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Appendix A Supporting Information

Enhancement of the catalytic performance of Co₃O₄ towards

butyl acetate oxidation by weakening the Co-O bond and

promoting oxygen activation

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1. Experimental section

1.1. Catalyst Preparation

CB1: 2.10 g of Co(NO₃)₂ • $6H_2O$ was added to a mixture containing 300 mL of ethylene glycol and 200 mL of ethanol, and 0.714 g of trimesic acid was added under magnetic stirring and stirred at room temperature for 2 h. Transfer the mixture into a 100 mL polytetrafluoroethylene (PTFE) liner and heat it to 150 °C and maintain this temperature for 24 hours. Separate the pink-purple precipitate by centrifugation, wash it with deionized water and ethanol, and then dry it overnight in an oven at 80 °C to obtain CB1¹.

ZIF67: 1.75 g of Co(NO₃)₂ • $6H_2O$ was dissolved in 12 mL of deionized water and 21.30 g of 2-methylimidazole was dissolved in 80 mL of deionized water. The two solutions were mixed well and stirred at room temperature for 6 h. The purple precipitate was collected by centrifugation, washed with deionized water and ethanol for three times, and then placed in an oven at 80 °C for overnight drying to obtain ZIF67².

CM71: 0.75 g of Co(NO₃)₂ • 6H₂O and 0.428 g of terephthalic acid were added to a mixture containing 48 mL of N,N-dimethylformamide (DMF) and 12 mL of ethanol, stirred until completely dissolved, and the mixture was transferred to 100 mL polytetrafluoroethylene (PTFE) liner and heated to 100 °C and kept for 12 h. The violet precipitate was separated by centrifugation and washed with DMF and ethanol, and then put in an oven at 80 °C.Overnight drying gave CM71³.

1.2. Catalyst Characterization

SEM tests were carried out using a Merlin-type scanning electron microscope from Zeiss (Germany). The samples were sprayed with gold for 60 s prior to testing.

TEM tests were performed using a Tecnai G2 F30 field emission transmission electron microscope from Thermo Fisher, USA.Samples were dispersed in anhydrous ethanol prior to testing.

XRD tests were carried out using an Empyrean type X-ray diffractometer from PANalytical, the Netherlands.The crystal structure of the catalysts was analysed using

an X-ray diffractometer with Cu-K α radiation (PANalytical Aeris). The scanning range was set between 2 and 90° and the test scan rate was 5° min⁻¹.

The N_2 adsorption-desorption tests were performed using a fully automated surface analyser (ASAP 2020) from Micromeritics, USA.The mass of the sample was about 100 mg, and the sample was degassed at 200 °C for 12 h. The specific surface area and pore size distribution of the sample were calculated and obtained by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations respectively.

FTIR tests were performed using using KBr as the matrix (Bruker Vertex 70, Germany), and scanning from 4000 to 400 cm⁻¹ with 32 scans at an effective resolution of 4 cm⁻¹ to measure the surface functional groups of samples.

Raman tests were performed using a LabRAM HR Evolution laser Raman spectrometer from Horiba, Japan. The light source wavelength of the test is 525 nm, the grating is 1800 grooves mm⁻¹, the objective lens is 50 times Visible lens, the laser intensity is 2.5 %, the detector is CCD.

The EPR test was carried out with an E500 spectrometer from Bruker, Germany, at a low temperature (85K-600K).

XPS tests were performed with an Escalab Xi+ X-ray photoelectron spectrometer from Thermo Fisher, USA. The excitation source was Al K α (hv = 1486.8 eV) and all spectra were C-corrected (C 1s = 284.6 eV).

The H₂-TPR tests were performed using a fully automated chemisorbent assay model Auto Chem II 2920 from Micromeritics, USA. About 100 mg of the samples to be tested were weighed into a U-shaped quartz tube and pre-treated in helium (30 mL min⁻¹) at a rate of 10 °C min⁻¹ to 300 °C for 1 h. After cooling down to 30 °C, the atmosphere was switched to 5% H₂/Ar (30 mL min⁻¹) and the temperature was increased to 900 °C at a rate of 10 °C min⁻¹. For O₂-TPD, the samples were exposed to a 5 vol% O₂/He gas mixture for 1 h following the same pretreatment procedure. Subsequently, the temperature was raised from 30 °C to 900 °C under helium flow.

BA-TPSR tests were performed using a HPR-20 EGA type mass spectrometer from Hiden Analytical, UK, to record the mass-to-charge ratio (m/z) signals corresponding to BA, CO₂ and H₂O during warming. All samples were pretreated in a nitrogen stream at 300 °C for 1 h to remove surface adsorption, and after saturated adsorption at 1000 ppm BA/N₂ (50 mL min⁻¹), the weakly adsorbed BA was discharged by a continuous purge with N₂ (30 mL min⁻¹) for 30 min before switching to either Air or N₂ (30 mL min⁻¹), and the temperature was increased to 600 °C at a 5 °C min⁻¹. The temperature was then increased to 600 °C at a rate of 5 °C min⁻¹.

In-situ DRIFTS tests were performed using a Nicolet iS50R FTIR Fourier transform infrared spectrometer from Thermo Fisher, USA, with a KBr window matched to the in-situ cell (thickness of 2 mm, diameter of 15 mm). The detector was a mercury cadmium telluride (MCT) cooled by liquid nitrogen. The scanning range was from 800 to 4000 cm⁻¹, and the number of scans was 64 times. All samples were pretreated in a nitrogen flow at 300 °C for 1 hour to remove the surface-adsorbed substances. After the temperature dropped to room temperature, the reaction atmosphere was introduced.

1.3 Activity tests

Information about the main instruments used for the performance evaluation is shown in Table S1.

Equipment	Model	Vender	
GC	GC 9720 Plus	Zhejiang Fuli Analytical	
		Instrument Co., Ltd	
Mass flow meter	D07-7K	Beijing Qixing Huachuang	
		Electronics Co., Ltd	
Hydrogen Generator	BRH300 II	Guangzhou Beirui	
		Precision Instrument Co.,	
		LTD	
Air Generator	GA5000A	Beijing Zhongxing Huili	
		Technology Development	
		Company	

Table S1 The main instruments for experiment.

As shown in Fig. S1, the evaluation test on the catalytic oxidation performance

of samples for BA was carried out on a temperature-programmed fixed-bed quartz reaction tube (Φ =6 mm). Before the test, 100 mg of the granulated catalyst (40 - 60 mesh) was uniformly mixed with 400 mg of quartz sand (40 - 60 mesh), and then fixed in the center of the quartz tube with quartz wool at both ends. The total flow rate was 100 mL min⁻¹ (including 1000 ppm of BA, 21 vol% of O₂ and the balance being N₂). The weight hourly space velocity (WHSV) was 60,000 mL g⁻¹ h⁻¹.



Fig. S1. Activity evaluation device diagram.

The reaction temperature (ranging from 100 to 300 °C) was precisely controlled by a digital temperature controller, and each temperature point was maintained for 50 minutes. BA vapor was generated through a metal bubbler in a warm water bath. The concentrations of BA and CO₂ at the outlet of the reactor were detected by a GC 9720 Plus gas chromatograph equipped with a flame ionization detector (FID) for subsequent analysis. The conversion rate of BA (X_{BA}) and the yield of CO₂ (Y_{CO₂}) were calculated according to equations (1) and (2).

$$X_{BA} = \frac{(C_{BA,in} - C_{BA,out})}{C_{BA,in}} \times 100\%$$
 Eq. (S1)

$$Y_{CO_2} = \frac{C_{CO_2,out}}{(M \times C_{BA,in})} \times 100\%$$
 Eq. (S2)

Among them, $C_{BA,in}$ and $C_{BA,out}$ represent the concentrations (in ppm) of BA at the inlet and outlet of the fixed-bed reactor respectively. T₅₀ and T₉₀ are usually used to evaluate the catalytic efficiency of the catalyst for BA, which represent the corresponding temperature when the conversion efficiency of BA reaches 50% and 90% respectively. In addition, $C_{CO_2,out}$ represents the concentration (in ppm) of CO₂ at the outlet of the reactor.

The kinetic measurements were carried out at a temperature of 140 °C and WHSV = 60,000 mL g⁻¹ h⁻¹. The reaction rate (r_{BA}) and specific activity (SA) of BA are calculated by the following equations⁴:

$$r_{BA} = \frac{C_{BA}X_{BA}VP_{atm}}{m_{cat}RT} (mol \cdot g^{-1} \cdot s^{-1})$$
 Eq. (S3)

$$SA = \frac{r_{BA}}{S_{BET}} \left(mol \cdot m^{-2} \cdot s^{-1} \right)$$
 Eq. (S4)

where m_{cat} , C_{BA} , V, X_{BA} , R, T, P_{atm} and S_{BET} are used to measure catalyst mass, BA concentration in feed gas, total flow rate, BA conversion rate, molar gas constant (equal to 8.314 Pa m³ mol⁻¹ K⁻¹), room temperature (K) and atmospheric pressure (equal to 101.3 Kpa) and specific surface area (m² g⁻¹) obtained by N₂ adsorptiondesorption.

The grain sizes of the samples were calculated from the XRD data using the Scherrer equation, depicted as Eq. (S5).

$$L = \frac{K\lambda}{\beta\cos\theta} \qquad \qquad \text{Eq. (S5)}$$

2. Experimental



Fig. S2. XRD patterns of CB1, ZIF67 and CM71.



Fig. S3. Performance of commercial catalysts catalyzing oxidation of BA.



Fig. S4. Cycle stability and different batches of (a,d) CM71-C, (b,e) ZIF67-C and (c,f) CB1-C for BA catalytic performance testing.



Fig. S5. In-situ DRIFTS spectra of CM71-C exposed to (a) 1000 ppm BA / N_2 and (c) 1000 ppm BA / Air, CB1-C exposed to (c,e) 1000 ppm BA / N_2 and (d,f) 1000 ppm BA / Air atmosphere.

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Р	Pore volu	S	Doro gizo		I ₁₉₂ /I ₆₈₄	Co ³⁺ /(Co ³	$O_{ads}/(O_{ads}$
Catalyst	me	$(m^2 \sigma^{-1})$	(nm)	D ^a (nm)		++Co ²⁺)	$+O_{latt})$
	$(cm^3 g^{-1})$	(m² g ²)	(mn)		(%)	(%)	(%)
CB1-C	0.1714	36.8207	12.1516	160.6	30.26	37.9	49.0
ZIF67-C	0.1589	27.0442	17.0076	155.6	0.21	45.1	49.4
СМ71-С	0.3255	44.1534	21.2708	125.1	0.02	48.1	50.2

 Table S2 Physicochemical parameters and surface element composition of CB1-C, ZIF67-C and CM71-C.

^a crystallite size is calculated by Scherrer's equation

Catalyst	T ₅₀ (°C)	T ₉₀ (°C)	$Y_{CO_2}(\%)$	Ea(kJ mol ⁻¹)	SA
СМ71-С	197	215	77.45	47.3	0.133
ZIF67-C	203	226	68.47	51.0	0.129
CB1-C	200	247	68.72	88.3	0.007
Commercial	253	281	63.58		

Table S3 Main data of catalysts for BA catalytic oxidation.

Table S4 Performance Comparison of Co₃O₄ catalysts with reported catalysts in BA oxidation.

Sample	BA concentration (ppm)	Space velocity (mL h ⁻¹ g ⁻ ¹)	T ₅₀ (°C)	T ₉₀ (°C)	Ref.
MnPA	1000	53050	150	180	5
MnO ₂	1000	53050	189	211	6
1%Pd/ZSM-5	1500	60000		310	7
2.5%Ag/Y	1000	30521		300~400	8
Ce ₁ Mn ₂	1000	15000	150	170	9

Part of the explanation for BA-TPSR:

By searching for BA in the mass spectrometry database of the National Institute of Standards and Technology (NIST), it can be known that after ionization, BA will show the strongest ion peak signal at m/z = 43, followed by that at m/z = 56. It was found that below 200 °C, both signals of the two catalysts could maintain good consistency. However, under anaerobic conditions, the two signals of CM71-C could not maintain consistency above 200 °C. This might be due to the fact that as the temperature increased, the adsorbed BA was partially oxidized by the catalyst ¹⁰, and the resulting intermediate products formed CH₃CO (methyl carbonyl) fragments with the same mass-to-charge ratio in the mass spectrometry. After introducing gaseous oxygen, the intermediate products were rapidly oxidized and could not be detected, so the two signals could maintain good consistency.

Position/cm ⁻¹	Assignment		
1760	C=O of aldehyde		
1700	Butyl acetate		
1640	N(C=C) of olefin		
1465	COO- of acetic acid		
1550-1520	Calleration		
1440-1400	Cardoxylate		
1384	$\delta(-CH_3)$ stretching vibrations of primary alcohols		
1373	CH ₃ bending vibration of butyl acetate		
1330	$\delta(OH)$ of ethanol		
1280	Stretching vibrations of C-OH in ethanol		
1035	Alpha (C-O) stretching vibrations of methanol		

Table S5 Assignment of infrared spectra in catalytic oxidation of BA.

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