An insight into the correlation of solid solution and surface active species in MnO_x-CeO_2 mixed oxides toward soot oxidation

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Introduction

MnO_x-CeO_2 has showed superior activity for soot abatement. It has been reported that the synergistic effect of the bimetal oxides in the solid solution favoring to soot oxidation, due to the incorporation of Mn into the ceria lattice, accelerated the oxygen mobility and promoted the evolution of lattice oxygen. However, the formation of solid solution and its correlation with these activity-determining parameters still need a further investigation.

Our previous works [1, 2] showed that oxygen species was critical in soot oxidation. This paper will focus on the activities of different Mn-doped ceria catalysts with various Mn/(Mn+Ce) ratios toward soot oxidation under O_2/Ar. The effect of Mn-doping content on generating MnOx-CeO_2 solid solution and its correlation with physicochemical properties of the catalysts are studied. Finally, the key factors in determining the catalytic activity and the reaction path way for soot oxidation are tentatively discussed.

Materials and Methods

All the samples were prepared by citric acid complex method[17].

Results and Discussion

Figure 1 shows the XRD patterns (a, b) of and TPO patterns (c) of soot oxidation on the CeO_2, MnOx(z)-CeO_2 and MnOx. And the calculated average crystallite size and lattice cell parameters [18-21] are listed in **Table 1**.

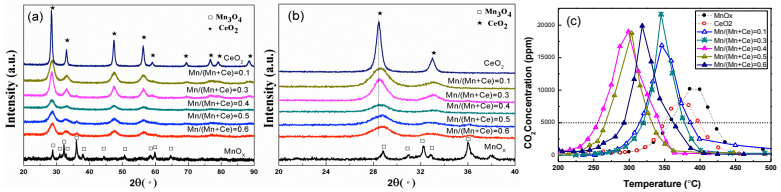

Figure 1. XRD profiles of various MnO_X(z)-CeO_2 catalysts (a:2θ=20°-80°; b: 2θ=20°-40°)

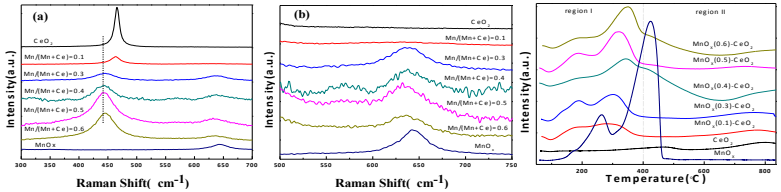

Figure 2. Raman spectra (a, b) and H_2-TPR profiles(c) of MnO_X(z)-CeO_2 catalysts

Figure 2 displays the Raman spectra (a, b) and H_2-TPR profiles(c) of catalysts. **Figure 3** shows the XPS analysis of fresh and reacted MnOx(z)-CeO_2 (z=0.3, 0.4). The surface atomic ratios calculated from the XPS spectra of the catalysts are summarized in Table 2.

Table 1. Specific surface area, average crystallite size and lattice parameter of MnO_x(z)-CeO_2

Catalyst	SSA/($m^2 \cdot g^{-1}$)	d^a （nm）	Lattice parameter (nm)
CeO_2	15.8	16.10	0.5402
MnO_x(0.1)-CeO_2	107.8	5.25	0.5385
MnO_x(0.3)-CeO_2	90.9	6.33	0.5399
MnO_x(0.4)-CeO_2	125.2	4.87	0.5375
MnO_x(0.5)-CeO_2	113.7	5.06	0.5381
MnO_x(0.6)-CeO_2	104.4	4.91	0.5389
MnO_x	5.7	24.06	-

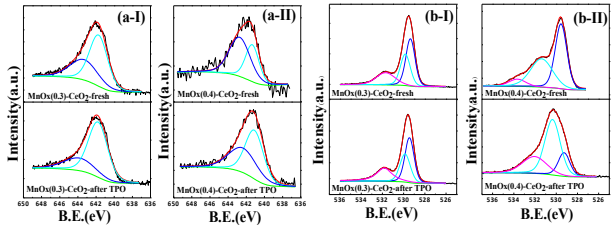

Figure 3. XPS spectra of Mn2p(a) and O1s(b) for MnO_x(0.3)-CeO_2(I) and MnO_x(0.4)-CeO_2(II)

Table 2. Atomic ratios by XPS surface compositional analysis

Sample	Mn/Ce	O/（at. %）			Ce^{4+}/Ce^{3+}	$Mn^{4+}/(Mn^{2+}+Mn^{3+})$
		O_{ads}	O_{sur}	O_{latt}		
MnO_x(0.3)-CeO_2-Fresh	0.30	23.5	32.0	44.5	4.41	0.63
MnO_x(0.3)-CeO_2-reacted	0.29	26.9	30.4	42.6	4.13	0.31
MnO_x(0.4)-CeO_2-Fresh	0.42	8.0	41.5	50.5	4.47	1.75
MnO_x(0.4)-CeO_2- reacted	0.37	26.5	55.6	17.9	4.05	0.78

Significance

Moderate Mn-doping amount favors to the formation of MnOx-CeO_2 solid solution, corresponding to smaller crystallite size, greater specific surface area and more oxygen vacancies, and then the redox properties of the catalyst are enhanced. Therefore, the mobility and transformation of oxygen species on the catalyst are improved, which promotes the catalytic oxidation of soot. Mn^{4+}, O_{latt}, O_{sur} and Ce^{4+} are proposed to play important roles in soot oxidation.

Acknowledgement

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