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Supplementary information

Hydroxyl groups attached to Co^{2+} on the surface of Co_3O_4: A promising structure for propane catalytic oxidation

Kun Chen[a], Wenzhi Li [a,*], Zean Zhou [a,*], Qifu Huang[b], Yang Liu[a], Qiuyan Duan[a]

[a] Laboratory of Basic Research in Biomass Conversion and Utilization, Department of Thermal Science and Energy Engineering, University of Science and Technology of China, Hefei 230026, China

[b] Beijing Mechanical Eqiupment Institute, Beijing 100854, PR China

Table S1. Frequencies of functional groups present on three samples analyzed by in situ DRIFTS.

Modes	Infrared band wavenumber(cm-1)		
	Co3O4-C	Co3O4-S	Co3O4-O
$\delta_{as}(CH_3)$	1464		
$\delta(CH_2)$	1432		
$\delta_s(CH_3)$	1398		
ν(C-O)			1273
ν(C=O)	1720	1740	1740
$\nu_{as}(COO)$	1560		1560
	1536		
ν(OH)	3200-3800	3709	3718
		3616	3560
$\nu(CO_3)$		1543	
		1346	
		1433	

Table S2. The catalytic activity of propane oxidation (0.9% C_3H_8 in air, 30,000 ml/(h·g), 150,000 ml/(h·g) and 300,000 ml/(h·g) gas weight hourly space velocity, respectively) on Co_3O_4-S catalyst in this paper and propane oxidation activity results on other catalysts in previous research.These results indicate that the Co_3O_4-S catalyst prepared in our work exhibited good catalytic activity no matter at low or high space velocity.

Catalyst	Mass of Catalyst	Gas Flow Rate	the Space Velocity	T_{100}(°C)
Co_3O_4-S(this paper)	40mg	20ml/min(0.9% C_3H_8)	30000h^{-1}	210
Co_3O_4-S(this paper)	40mg	100ml/min(0.9% C_3H_8)	150000h^{-1}	220
Co_3O_4-S(this paper)	40mg	200ml/min(0.9% C_3H_8)	300000h^{-1}	250

Co_3O_4-GC-6[1]	200mg	100ml/min(1% C_3H_8)	30000h^{-1}	240
$Ni_{0.27}Co_{2.73}O_4$[2]	-	150ml/min(1% C_3H_8)	45000h^{-1}	420
CeCo30[3]	600mg	100ml/min(1% C_3H_8)	10000h^{-1}	260
MnO_2[4]	250mg	50ml/min(0.8% C_3H_8)	12000h^{-1}	280
Ru/CeO_2-R[5]	100mg	50ml/min(0.2% C_3H_8)	30000h^{-1}	200
Pd/Al_2O_3[6]	25mg	320ml/min(0.05% C_3H_8)	768000h^{-1}	500
$Pd_{55}Au_{45}/TiO_2$[7]	-	20ml/min(0.8% C_3H_8)	16000h^{-1}	300

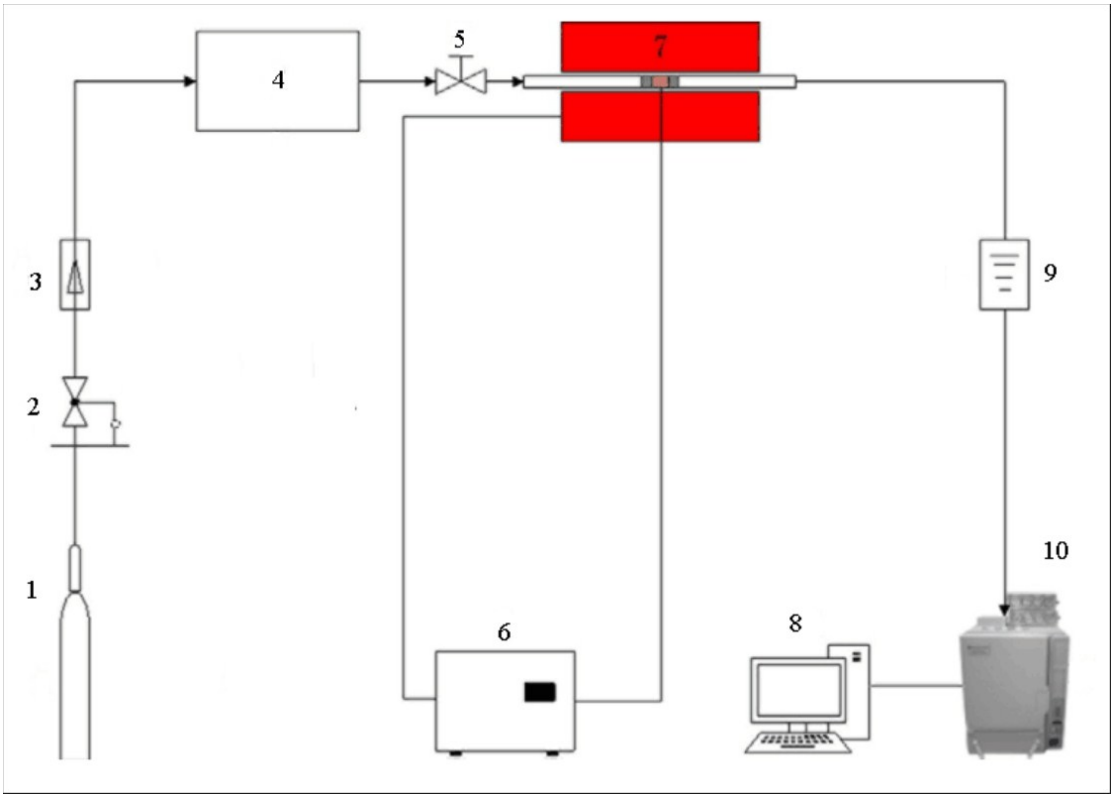
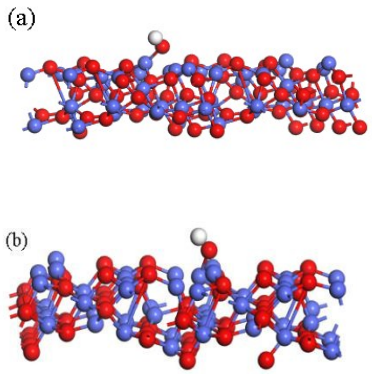


Figure S1. System of propane catalytic oxidation: 1) 0.9% propane in Air, 2) pressure-reducing valve, 3) flowmeter, 4) premixer, 5) check valve, 6) temperature controller equiped with thermocouple, 7) electric heating furnace, 8) computer to record chromatography data, 9) gas dryer, and 10) gas chromatograph(GC-1690).

Figure S2. DFT calculation models of a hydroxyl group attached to Co^{2+} (a) and a hydroxyl group attached to Co^{3+} (b) on the (311) planes of Co_3O_4. White: Hydrogen atom, red: Oxygen atom, blue: Cobalt atom. DFT calculations in this study were performed using CASTEP Tools in Materials Studio 7.0. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional for geometry optimization and energy calculations of these models was applied. Initially, the bulk spinel structure of Co_3O_4 was optimized by PBE functional and the kinetic cutoff energy was 340 eV. The (220) and (311) planes were modeled from the optimized Co_3O_4 spinel structure and the top layer was fixed and other layers were relaxed during the calculations. The vacuum space of 20Å along the c axis was applied to avoid the interactions between the neighboring slaps. The final energy of these systems was collected. More energy is released when the hydroxyl group is attached to Co^{2+} on the catalyst surface, indicating that the binding of the hydroxyl group to the Co^{2+} on the catalyst surface is more stable, which is in agreement with the experimental results.



Notes and references

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