Facile Fabrication of Shape-controlled $Co_x Mn_y O_\beta$ Nanocatalysts for Benzene Oxidation at Low Temperature

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Experimental

Catalysts preparation

The preparation of Co-Mn oxides consists of the following steps. Using the formation of Co₁Mn₁O (Mn/Co molar ratio = 1/1) as an example: 1 mmol of Co(NO₃)₂·6H₂O, 1 mmol of Mn(NO₃)₂·4H₂O and 100 mg of urea were dissolved into a mixture of water (35 mL), ethanol (15 mL) and HCl (3 M, 1 mL) under stirring to form a clear solution. The solution was then transferred to a Teflon-lined stainless-steel autoclave of 100 mL, and the sealed autoclave with its content was heated at 140 °C for 10 h. Thereafter, the obtained precipitate was washed with deionized water and anhydrous ethanol for several times, followed by vacuum freeze-drying at -46 °C for 10 h and successive drying overnight. Finally, the powders were calcined at 400 °C in air for 3 h, and the obtained catalyst is labeled herein as Co₁Mn₁O (also as Co-Mn-S). The synthetic procedures for the generation of Co₃O₄, Co₅Mn₁O (also as Co-Mn-F), Co₃Mn₁O, Co₂Mn₁O, Co₁Mn₂O, Co₁Mn₃O and MnO₂ were similar to that of Co₁Mn₁O except for the adoption of different Mn/Co molar ratios.

Catalytic Activity test

The catalytic oxidation of C_6H_6 was conducted in a continuous flow fixed-bed quartz reactor (i.d.= 6.0 mm). Before activity measurement, the samples were pretreated under a Ar flow of 30 mL/min at 350 °C for 1 h. To minimize the effect of

hot spots, 0.05 g of the sample (40–60 mesh) was diluted with 0.25 g of quartz sands (40–60 mesh). The gas mixture composed of 1000 ppm C_6H_6 , 20% O_2 and balance N_2 . The total flow rate was set at 75 mL/min using a mass flow controller, corresponding to a weight hourly space velocity (WHSV) of 90,000 mL/(g·h). After steady operation of 30 min, the inlet and outlet gases were analyzed by an on-line gas chromatograph (Agilent 7890A, USA) equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). In the case of water vapor addition, 9.5 vol% of H_2O was introduced via a mass flow controller using a water saturator at a reaction temperature of 350 °C. The benzene conversion (X) were calculated according to the following equations:

$$X_{benzene} = \frac{C_{in} - C_{out}}{C_{in}} * 100\%$$
 [1]

where C_{in} and C_{out} are the inlet and outlet benzene concentration, respectively; External and internal mass transport limitation was obviated by varying the ratio of catalyst weight to total flow rate (W/F) and the catalyst particle size, respectively. The estimation of the Damköhler number under the most unfavorable conditions indicates that the external diffusion mass transfer resistance was negligible. A dimensionless Weisz-Prater (W–P) parameter of less than 0.3 with an effectiveness factor higher than 0.95 and reaction order of 1 provide sufficient conditions for overcoming the significant pore diffusion limitations. The W–P value was calculated by the following equation:

$$C_{wp} = \frac{-r'_{A(obs)}\rho_c R^2}{D_e C_{As}}$$
[2]

Herein, $-r'_{A(obs)}$ is the reaction rate, R and ρ_c represent the catalyst particle radius and solid catalyst density, respectively. D_e and C_{As} are effective gas-phase diffusivity and gas concentration of A at the catalyst surface, respectively. When the catalytic oxidation of benzene oxidized at 162.5 °C in MnO₂, the W–P value was calculated to be 0.21, which is less than 0.3. Therefore, no significant mass transfer limitations existed in our catalytic systems. The catalytic combustion of benzene follows first-order kinetics as expressed in the following equations [3–4]:

$$r_{c_{6H6}} = \left[\frac{-N_{c_{6H6}} * \eta_{c_{6H6}}}{W_{cat}}\right] \qquad [3]$$

$$r = -kc = -A \exp\left[\frac{-E_a}{RT}\right]c \qquad [4]$$

where N, η , W, E_a, A, κ and γ are the benzene gas flow rate (mol/s), gas conversion, catalyst weight (g), apparent activation energy (kJ/mol), pre-exponential factor, rate constant (s⁻¹) and reaction rate [μ mol/(g·s)], respectively.

The normalized initial reaction rate (r, $mol \cdot m^{-2} \cdot s^{-1}$) is calculated according to the following equation:

$$r = -\frac{F}{M_{CAT} * S_{BET}} * \frac{P}{RT} * \ln\left(1 - X_{Benzene}\right) * C_{Benzene in}$$
[5]

Characterizations

Powder X-ray diffraction (XRD) was performed on a Panalytical X'Pert Pro diffractometer using Co-K_a radiation. The specific surface areas and pore volume measurements were carried out at 77 K on an ASAP 2020 apparatus using the nitrogen adsorption/desorption approach. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out using an Ultima2 spectrometer. Scanning Electron Microscope (SEM) was performed on a JSM6700-F instrument. Scanning Electron Microscope (SEM) was performed on a JSM6700-F instrument. High-resolution transmission electron microscopy (HR-TEM) measurements were carried out on a JEM-2010 microscope operating at 200 kV in the bright-field mode. H₂ temperature-programmed reduction (H₂-TPR) was performed on an AutoChem II 2920 equipment using TCD, having the sample pretreated in an Ar flow (30 mL/min) at 400 °C for 0.5 h. After cooling to room temperature, the sample was heated to 700 °C at 5 °C/min in a gas flow of H₂/Ar (vol/vol = 10/90; rate = 30 mL/min). O₂-TPD-MS experiment was carried out on a Micromeritics Autochem II 2920 instrument equipped with a Hiden QIC-20 mass spectrometer.

Oxygen-temperature-programmed surface reaction (O₂-TPSR) experiments were also performed on the AutoChem II 2920 apparatus. Prior to each experiment, the sample was pretreated at 300 °C in He for 0.5 h. After the sample was cooled to 50 °C, the He flow was switched for pulse injection of C₆H₆/Ar (vol/vol = 10/90) until complete C_6H_6 adsorption, followed by He purging for 10 min. Finally, the O₂-TPSR run was started with the sample heated at 5 °C/min to 500 °C in a flow (40 mL/min) of 3%O₂/He. A mass spectrometer (Cirrus) was used for on-line monitoring of effluent gases, having signals at m/z ratios of 18 (H₂O), 28 (CO), 44 (CO₂) and 78 (C₆H₆) followed.

X-ray photoelectron spectroscopy (XPS) analysis was performed on Physical Electronics Quantum 2000, equipped with monochromatic Al-K_a source (K_a = 1,486.6 eV) and a charge neutralizer. The X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) measurements were undertaken at Beamlines 1W1B at Beijing Synchrotron Radiation Facility (BSRF) using transmission and fluorescence modes. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k³-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k3-weighted $\chi(k)$ data of Fe K-edge were Fourier transformed to real (R) space using a hanning windows (dk=1.0 Å-1) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.

In situ DRIFTS

In situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nicolet Nexus FT-IR spectrometer in the range of 650–4000 cm⁻¹ (32 scans at a resolution of 4 cm⁻¹). Before experiment, samples were held at 300 °C under N₂ flow (50 mL/min) for 0.5 h and cooled to a desired temperature for getting a background spectrum, which would be subtracted from the sample spectrum for each measurement. Subsequently, 1000 ppm C₆H₆ balanced with N₂ was introduced to the cell at a flow rate of 30 mL/min at 150 and 250 °C, respectively, for the record of DRIFTS spectra. After the removal of physiosorbed C₆H₆ by flushing wafer with N₂ for 3 h, 20%O₂/N₂ was introduced to investigate the reactivity of pre-adsorbed C₆H₆ with N₂ + O₂ at different temperatures.

DFT calculation

All density functional theory calculations with dispersion corrections (DFT-D2) were performed utilizing the Vienna *ab initio* simulation package (VASP) and the projected augmented wave (PAW) method. The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals was employed. The kinetic energy cutoff for the plane-wave expansion was set to 500 eV, and the Brillouin-zone integrations were sampled using the Γ -point. The effects of spin polarization were considered and the dipole correction in the surface normal direction was applied. The convergence thresholds of the energy change and the maximum force for the geometry optimizations were set to 10⁻⁵ eV and 0.03 eV/Å, respectively.



Figure S1 different nucleation modes on the surface of Mn_7O_{13} : heterogeneous nucleation and homogeneous nucleation in the reaction solution.

In the present synthesis strategy, three steps are involved: the urea-assisted hydrothermal and vacuum freeze drying (-46 $^{\circ}$ C) processes to generate a Co-Mn oxides precursor, then a post-calcination treatment to generate the corresponding Co-Mn oxides. Taking MnO₂ nanocube as an example, the reaction can be illustrated by the following equations:

$$H_2NCONH_2 + H_2O \longrightarrow 2NH_3 + CO_2 \quad [6]$$
$$NH_3 \cdot H_2O \longrightarrow NH_4^+ + OH^- \quad [7]$$

The Mn^{2+} ions react with the hydroxyl ions to generate MnOOH, and MnO_2 was obtained by calcination of the precipitate MnOOH at 400 °C. Generally, the shape of nanomaterials can be controlled by modifying the nucleation, seeds and growth process in solution synthesis. Herein, upon the addition of Co^{2+} into Mn^{2+} solution, oxygen from air oxidizes $Co(NH_3)_6^{2+}$ to $Co(NH_3)_6^{3+}$.

Subsequently, there is the generation of MnOOH which is gradually oxidized to Mn_7O_{13} by $Co(NH_3)_6^{3+}$ following the equation:

7MnOOH + $5Co(NH_3)_6^{3+} \longrightarrow Mn_7O_{13} + 5Co(NH_3)_6^{2+}$ [8] (standard Gibbs free energy: -139.53 kJ/mol)

Notably, the concentration of Mn_7O_{13} increases with increasing Mn/Co molar ratio, which reaches the highest in Co_1Mn_1 oxides solid microspheres. When further increasing Mn/Co molar ratio, inadequate $Co(NH_3)6^{3+}$ cannot oxidize MnOOH to form Mn_7O_{13} , resulting in a reduced concentration of Mn_7O_{13} and in turn the "exploded" microspheres. The results suggest that the shape of Co-Mn oxides is extremely sensitive to the concentration of Mn_7O_{13} , which is "effectively infinite" upon surpassing a certain threshold. Meanwhile, Mn_7O_{13} is associated with the free energy change in the nucleation process. Different nucleation modes of Co-Mn oxides are presented in Figure 2B. Pure Co_3O_4 and MnO_2 obey the homogeneous nucleation, while the existence of Mn_7O_{13} favors the heterogeneous nucleation. A lower energy barrier is required for heterogeneous nucleation with respect to homogeneous nucleation, both homogeneous and heterogeneous nucleation occur concomitantly, resulting in diverse shapes of Co-Mn composite oxides.

Mn and Co oxidation states are strongly influenced by the local geometric, therefore, the coordination environments of Mn and Co ions were further investigated by Mn K-edge EXAFS spectra (Figure 3A) show that three main (< 4 Å) Fourier-transformed (FT) peaks at 1.5, 2.4 and 3.0 Å, corresponding to "Mn/Co-O" shell, edge-shared and corner-shared "Mn/Co-Mn/Co" shells (Figure 3B), respectively. Meanwhile, the Co K-edge EXAFS spectra display three obvious peaks below 4 Å in the cases of Co-Mn-S, Co-Mn-F and Co₃O₄ (Figure 3C). The first peak below 2 Å matches well with that of Co-O shells. The Co-Co coordination shell at ~2.5 Å (coordination number, CN: 8) and ~3.0 Å (CN: 4) contribute to the other two peaks (Figure 3D).



Figure S2 HR-TEM images of (A–B) MnO_2 , (C) Co_1Mn_1O and (D) Co_3O_4 ; (E) pore size distribution curves of Co_3O_4 , Co_1Mn_1O , Co_5Mn_1O and MnO_2 ; and (F) XRD patterns of Co_3O_4 , Co_1Mn_1O , Co_5Mn_1O and MnO_2 .



Figure S3 N_2 physisorption isotherms curves of Co₃O₄, Co-Mn-F, Co-Mn-S and MnO₂.



Figure S4 (A) O₂-TPSR profiles of MnO₂ at 300 °C; (B) Toluene reaction rate as a function of temperature over as-prepared catalysts.



Figure S5 SEM images of MnO₂ after activity and thermal stability test.

MnO₂ at 500°C



Figure S6 H₂-TPR profiles of Co₃O₄, Co-Mn-F, Co-Mn-S and MnO₂.

The peak at 353 °C can be assigned to surface oxygen species, while the ones at 445 and 492 °C are associated with the reduction of Co³⁺ to Co²⁺ and Co²⁺ to Co⁰, respectively. ¹As for MnO₂, the reduction process could be reasonably divided into two stages: (1) Mn⁴⁺ to Mn³⁺ and (2) Mn³⁺ to Mn^{2+. 2} The reduction temperatures of Mn species in MnO₂ (290 and 413 °C) are lower than those of Co-Mn-S (302 and 482 °C) and Co-Mn-F (303 °C), suggesting better low temperature reducibility and stronger lattice oxygen mobility in MnO₂.³Another broad peak located at 450 °C in Co-Mn-F is associated with the co-reduction of Co³⁺ to Co²⁺ and Co²⁺ to Co⁰. Furthermore, the amount of H₂ consumption (8.2 mmol/g) is smaller than the theoretical amount (11.5 mmol/g) required for full reduction of MnO₂ to MnO. The result implies the existence of Mn species of lower valence (< +4), which is in consistent with the Mn2p_{2/3} XPS and Mn K-edge XANES results.



Figure S7 O₂-TPD-MS profiles of Co₃O₄, Co₅Mn₁O, Co₁Mn₁O and MnO₂.



Figure 8 *In situ* DRIFTS spectra of (A-C) C_6H_6 adsorption at 150 °C on catalysts; (D-F) O_2 reacting with C_6H_6 pre-adsorbed at 150 °C on catalysts; (G-

I) O_2 reacting with C_6H_6 pre-adsorbed at 250 °C on catalysts.



Figure S9 DFT calculation of the simulated vibration models of benzene species over $MnO_2(101)$ surface.



Figure S10 DFT calculation of the simulated vibration models of carboxylate species over MnO_2 .



Figure S11 *In situ* DRIFTS spectra of Co₃O₄, Co-Mn-S and MnO₂ at 150 °C (test condition: 1000 ppm benzene+N₂).

 $\label{eq:table S1} \begin{array}{l} \mbox{Table S1 Textural properties, reaction temperature, $O_{latt}/(O_{ads}+O_{latt})$ ratio and $activation energy (E_a)$ of catalysts $$ \end{array}$

Sample		Pore	T _{50%}	T _{90%}	$O_{latt} / (O_{ads} + O_{latt)}$	Ea
	S_{BET} (m ² ·g ⁻¹)	volume (cm ³ ·g ⁻¹)	(°C)	(°C)	(%)	(kJ/mol)
Co ₃ O ₄	25	0.119	233	292	55	89
Co-Mn-F	49	0.181	232	259	48	78
Co-Mn-S	55	0.139	212	253	41	56
MnO ₂	78	0.100	171	207	58	43

Sample	Mn/Co	Mn^{4+}/Mn^{3+}	O/Mn
	molar ratio	molar ratio	molar ratio ^a
Co ₃ O ₄	-	-	-
Co-Mn-F	1/5.03	0.61	-
Co-Mn-S	1/1.02	0.63	-
MnO ₂	-	1.69	3.28

Table S2 XPS data ICP-AES results of Co3O4, Co-Mn-F, Co-Mn-S and MnO2catalysts.

Table S3 Summary of the EXAFS fitting results for Mn-containing samples.

Sample	Shell	CN ^a	R (Å) ^b	$\sigma^2 (Å^2 \cdot 10^3)$ °	$\Delta E_0(eV)_d$	R factor (%)
MnO ₂ -std	Mn-O	6	1.89	3.1	-0.2	0.5
MnO ₂ -sample	Mn-O	4.1	1.88	3.5	1.1	0.8
Co-Mn-S	Mn-O	4.9	1.90	3.3	-0.6	0.6
Co-Mn-F	Mn-O	4.7	1.90	2.9	-0.7	0.6

^{*a*} *CN*: coordination numbers; ^{*b*} *R*: bond distance; ^{*c*} σ^2 : Debye-Waller factors; ^{*d*} ΔE_0 : the inner potential correction. *R* factor: goodness of fit. S_0^2 , 0.75, was obtained from the experimental EXAFS fit of MnO₂ reference by fixing CN as the known crystallographic value and was fixed to all the samples.

Sample	T ₁ (T<600 °C)		The amounts of O ₂ desorption		
		T ₂	(µmol/g)		
		(T>600 °C)	T_1	T_2	
Co ₃ O ₄	-	851	-	581	
Co-Mn-F	128, 547	847	8	-	
Co-Mn-S	426, 560	836	200	-	
MnO ₂	105, 479, 499	763	1201	215	

Table S4 O₂-TPD-MS data of Co₃O₄, Co-Mn-F, Co-Mn-S and MnO₂.

References

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