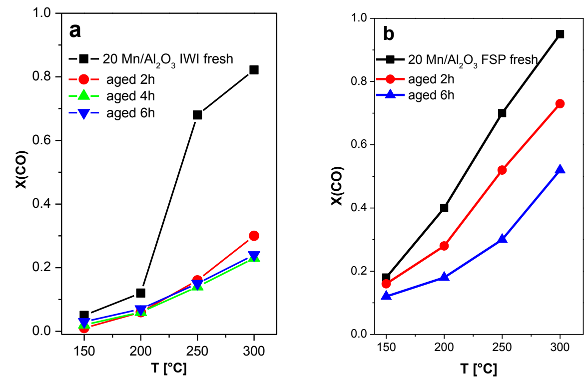

Fig. 1. CO conversion of fresh and aged 20 wt.% Mn/Al_2O_3 monolith catalysts prepared by (a) IWI and (b) FSP methods.

Results

Fig.1 demonstrates a loss of activity for supported catalysts coated on the monoliths during the hydrothermal ageing. This is especially pronounced for the IWI prepared samples, i.e. the catalytic activity drops after 2 h at 300°C from 80% to 30%, while only a small activity decrease from 95% to 70% was observed for the corresponding FSP catalyst. Alumina seems (unsupported catalysts are not shown) to stabilize the active site and protect early deactivation of the catalyst. The loss of BET surface area (Table 1) of the support probably occurs due to agglomeration, which is especially pronounced for the IWI sample. All investigated catalyst showed phase transitions after ageing to more reduced manganese oxides. A decrease of catalytic activity at low-temperature was observed after sulfur poisoning for both 20 Mn/Al_2O_3 prepared by IWI and FSP catalysts. The deactivation takes place due to formation of $MnSO_4$, which could be decomposed by heating up in the oxygen atmosphere and in the case of the FSP sample almost the same activity as in the beginning could be regained.

Significance

The decrease of the CO oxidation activity has been observed for both FSP and IWI catalysts upon hydrothermal ageing. However, the flame spray pyrolysis seems to lead to significantly more thermally stable materials. Furthermore, the higher dispersion of Mn phases in the FSP sample allows the regeneration of the catalytic activity for the sulfur poisoned catalysts.

References

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