Catalysis Today 258 (2015) 498–506

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Study on the hydrothermal and SO_2 stability of Al_2O_3-supported manganese and iron oxide catalysts for lean CO oxidation

M. Tepluchin [a], S. Kureti [b,*], M. Casapu [a], E. Ogel [a], S. Mangold [c], J.-D. Grunwaldt [a,d]

[a] Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstr. 20, D-76131 Karlsruhe, Germany
[b] Technical University of Freiberg, Institute of Process Engineering and Chemical Engineering, Chair of Reaction Engineering, Fuchsmühlenweg 9, D-09599 Freiberg, Germany
[c] ANKA, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[d] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form 12 January 2015
Accepted 14 January 2015
Available online 19 February 2015

Keywords:
Exhaust gas catalysis
Flame spray synthesis
Thermal stability
Manganese oxide
Iron oxide

ABSTRACT

This paper addresses the hydrothermal stability and SO_2 poisoning resistance of Al_2O_3-supported manganese and iron oxide catalysts for lean CO oxidation. Catalysts were used in the form of powders and coated cordierite monoliths. Bare catalysts mostly comprised Mn and Fe loadings of 20 wt% and were prepared by impregnation and flame spray pyrolysis (FSP). The hydrothermal treatment was conducted at 700 °C. Monolithic catalysts were evaluated toward CO oxidation, and powders were characterized by X-ray diffraction, N_2 physisorption, X-ray absorption near-edge spectroscopy and transmission electron microscopy. Catalytic tests indicated higher hydrothermal stability of the FSP samples, whereas the corresponding Mn catalyst was most stable and most active. The superior stability of the FSP catalysts was associated with the maintenance of their nanocrystallinity and high active surface area. Furthermore, the hydrothermal treatment of the manganese oxide catalysts was accompanied by formation of the thermodynamically preferred Mn_3O_4.

The SO_2 poisoning of selected Mn-based powders was performed at 150 °C and led to strong decrease in catalytic performance, likely due to formation of sulfate species on Mn sites and alumina surface. The FSP catalyst could be partially regenerated by annealing at 700 °C, related to its thermal stability and homogeneous dispersion of the manganese moieties.

1. Introduction

Diesel engines are the most effective internal combustion engines for vehicles reflected by reduced fuel consumption and CO_2 emission. However, a constraint of diesel engines is the output of harmful pollutants such as nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbons (HC) and soot. Consequently, emission limits were introduced and continuously tightened in the past few years worldwide. For removal of HC, CO and soot from the oxygen-rich diesel exhaust, so-called diesel oxidation catalysts (DOC) are used, while for NO_x abatement the selective catalytic reduction and NO_x storage-reduction catalysts are employed [1,2]. DOC systems imply Pt and Pd as active components associated with their high catalytic efficiency and hydrothermal stability [3]. Nevertheless, the increased demand for noble metals becomes more and more an issue related to their limited natural resources. Hence, alternative catalytic components are of immense interest for the substitution of precious metals in pollution control.

For CO oxidation, a multitude of metal oxides were reported to reveal considerable catalytic performance [4,5], particularly cobalt, copper or chromium oxides [6]. Furthermore, prospective CO oxidation activity was also shown for manganese oxide [7–10] and iron oxide catalysts [11–13]. Recently, we evaluated a series of γ-Al_2O_3-supported manganese and iron oxide catalysts for the oxidation of CO under O_2-rich conditions by systematically varying the metal loading as well as preparation procedure [14,15]. Promising activity even at low exhaust temperatures (150–200 °C) was observed for highly loaded Mn/Al_2O_3 prepared by flame spray pyrolysis and incipient wetness impregnation.

For automotive applications, the long-term stability of the catalysts toward SO_2 and hydrothermal exposure is a crucial requirement. SO_2 is known as strong catalyst poison blocking both precious metal sites as well as substrate components especially at low temperatures [16–18]. The deactivating SO_x species

* Corresponding author. Tel.: +49 3731 39 4482; fax: +49 3731 39 4555.
E-mail address: kureti@iec.tu-freiberg.de (S. Kureti).

http://dx.doi.org/10.1016/j.cattod.2015.01.010
0920-5861/

can partially be removed by thermal treatment, whereas the efficiency is enhanced under rich conditions [16,19]. Furthermore, high temperatures (>600 °C) can cause irreversible degradation of the catalysts implying sintering as well as phase transformation and crystallization of substrate and precious metal particles [18,20–24]. Thus, the thermal aging of automotive catalysts is currently inhibited by using sintering barriers such as La_2O_3, ZrO_2 and CeO_2 [25,26]. Additionally, for supported metal oxide catalysts, the stability of the substrate is also of importance. For instance, iron oxide catalysts carried on BEA zeolite showed significant decrease in catalytic performance already after moderate hydrothermal exposure at 550 °C associated with sintering of the support [27]. But, iron oxide on thermally resistant WO_3/ZrO_2 maintained its catalytic activity even after prolonged treatment at 600 °C [28]. On the contrary, only minor change in oxidation activity was demonstrated for full manganese oxide catalysts even after handling at 750 and 1050 °C despite strong structural degradation and strong loss of surface area [29]. Moreover, the preparation route has a significant influence, e.g. flame-derived catalysts are expected to show high thermal stability [30,31].

As a consequence, for the development of advanced exhaust gas catalysts, the evaluation of hydrothermal stability and resistance toward SO_2 including potential deactivating mechanisms [32,33] is a crucial feature. For this purpose, it is advantageous to test the catalysts in the practical form of washcoated honeycomb monoliths. Hence, the objective of this study was the systematic investigation of the effect of hydrothermal exposure of Al_2O_3-supported iron and manganese oxide catalysts prepared by flame spray pyrolysis as well as conventional impregnation. These catalysts recently reported to reveal substantial potential for the after-treatment of lean exhaust [14] were coated on honeycomb carriers. The oxidation of CO was taken as test reaction relevant for the pollution control of diesel engines. Finally, the resistance toward SO_2 was examined with powder catalysts, which also served as basis for deeper characterization studies using X-ray diffraction (XRD), N_2 physisorption (BET), X-ray absorption near-edge structure (XANES) spectroscopy and transmission electron microscopy (TEM).

2. Experimental

2.1. Catalyst preparation

Fe/Al_2O_3 and Mn/Al_2O_3 catalysts were synthesized by incipient wetness impregnation (IWI) and flame spray pyrolysis (FSP). The preparation resulted in metal loadings of 10 and 20 wt% relative to bare alumina substrate. For simplicity, sample codes are used throughout the paper implying loading as well as metal component, e.g. 20 Mn/Al_2O_3.

For IWI, the γ-Al_2O_3 carrier (Disperal, Sasol) was calcined at 600 °C for 3 h in static air. The substrate was then impregnated with an aqueous solution of iron(III)nitrate nonahydrate (Sigma-Aldrich, □97%) or manganese(III)nitrate tetrahydrate (Alpha Aesar, □98%) such that the solution was completely absorbed. The metal loading was controlled by adjusting the Mn and Fe precursor concentrations. After drying overnight at 100 °C, the samples were calcined for 3 h at 500 °C in static air, which resulted in nitrate decomposition and formation of respective metal oxides.

For FSP, the corresponding soluble precursors iron(III)acetylacetonate (Merck, □97%) and aluminum acetylacetonate (Merck, □99%) dissolved in toluene (Prolabo, □99.7%) or manganese(II)-acetylacetonate and aluminum acetylacetonate dissolved in methanol/toluene (1:1 by volume) were taken. The used FSP bench was very similar to that reported recently [34] based on earlier ones by Mädler, Pratsinis and Stark [35,36]. The precursor solutions were fed in a capillary tube at 5 ml/min taking a syringe pump and were dispersed by a small annulus located at the outlet of the capillary supplying an O_2 flow of 5.0 l/min at 3 bar pressure drop. The spray was ignited by an annular premixed CH_4 flame comprising 1.60 l/min O_2 and 0.75 l/min CH_4. Gas flows were adjusted by mass flow controllers from MKS Instruments. The produced catalyst particles (ca. 0.8 g) were collected on glass fiber filters (75 cm diameter, Whatman GF6) employing a water-cooled holder connected to a vacuum pump. The pressure drop across the filter was about 180 mbar. As a reference, bare Al_2O_3 was also synthesized by FSP.

Monolithic honeycomb cores (D = 21 mm, L = 11 mm) were taken from a full cordierite honeycomb with a cell density of 400 cpsi (Corning). For the coating, a mixture of 10 g powder catalyst and Al-based binder Disperal 2 (Sasol) or Si-based Ludox (Aldrich) in a 10:1 mixture (by weight) was diluted in 30 ml water. The monoliths were dipped into this slurry, dried overnight at 80 °C and finally calcined for 3 h in static air at 550 °C. The catalyst loading was gravimetrically checked, and the coating procedure was repeated until a mass of 0.5 g was deposited corresponding to a load of ca. 130 g/l.

2.2. Hydrothermal and SO_x exposure

The coated monoliths as well as bare powder samples were hydrothermally treated in a tubular quartz glass reactor. For this purpose, a blend of 10 vol.% H_2O and 10 vol.% O_2 balanced by N_2 was fed at a total flow rate of 1.0 l/min resulting in a gas hourly space velocity (GHSV) of 20,000 1/h for the monoliths. The powders were put in a ceramic crucible placed in the tubular reactor. All the samples were hydrothermally aged at 700 °C mimicking the peak temperature in the exhaust pipe of diesel engines. After hydrothermal exposure for 2, 4, 6 and 8 h, the catalytic CO oxidation activity of the honeycomb-supported catalysts was measured and then the aging procedure was continued. Powder catalysts were aged for 12 h.

The SO_2 poisoning was exclusively performed for the Mn/Al_2O_3 powder catalysts, i.e. IWI-prepared 10 Mn/Al_2O_3 and the FSP-made 20 Mn/Al_2O_3. These catalysts were exposed for 1.5 h at 150 °C to a gas mixture comprised of 10 ppm SO_2, 10 vol.% O_2 taking N_2 as balance. No SO_3 evolved under these conditions. The feed was obtained by diluting a special mixture of 100 ppm SO_2 in N_2 by pure N_2 and O_2 flows (Air Liquide). The total flow was kept at 1.0 l/min equal to a GHSV of 30,000 1/h. After the SO_2 exposure, the CO oxidation performance of the catalysts was evaluated. Subsequently, the thermal regeneration of these samples was evaluated by heating to 700 or 750 °C with a ramp of 25 K/min, while dosing a gas mixture of 20 vol.% O_2 and 80 vol.% N_2 at a total flow of 1.0 l/min.

2.3. Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, X-ray absorption near-edge structure (XANES) spectroscopy and transmission electron microscopy (TEM). XRD patterns were taken on a D8 Advance from Bruker using Ni-filtered Cu Kα radiation. The diffractograms were recorded in the 2θ range from 20° to 80° with a holding time of 2 s and steps of 0.016. The accelerating voltage and anode current were 40 kV and 35 mA, respectively. Data evaluation was conducted with the data bank of Join Committee for Powder Diffraction Standards.

N_2 physisorption was performed on a Sorptomatic 1990 from Porotec. The samples were degassed at 350 °C in vacuum (10^{-4} mbar) for 2 h and then the N_2 adsorption/desorption isotherm was recorded at 77 K. The BET surface area (S_{BET}) was derived from the BET line referring to 11 data points taken in the p/p_o range from 0.05 and 0.3.

XANES studies were conducted at the XAS beam line of the ANKA synchrotron radiation light source (Karlsruhe). A Si(1 1 1) double-crystal monochromator detuned to about 70% of the maximum