

Electronic Supplementary Information

ANbO₃ (A=Na, K) and A₂Nb₂O₇ (A'=Ca, Sr) composite oxides for oxidative coupling of methane and oxidative dehydrogenation of ethane: Perovskite vs. layered perovskite

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1. Supplementary Experimental Information

1.1 Catalyst characterization

The crystal phase structure of the fresh and spent catalysts was analyzed by X-ray powder diffraction (XRD) which was carried out in a Bruker AXS D8 Focus of 40KV acceleration voltage and 30 mA emission current using a Cu target and K α -ray irradiation, 2 θ gap of 10° to 80° with step of 0.02°/s.

X-ray photoelectron spectroscopy (XPS) characterization was carried out in a ESCALAB250xi X-ray photoelectron spectroscopy system equipped a single MgK α X-ray source operated at 300 W and 15 kV voltage. The binding energies were calibrated based on the C 1s peak of graphite at 284.6 eV.

The specific surface area of the fresh and spent catalysts was measured by nitrogen adsorption-desorption at 77 K on an ST-08B instrument and determined using the Brunauer–Emmett–Teller (BET) equation.

In situ Raman spectra of all the catalysts were performed on a Renishaw in Via instrument using a 532 nm laser source equipped with a Linkam TS 1500 micro-size in situ cell, with a scanning Raman shift range of 100-1000 cm^{-1} . All samples were pretreated in an Ar atmosphere with a gas flow rate of 30 mL/min at 800 °C for half an hour and then cooled to room temperature. An air flow was introduced at a rate of 30 mL/min and heated at a rate of 10 °C/min from ambient temperature to 800 °C. Raman spectra were collected at 25, 200, 400, 600, and 800 °C.

CH_4 -TPSR-MS, C_2H_6 -TPSR-MS, CH_4 -pulse and C_2H_6 -pulse test were performed on a BelCata II apparatus equipped with a BelMass using quadruple as a mass analyzer. The outlet products (C_2H_4 $m/z=27$, C_2H_6 $m/z=30$ CO $m/z=28$ and CO_2 $m/z=44$) were measured instantaneously with the mass spectrometer system. Typically, a certain weight of the samples was pretreated at 800 °C under a pure He atmosphere (30 mL/min) for 30 min, which was then cooled to 50 °C. The sample pre-treatment for all subsequent testing experiments is the same as this process.

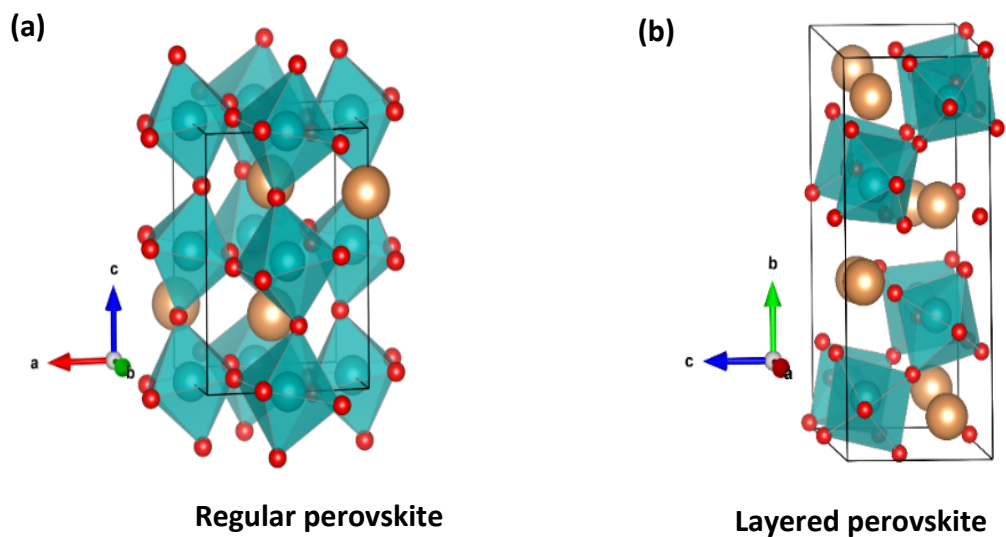
For CH_4 -TPSR-MS experiment, 200 mg of a catalyst sample was first heated at a rate of 10 °C/min in a He atmosphere (60 mL/min) to 800 °C for removing surface impurities. The sample was then cooled to 50 °C and introduced into a mixed gas (CH_4 :He=3:4) with a flow rate of 60 mL/min at the same temperature; subsequently, it was heated to 800 °C at a rate of 10 °C/min to record the relevant mass spectrometry signals.

For CH_4 -pulse experiment, 200 mg of catalyst is heated for half an hour at 10 °C/min in a 10% O_2 -He (flow rate of 30 mL/min) atmosphere from room temperature to 800 °C to achieve saturation of oxygen adsorption. After He gas (flow rate of 30 mL/min) was incorporated for 15 min to remove physically adsorbed O_2 on the surface, 1 mL of methane was pulsed every 3 min to collect relevant mass spectrometry signals.

For C_2H_6 -TPSR-MS experiment, the samples were subjected to a C_2H_6 :He=1:8 flow rate of 60 mL/min at 50 °C and then heated to 700 °C at a rate of 10 °C/min to record the relevant mass spectrometry signals.

Electron paramagnetic resonance (EPR) spectra of reactive oxygen species were recorded with a JEOL FA-200 EPR Spectrometer, operating with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

2. Supplementary Results



Scheme S1. Crystalline phase structures of the (a) regular perovskite and (b) monoclinic layered perovskite.

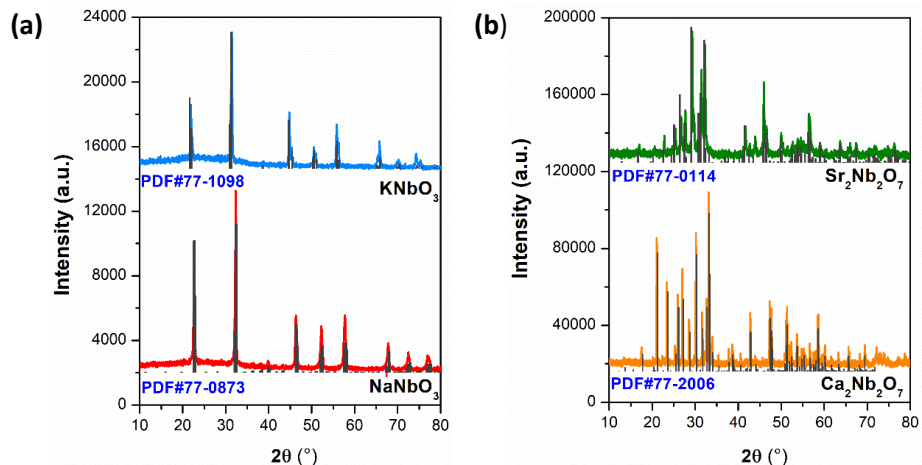


Fig. S1 XRD patterns of the (a) ANbO_3 (A=Na, K) and (b) $\text{A}_2\text{Nb}_2\text{O}_7$ (A=Ca, Sr) samples.

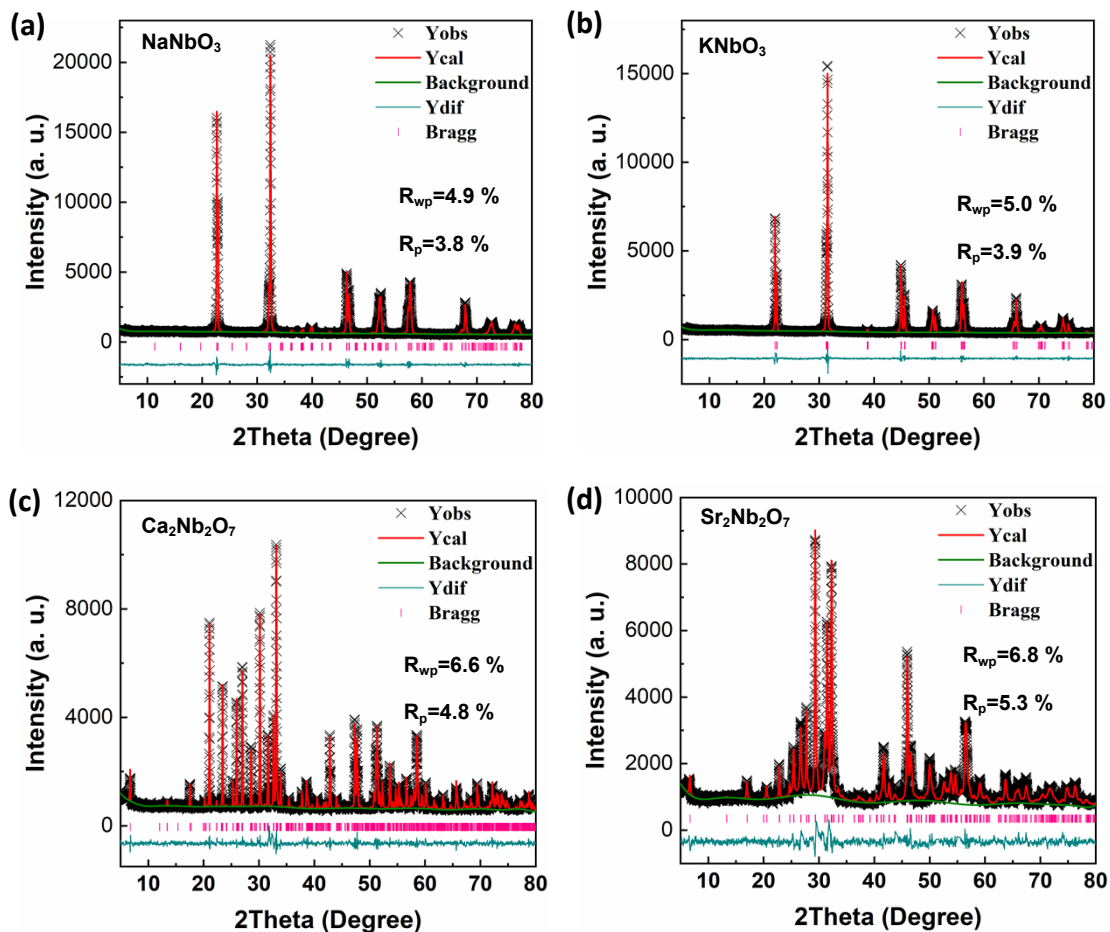


Fig. S2 The Rietveld refinement XRD patterns of (a) NaNbO_3 , (b) KNbO_3 , (c) $\text{Ca}_2\text{Nb}_2\text{O}_7$, (d) $\text{Sr}_2\text{Nb}_2\text{O}_7$.

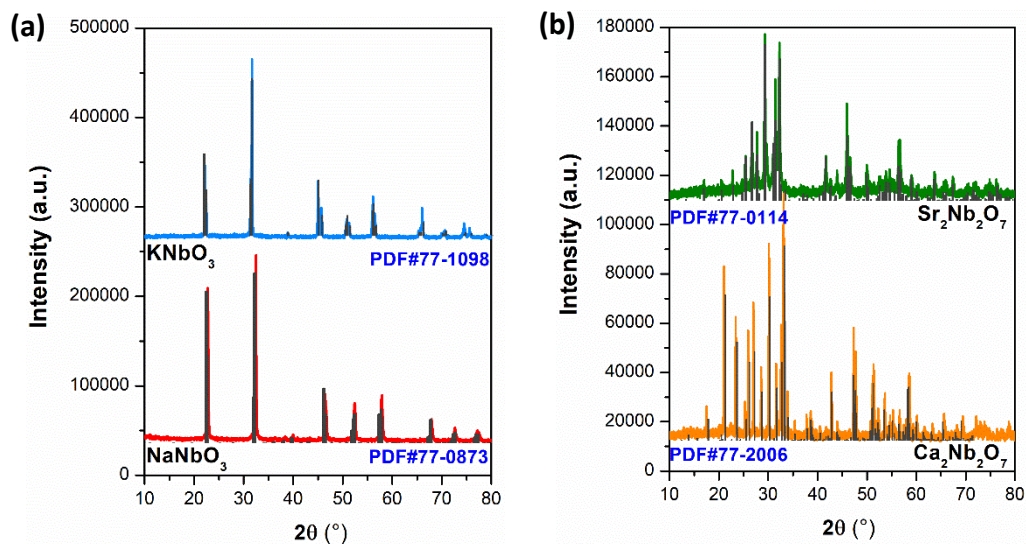


Fig. S3 XRD patterns of the spent catalysts after OCM reaction (a) ANbO_3 (A=Na, K) and (b) $\text{A}_2\text{Nb}_2\text{O}_7$ (A=Ca, Sr) samples.

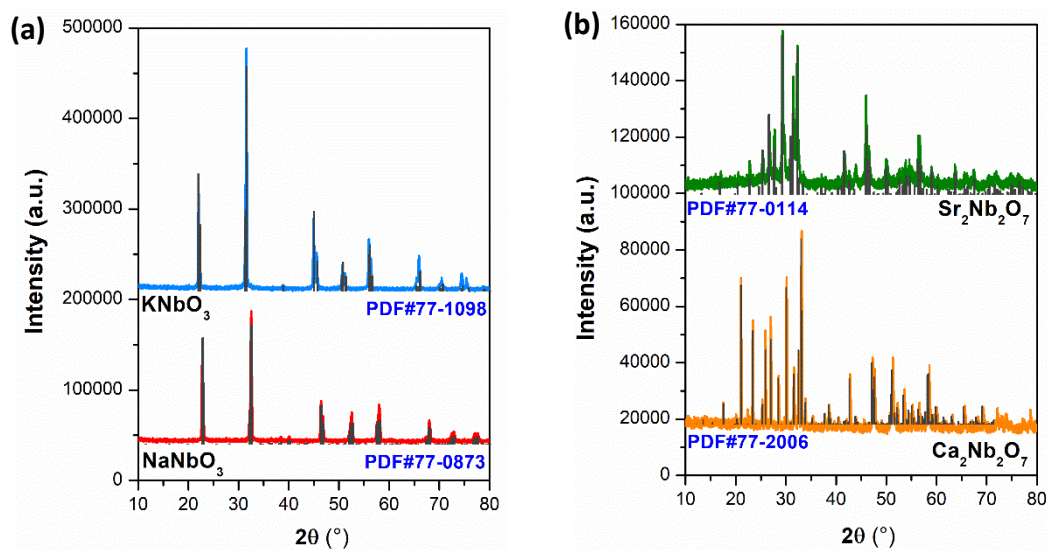


Fig. S4 XRD patterns of the spent catalysts after ODHE reaction (a) ANbO_3 (A=Na, K) and (b) $\text{A}_2\text{Nb}_2\text{O}_7$ (A=Ca, Sr) samples.

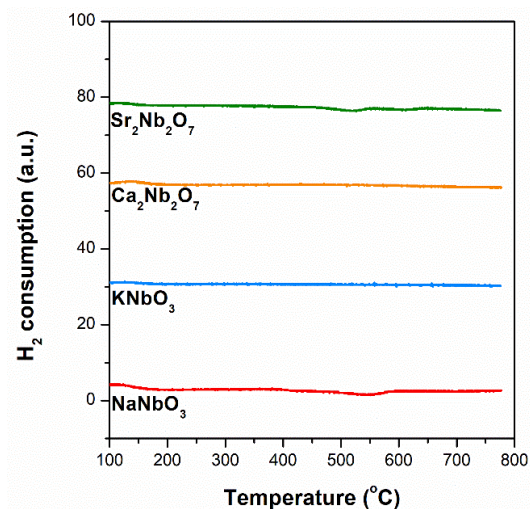


Fig. S5 H₂-TPR profiles of the ANbO₃ (A=Na, K) and A₂Nb₂O₇ (A=Ca, Sr) samples.

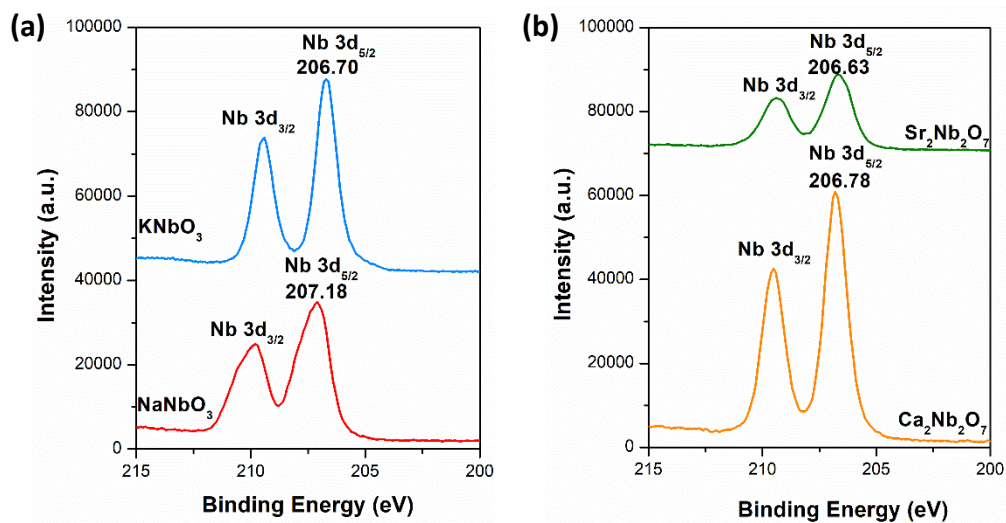


Fig. S6 Nb 3d spectra of (a) ANbO₃ (A=Na, K) and (b) A₂Nb₂O₇ (A=Ca, Sr) samples.

Table S1 Refined Nb-O bond lengths of ANbO₃ (A=Na, K) and A₂Nb₂O₇ (A=Ca, Sr) samples.

Samples	Nb-O bond length (Å)	Average Nb-O bond length (Å)	Samples	Nb-O bond length (Å)	Average Nb-O bond length (Å)
NaNbO ₃	Nb-O1 1.982 (1)	1.992	Ca ₂ Nb ₂ O ₇	Nb-O2 2.575 (6)	2.052
	Nb-O2 1.980 (1)			Nb-O3 2.003 (4)	
	Nb-O3 2.103 (2)			Nb-O3 2.003 (4)	
	Nb-O3 1.884 (1)			Nb-O4 2.120 (5)	
	Nb-O4 2.096 (2)			Nb-O5 1.760 (5)	
	Nb-O4 1.904 (1)			Nb-O6 1.851 (4)	
KNbO ₃	Nb-O1 2.037 (1)	2.011	Sr ₂ Nb ₂ O ₇	Nb-O4 1.786 (1)	2.062
	Nb-O2 1.958 (1)			Nb-O5 1.999 (1)	
	Nb-O2 2.124 (1)			Nb-O6 2.357 (2)	
	Nb-O2 2.124 (1)			Nb-O7 1.867 (1)	
	Nb-O2 1.910 (2)			Nb-O8 2.253 (2)	
	Nb-O2 1.910 (1)			Nb-O9 2.109 (2)	