Supporting Information

The Role of Various Oxygen Species in Mn-based Layered Double Hydroxide Catalysts on Selective Alcohol Oxidation

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In the preparation of MMgMn-LDH, 0.0015 mol $Mg(NO_3)_2 \cdot 6H_2O$, 0.0075 mol $Mn(NO_3)_2 \cdot 4H_2O$ and 0.0030 mol M^{m+} nitrate were dissolved in 100 mL water. This salt solution was then added drop-wise at a rate of 2 mL·min⁻¹ to an alkali solution including 0.02 mol NaOH and 0.01 mol Na₂CO₃ in 100 mL water under stirring with the speed of 500 rpm. The obtained suspension was aged for 20 h at room temperature. Subsequently, the precipitates were separated and washed by centrifugation until pH=7 and dried at 60 °C overnight.

X-ray diffraction (XRD) patterns were carried out by a Shimadzu XRD-6000 diffractometer using a Cu K α source ($\lambda = 0.154$ nm) at a scan step of 10° min⁻¹ from 3° to 70°. The content of metals in catalysts was performed by inductively coupled plasma emission spectroscopy (ICP-AES, Shimadzu ICPS-75000). The powders were dissolved by a small quantity of aqua regia, and the obtained acid solution was further attenuated. Low-temperature nitrogen adsorption–desorption experiments were worked on a Quantachrome Autosorb-1C-VP analyzer. 0.1000 g samples were accurately weighed and pretreated by heating to 150 °C for 6 h. The specific surface area was then calculated according to the Brunauer–Emmett–Teller (BET) method

based on the adsorption isotherm. The average sizes of LDHs were measured by malvern mastersizer 2000 particle size analyzer. Before testing, traces of LDHs were dispersed in 100 mL deionized water and pretreated by high-power ultrasonic for 30 min. DRIFT spectroscopy studies were performed by a Bruker Tensor 27 spectrometer fitted with a high sensitivity MCT detector and a diffusIR heated chamber equipped with KBr windows. ~0.1 g samples were pretreated with N2 at 100 °C for 1 h. Experiencing an initial scan as the background spectra, CO₂ was then inlet for 1 h. After purging with N₂ to remove CO₂ for few minutes, spectra were collected in the range of 4000-600 cm⁻¹ with 64 accumulation scans at room temperature below a pressure of 10⁻³ Pa. X-ray photoelectron spectroscopy (XPS) spectra were collected using a Thermo VG ESCALAB 250 spectrometer equipped with an Al Ka anode, and the peaks were calibrated by the C 1s peak at 284.6 eV. After the centrifugal separation, the samples were dried in a vacuum drying oven and reserved in specimen tubes full of N₂. In all cases, the FWHM was constrained to be equal in each sample for all deconvoluted peaks from the photoemission spectra of the same species using an 70%/30% Gaussian/Lorentzian sum and a Shirley background. Error bars of the peak-fitting parameters (taken as 95% confidence intervals) were determined from the variances of the fitted peak parameters, which was caused by Monte Carlo simulations of the experimental noise. The curves of the 2p electron in Cr were fitted well to double groups of peaks, corresponding to $2p_{3/2}$ and $2p_{1/2}$, with the same peak area ratio (2:1) per pair of corresponding peaks. Temperature-programmed desorption (TPD) was carried out by a Micromeritic ChemiSorb 2750 chemisorption instrument with a thermal conductivity detector (TCD). 0.1000 g fresh catalysts were pretreated at 150 °C for 1 h in He or O_2 , and then cooled to room temperature. It was kept in pure oxygen steam for 1 h, and then purged with He. The curve was recorded from 30 °C to 950 °C in 40 mL·min⁻¹ He steam with a heating rate of 10 °C min⁻¹. The Raman spectra were obtained on a Jobin Yvon Horiba HR800 spectrometer using a 532 nm line of Ar⁺ ion laser as the excitation source at room temperature.

Solvent-free benzyl alcohol oxidation was carried out in a glass stirred reactor with gas intake but without outtake. 0.1 g catalyst and 1 mL benzyl alcohol were mixed by magnetic stirring at 1000 rpm, and purged with O₂ for three times to remove air. The reaction temperature was maintained at 140 °C and the O₂ pressure was maintained at 1 bar (relative pressure). After 4 h, the stirring was stopped and the reactor was rapidly cooled in an ice bath. After cooling for 10 min, the reactor was opened slowly and the contents were centrifuged. The recycled catalyst was sequentially washed with acetone and 10% Na₂CO₃ solution for 3 times, then washed with deionized water until pH=7, and dried at 60 °C overnight.

An aliquot of the clear supernatant reaction mixture (0.5 mL) was diluted with mesitylene (0.5 mL, external standard for GC analysis), and was analyzed by an Agilent J&W GC-FID (DB-Wax, 30 m × 0.320 mm, $d_f = 0.25 \mu m$). For the quantification of the amounts of reactants consumed and products generated, an external standard method was used. The selectivity was calculated as mol of product formed per mol of reacted benzyl alcohol and the carbon balance was within 100±5%.

Each group of data had been repeated for more than 3 times with the standard deviation less than 2%.

Catalyst	S ^a (m ² ·g ⁻¹)	M ^b wt.%	Conversion ^c (%)	Selectivity ^c (%)				TOF ^d	Specific activity	Carbon
				Benzaldehyde	Toluene	Benzoic acid	Benzyl benzoate	(10 ⁻³ s ⁻¹)	(10 ⁻⁴ m ⁻ ² •s ⁻¹)	(%)
ZnMgAl-LDH	138	9.42	3.03	98.33	0.57	0.17	0.93	0.42	0.03	99
CuMgAl-LDH	96	9.14	5.89	97.62	0.27	0.13	1.98	0.96	0.10	98
NiMgAl-LDH	208	8.44	5.67	96.34	1.24	0	2.42	0.84	0.04	95
CoMgAl-LDH	179	6.74	7.35	93.88	0.78	0.15	5.19	1.26	0.07	102
FeMgAl-LDH	115	7.86	5.00	97.63	0.50	0	1.87	1.07	0.09	105
MnMgAl-LDH	119	10.44	12.29	99.40	0.06	0.05	0.49	1.51	0.13	99
CrMgAl-LDH	176	7.94	3.33	98.79	0.30	0	0.91	0.43	0.02	104

 Table S1 Textural and catalytic properties of various MMgAl-LDH catalysts.

^a Determined by BET. ^b Determined by ICP. ^c Reaction conditions: benzyl alcohol (1 mL), catalysts (0.1 g), O₂ pressure (1 bar),

140 °C, 4 h. d Based on the data at 30 min.

Mass Transfer limitation was calculated and neglected for solvent-free alcohol oxidation on a series of MMgMn-LDH catalysts by Weisz-Prater and Mears Criterion.

1. Weisz-Prater Criterion for Internal Diffusion (Fogler, p839)

If $C_{WP} = \frac{-r_A^{'}\rho_b R^2}{C_{Ab}D_e} < 1$, then internal mass transfer effects can be neglected. $\frac{-r_A^{'}\rho_b R^2}{C_{Ab}D_e} < \frac{4.85 \times 10^{-6} \times 1000 \times (1.3 \times 10^{-7})^2}{10.68 \times 1.34 \times 10^{-12}} = 5.73 \times 10^{-6} < 1$

2. Mears Criterion for External Diffusion (Fogler, p841; Mears, 1971)

$$\frac{-\dot{r_A}\rho_b Rn}{k_c C_{Ab}} < 0.15, \text{ then external mass transfer effects can be neglected.}$$

$$\frac{-\dot{r_A}\rho_b Rn}{k_c C_{Ab}} < \frac{4.85 \times 10^{-6} \times 1000 \times 1.3 \times 10^{-7} \times 1}{0.33 \times 10.68} = 1.72 \times 10^{-10} < 0.15$$

3. Mears Criterion for External (Interphase) Heat Transfer (Fogler, p842)

$$\begin{aligned} \left| \frac{-\Delta H_{r}(-r_{A}^{'})\rho_{b}RE}{h_{t}T_{b}^{2}R_{g}} \right| &< 0.15, \text{ then external heat transfer effects can be neglected.} \\ \\ \left| \frac{-\Delta H_{r}(-r_{A}^{'})\rho_{b}RE}{h_{t}T_{b}^{2}R_{g}} \right| &< \frac{-(-336) \times 4.85 \times 10^{-6} \times 1000 \times 1.3 \times 10^{-7} \times 60}{3.08 \times 10^{4} \times 413^{2} \times 8.314 \times 10^{-3}} = 2.80 \times 10^{-13} < 0.15 \end{aligned}$$

4. Mears Criterion for Combined Interphase and Intraparticle Heat and Mass

Transport (Mears, 1971)

$$\frac{-r_{A}^{'}R^{2}}{C_{Ab}D_{e}} < \frac{1 + 0.33\gamma\chi}{|n - \gamma_{b}\beta_{b}|(1 + 0.33n\omega)}$$

$$\frac{-r_{A}^{'}R^{2}}{C_{Ab}D_{e}} = \frac{4.85 \times 10^{-6} \times (1.3 \times 10^{-7})^{2}}{10.68 \times 1.34 \times 10^{-12}} = 5.73 \times 10^{-9}$$

$$\frac{1 + 0.33\gamma\chi}{|n - \gamma_{b}\beta_{b}|(1 + 0.33n\omega)} = 1.00$$

$$5.73 \times 10^{-8} < 1.00$$

Table S2. Parameters used in the Weisz-Prater criterion and Mears Criterion for

 estimating mass transfer limitations in solvent-free alcohol oxidation.

Parameters	Value
Reaction rate: $-r_A'$ (kmol/kg _{cat} s)	< 4.85×10 ⁻⁶ , as shown in Fig. S1
Density of catalyst: $\rho_b (kg/m^3)$	~ 1000
Radius of catalyst: R (m)	< 1.3×10 ⁻⁷
Reaction order: n	~ 1
Liquid-phase diffusivity: D_{AB} (m ² /s)	$\sim 9 \times 10^{-10}$
Effective liquid-phase diffusivity: $D_e (m^2/s)^a$	~1.34×10 ⁻¹²
Concentration of benzyl alcohol at 140 °C: CAb (kmol/m3) b	~ 10.68
Viscosity of the reactant mixture fluid at 140 °C: μ (Pa \cdot s) $^{\circ}$	$\sim 6 \times 10^{-4}$
Density of reactant mixture fluid at 140 °C: ρ (kg/m ³) b	~ 1155.3
Schmidt number: Sc ^d	~ 577
Superficial velocity: U (m/s)	~ 10
Reynolds number: Re ^e	< 1.16
Sherwood number: Sh ^f	< 7.38
Mass transfer coefficient: $k_c (m/s)^{f}$	~ 0.33
Heat of reaction: Δ Hr (kJ/mol)	~-336
Activation energy: E (kJ/mol)	~ 60
Thermal conductivity: λ (W/m·K)	~ 0.25
Heat transfer coefficient: $h_t (kJ/m^2 \cdot K \cdot s)^g$	$\sim 3.08 \times 10^4$
Bed temperature: $T_b(K)$	~ 413
Arrhenius number: γ_b^{h}	~ 17.47
Damköhler number for interphase heat transport: χ^{i}	< 3.84×10 ⁻¹⁸
Heat generation function: $\beta_b{}^j$	~ 3.13×10-6
Damköhler number for interphase mass transport: ω^{k}	< 4.90×10 ⁻⁴

$$D_{AB}\phi_p\sigma_c$$

^a $D_e = \tau$, effective liquid-phase diffusivity [Fogler, p815], where ϕ_p is porosity, σ_e is constriction factor, and τ is tortuosity.

^b estimated based on liquid component.

^c estimated based on Wilke formula.

$${}^{d} S_{c} = \frac{\mu}{\rho D_{AB}}.$$

$${}^{e} R_{e} = \frac{2UR\rho}{\mu}.$$

$${}^{f} S_{h} = \frac{2k_{c}R}{D_{AB}} = 2+0.6Re^{1/2}Sc^{1/3}.$$

$${}^{g} Nusselt number (Nu) = 2 + 0.6Re^{1/2}Sc^{1/3} = \frac{2Rh_{t}}{\lambda}.$$

$${}^{h} \gamma_{b} = \frac{E}{R_{g}T_{b}}.$$

$${}^{i} \chi = \frac{(-\Delta H_{r})(-r_{A}')R}{h_{t}T_{b}}.$$

$${}^{j} \beta_{b} = \frac{(-\Delta H_{r})D_{e}C_{Ab}}{\lambda T_{b}}.$$



Fig. S1. Time–conversion plots for solvent-free BA oxidation over various catalysts. Reaction conditions: 1 mL benzyl alcohol, 0.1 g catalyst, 1 bar O₂, 140 °C.

Catalyst	LDH average size (nm) ^{<i>a</i>}			
ZnMgMn-LDH	250.3			
CuMgMn-LDH	196.5			
NiMgMn-LDH	109.2			
CoMgMn-LDH	217.5			
FeMgMn-LDH	111.6			
CrMgMn-LDH	190.7			

Table S3. Mean particle sizes of various LDH catalysts.

^a Determined by laser diffraction analyzer.