The relationship between the surface oxygen species and the acidic properties of mesoporous metal oxides and their effects on propane oxidation

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Characterizations

Raman

The Raman spectra were collected with an HR LabRaman 800 configuration, equipped with a liquid nitrogen-cooled CCD detector using the 514.5 nm line of an Ar^+ laser. The laser power was 10 mW. Scan time was 30 s and the spectral range was 100-2000 cm^{-1}.
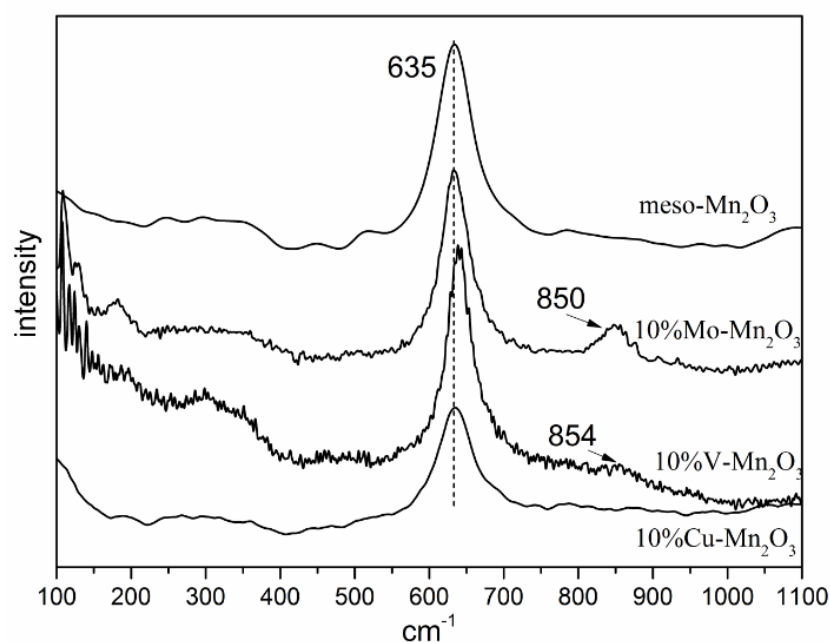

Fig. S1 Raman spectra of 10% V-Mn_2O_3, 10% Cu-Mn_2O_3, 10% Mo-Mn_2O_3, meso-Mn_2O_3 samples.

Raman band located at 635 cm^{-1} can be assigned to the Mn-O stretching vibration of the MnO_6 group.[S1] On the Mo-Mn_2O_3 catalyst, the vibration at 850 cm^{-1} is Mo-O-Mo vibration in highly dispersed surface molybdate ($[MoO_4]^{2-}$).[S2] As the vibrations at 300-340 cm^{-1} for small crystallites of bulk structure and at 955 cm^{-1} for surface molybdate were not detected, we consider that the Mo-O-Mo species on the Mo-Mn_2O_3 catalyst are dominated in highly

dispersed surface molybdate ($[MoO_4]^{2-}$). About the state of vanadia, researchers have reported that the vibrations at 1020~1035 cm^{-1} belong to the V=O vibrations of monovanadate species and the bands in the 860 cm^{-1} or 930 cm^{-1} can be ascribed to the stretching modes in polyvanadate species. [S3, S4, S5] In the present study, the vibrations at 1020~1035 cm^{-1} region did not be detected. We observed a very weak V-O-V bond centered at 854 cm^{-1}, if the band might be considered a peak. The V species could disperse well on V-Mn_2O_3 catalyst surface. Vibration peak of Cu aggregated state species were not detected on the Cu-Mn_2O_3.

HAADF-STEM and elemental mapping images

HAADF-STEM were performed using a Tecnai F20 G2 High-Resolution TEM (HRTEM) electron microscope. The composition of V-Mn_2O_3 and Mo-Mn_2O_3 were characterized using energy dispersive X-ray spectroscopy (EDX)–elemental mapping analysis. The FEI TIA software was used to control the STEM-EDX mapping.

Fig.S2A and Fig.S2B show HAADF-STEM and elemental mapping images of loaded V and Mo on meso-Mn_2O_3 surface. The V and Mo mapping prove the well distribution of the element signals on the surface of the particles.
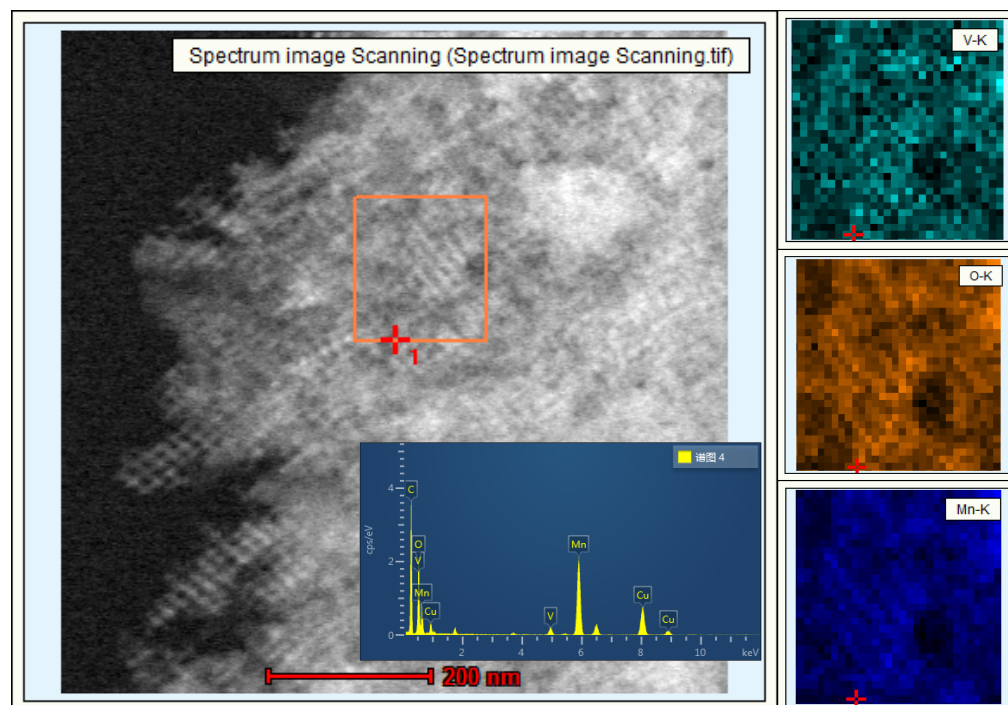

Fig. S2A HAADF-STEM and elemental mapping images of V are presented. Scale bar: STEM 200 nm, elemental mapping 100 nm.
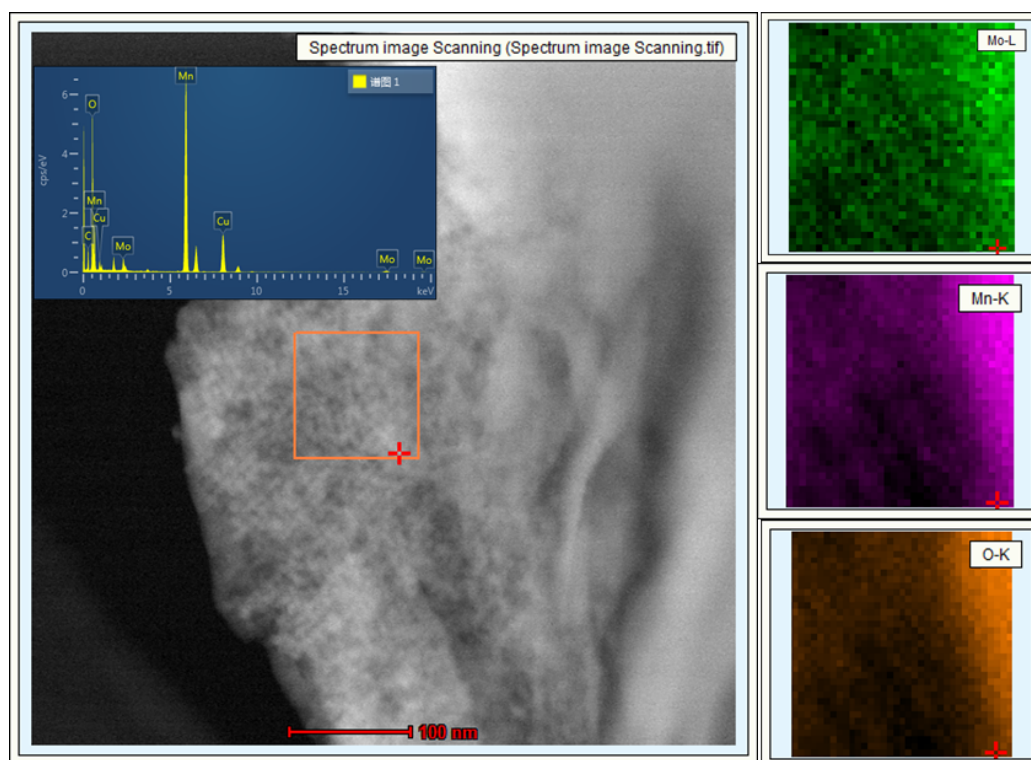
Fig. S2B HAADF-STEM and elemental mapping images of Mo are presented. Scale bar: HAADF-STEM 100 nm, elemental mapping 100 nm.

Table 1S. The performance of the catalysts. Reaction condition: Temperature 480ºC, GHSV = 4500 mL (g h)$^{-1}$, and $C_3H_8 : O_2 = 1 : 1$ (molar ratio)

catalyst	Conversion (%)	Selectivity (%)									
		C_1	$C_{2=}$	$C_{3=}$	CH_2O	ALD	ACR	AcT	AcA	CO	CO_2
Meso-Mn_2O_3	24.3	2.2	20.6	18.6	0.0	0.0	0.0	0.0	0.0	0.0	58.2
bulk-Mn_2O_3	21.1	4.8	30.6	22.8	0.0	0.0	0.0	0.0	0.0	0.0	41.1
10%Mo-Mn_2O_3	22.2	1.3	12.0	37.2	1.5	1.2	2.2	0.0	0.0	11.6	33.0
10%Cu-Mn_2O_3	19.7	0.9	12.2	29.5	0.2	0.6	0.0	0.0	0.0	0.0	56.6
1‰V-Mn_2O_3	25.7	3.4	27.5	17.4	1.1	0.0	0.0	0.0	0.0	0.0	50.2
1%V-Mn_2O_3	24.4	7.1	35.8	28.7	3.3	1.0	0.0	0.0	0.0	0.0	23.5
5%V-Mn_2O_3	<u>25.6</u>	6.0	27.8	31.0	3.3	3.2	0.1	0.0	1.1	0.0	26.9
10%V- Mn_2O_3	28.8	1.5	9.0	51.0	1.3	1.2	1.1	1.1	1.0	21.1	11.6
15%V-Mn_2O_3	11.9	0.3	4.9	41.6	0.0	0.0	0.0	0.0	0.0	36.4	16.8

[a.] C_1: methane, $C_{2=}$: ethylene, $C_{3=}$: propylene, CH_2O: formaldehyde, ALD: acetaldehyde, ACR: acrolein, AcT: acetone, AcA: acrylic acid, AA: acetic acid
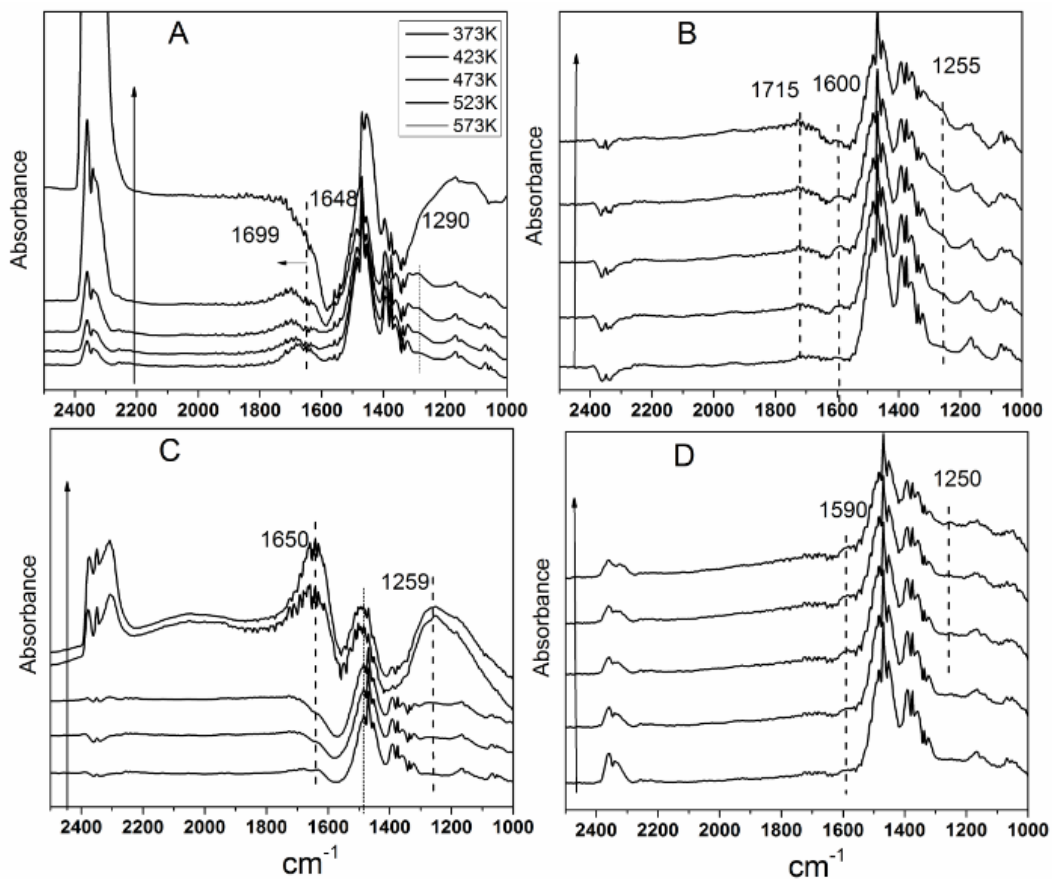
IR of propane + O₂ adsorption

Fig. S3 FT-IR spectra of reaction atmosphere (propane : O_2 =1 : 1) adsorbed on   (A) meso-Mn_2O_3, (B) 10% V-Mn_2O_3, (C) 10% Cu-Mn_2O_3 , and (D) 10% Mo-Mn_2O_3 at 373, 423, 473, 523 and 573 K.
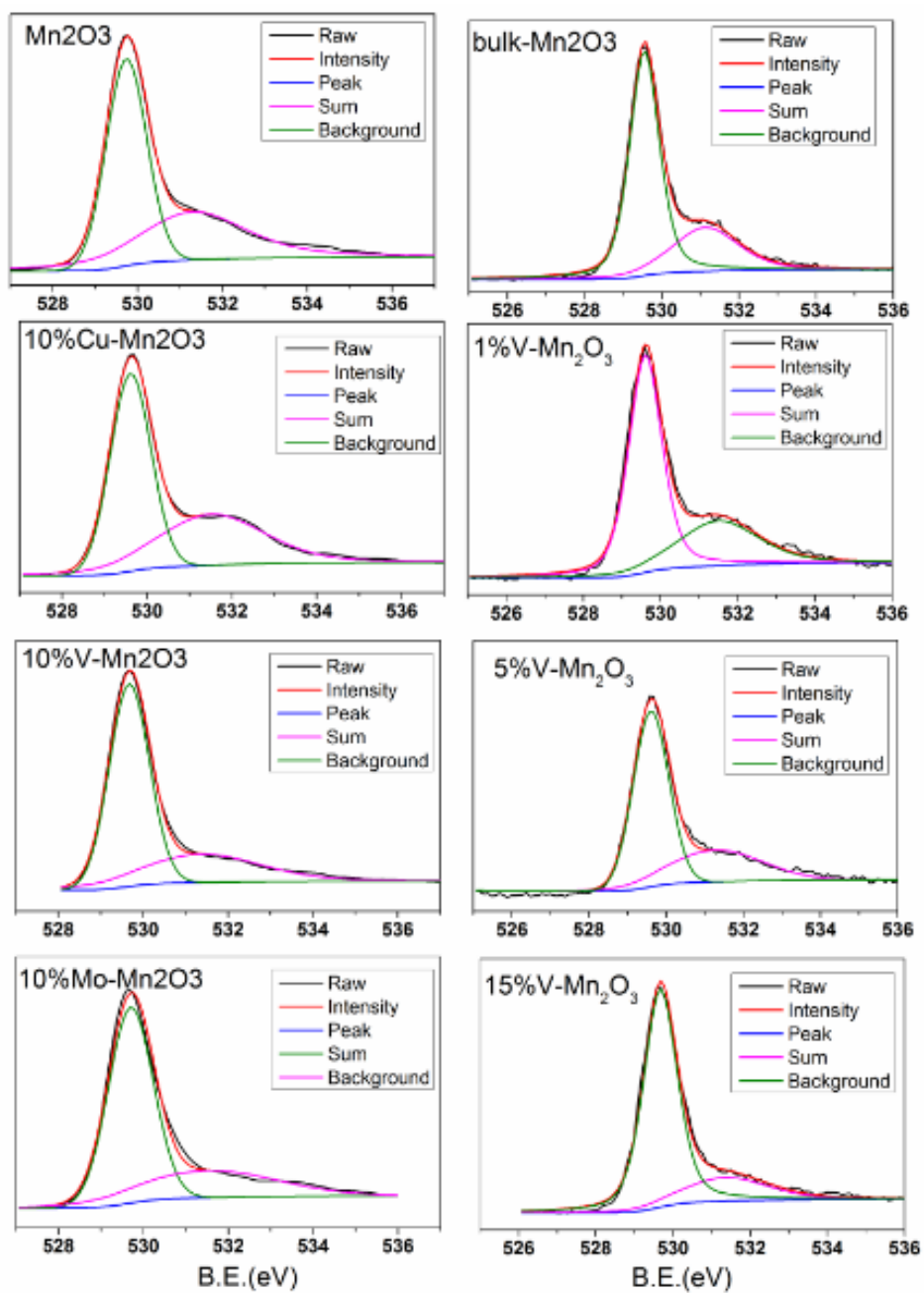
XPS

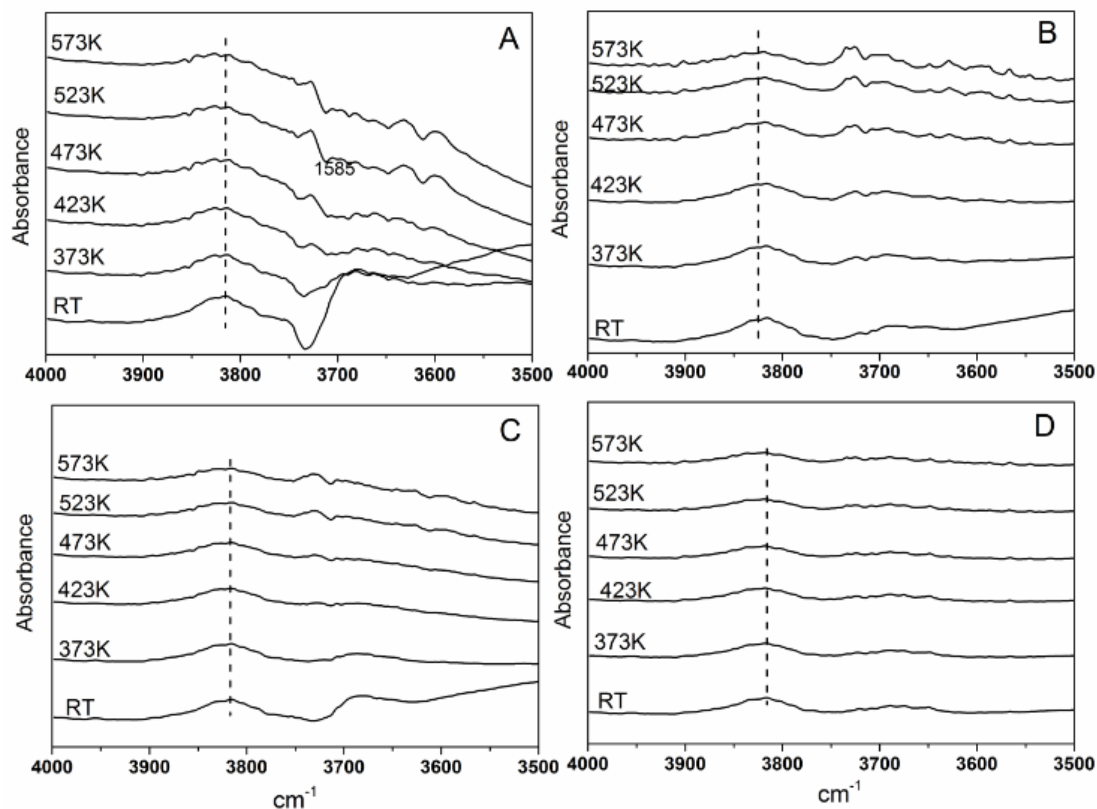**Fig. S4** X-ray O1s photoelectron emission spectra from the indicated materials.

Fig.S5 FT-IR spectra of -OH (in the absence of O_2) on (A) meso-Mn_2O_3, (B) 10% V-Mn_2O_3, (C) 10%Cu-Mn_2O_3 10%Mo-Mn_2O_3, and (D) 10%Mo-Mn_2O_3,10%Cu-Mn_2O_3 from 323 to 573K.

References

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