Supplementary Information (SI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2024

**Supplementary Information (SI) for Catal. Sci. Technol.
This journal is © The Royal Society of Chemistry 2024**

Supporting Information

Co-catalysis of Al_2O_3-supported Ni nanoparticles and VO_x in propane dehydrogenation

Guomin Li [a,b, c], Bin Wang [a], Xingchao Dai [a], Feng Shi [a], Yong Ding [b], Xinjiang Cui [a]*

[a] State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou 730000, China.

[b] Key Laboratory of Advanced Catalysis of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, No. 222 South Tianshui Road, 730000, Lanzhou, China.

[c.] University of Chinese Academy of Sciences, No. 19 A, Yuquanlu, Beijing, 100049, China.

* Corresponding author: xinjiangcui@licp.cas.cn（Prof. Dr. Xinjiang Cui）

Experimental

Catalyst preparation

The catalyst was prepared by the gel method. The preparation of NiV_2O_X/Al_2O_3 was exemplified: 5.50 g of ammonium carbonate was dissolved in 35ml of water to obtain an ammonium carbonate solution. 0.50 g of $Ni\ (NO_3)_2\ 6H_2O$, 0.56 g of $VOSO_4$, and 14.70 g of $Al\ (NO_3)_3\ 9H_2O$ were dissolved in 20 ml of water in a 150 ml beaker, and then the beaker was transferred to an oil bath at 70 °C and stirred. Add ammonium carbonate solution into it to form gel, and then continue stirring for 2 h. Subsequently, the gel was transferred into a surface dish and dried in a 100 °C oven for 10 h. The dried samples were placed in a muffle furnace and calcined at 500 °C for 3 h under air atmosphere to obtain the catalyst NiV_2Ox-Al_2O_3. The NiV_2Ox-Al_2O_3 was reduced for 2 h at 500 °C in a flow of 2 ml/min H_2 and 18ml/min Ar, denoted as NiV_2Ox-Al_2O_3-fresh. After reduction, turned off H_2 and kept Ar blowing for 30 minutes. Then, introduced 3.6 ml/min of C_3H_8, and the sample reacted for 2 h was recorded as NiV_2Ox-Al_2O_3-act. where "fresh" represents the reduced sample and "act" represents the activated sample. Other catalysts were prepared according to the same procedure, and the raw material samples were weighed as needed.

catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Smartlab-SEX X-ray diffractometer. The contents of various metal elements in the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The TEM images were obtained on a Talos F200S microscope instrument. Textual properties of the catalysts were measured with Quantachrome IQ2 by nitrogen adsorption at -196 °C. The samples were outgassed at 300 °C for 3h before measurements. The data was analyzed using the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was obtained by a VG ES-CALAB 210 instrument equipped with a 5 keV Ar ion gun. To obtain a fresh surface state of the active species, the sample were etched with Ar ions for 40 s in a low-energy state of 2000 eV and then analyzed again by XPS.

H_2 temperature programmed reduction (H_2-TPR) was conducted on the chemical adsorption analyzer (TP-5080d-tianjin Xianquan industry and Trade Co., Ltd.). The catalyst was pretreated at 400 ^oC for 1 h with flowing He, and then cooled to room temperature. Subsequently, the sample was flushed by 5% H_2/N_2 (40 ml/min) until the baseline is stable. The catalyst was reduced from room temperature to 900 ^oC at the rate of 10 ^oC/min and maintain for 20 minutes, while recording the reduction curve.

NH_3 temperature-programmed desorption (NH_3-TPD) was conducted on the chemical adsorption analyzer (TP-5080d-tianjin Xianquan industry and Trade Co., Ltd.). 0.1 g of the corresponding catalyst was pretreated in situ in the reaction tube, and then cooled to room temperature with flowing He. At room temperature, 5% NH_3/He (15 ml/min) was introduced for 30 min, and then switched back to He (40 ml/min) to purge the sample to a stable baseline. Subsequently, it was heated to 700 °C at a heating rate of 10 °C/mind, and the desorption curve was recorded at the same time.

C_3H_8/H_2 temperature-programmed desorption (C_3H_8/H_2-TPD) and the temperature programmed surface reaction of propane (C_3H_8-TPSR) experiments were performed on a fixed bed reactor equipped with an on-line mass spectrometer (Shanghai Pro-tech Limited Company). 0.5 g of the sample was placed in a fixed bed reactor for in-situ pretreatment as needed, and then lower it to room temperature. C_3H_8/H_2-TPD: C_3H_8/H_2 (15 ml/min) was introduced for 30 min, and then switched to Ar (18 ml/min) to purge the sample to a stable baseline. Subsequently, it was heated to 500 °C at a heating rate of 10 °C/min and maintain for 30 minutes, while recording the desorption curve. C_3H_8-TPSR: 3.6 ml/min of C_3H_8 and 18 ml/min of Ar were introduced and the mass spectrometry signal was recorded. When the mass spectrometry signal stabilized, the heating was started at a heating rate of 10 °C/min to 550 °C, and the corresponding m/z signal curve was recorded. The mass spectrometry signals to be detected included H_2 (m/z=2), C_3H_8 (m/z=29), and C_3H_6 (m/z=41).

In situ FTIR was collected on the experimental device built in our institute. After in situ reduction of the catalyst in the sample cell, propane (10 ml/min) and N_2 (20 ml/min) were introduced at 500 °C and maintained for 2h. Subsequently, flushed with N_2 for 20 min (20 ml/min). The infrared spectrum was continuously collected from the time when propane was introduced to the time when purging was completed.

Catalytic evaluation

0.5 g of calcined catalyst was placed in a fixed bed reaction tube. The catalyst was reduced in situ at 500 °C in a stream of 2 ml/min of H_2 and 18 ml/min of Ar for 2 h. After reduction, H_2 was turned off, and the catalyst was purged with Ar for 30 min, and then introduce 3.6 ml/min of C_3H_8 to start the reaction. The gas from the reactor outlet was introduced into Agilent gas chromatography for in-line detection, and the gas after the reaction was quantified by the standard curve method. The propane conversion and propylene selectivity were calculated by Equations (1) and (2), respectively:

$$C = \left(1 - \frac{3 \times F_{C_3H_8}}{\sum_i i \times F_{Ci\%}}\right) \times 100\% \qquad (1)$$

$$S_i = \frac{i \times F_{Ci}}{\sum_i i \times F_{Ci\%}} \times 100\% \qquad (2)$$

Where F means the mole fraction of each component in the outlet gas of the fixed bed, and i means the number of C atoms contained in each component.

Regeneration stability

After 12 h of reaction, the feed was switched to Ar gas purge catalyst and reduced to room temperature. The spent catalyst was heated to 500 °C at a rate of 5 °C/min in an air-atmosphere muffle furnace for 2 h, after which the performance was retested under the same conditions.

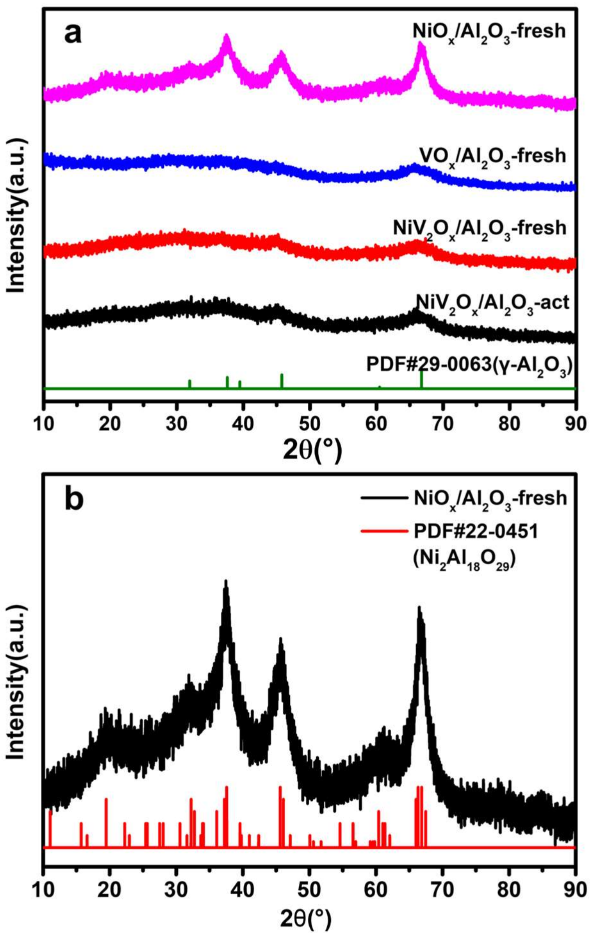

Fig.S1 XRD patterns of different catalysts

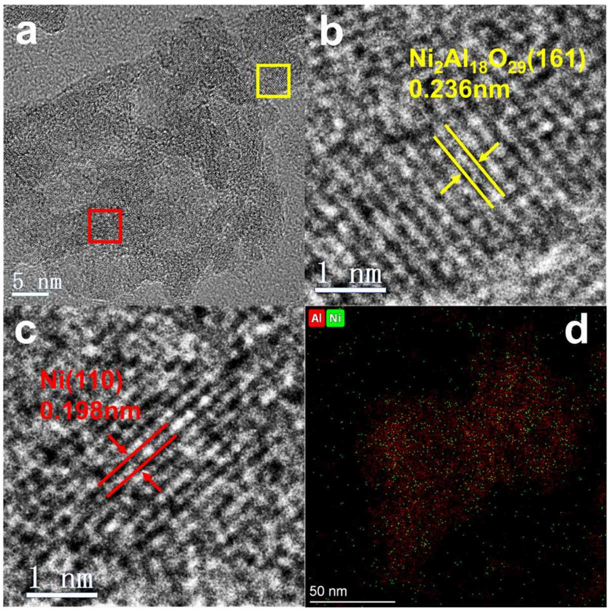

Fig.S2 (a) TEM image of NiO_x/Al_2O_3-fresh; The lattice information within the corresponding color box in a: (b) $Ni_2Al_{18}O_{29}$, (c) Ni; (d) EDS mapping of the NiO_x/Al_2O_3-fresh with the signals attributed to the different elements shown as Ni and Al.

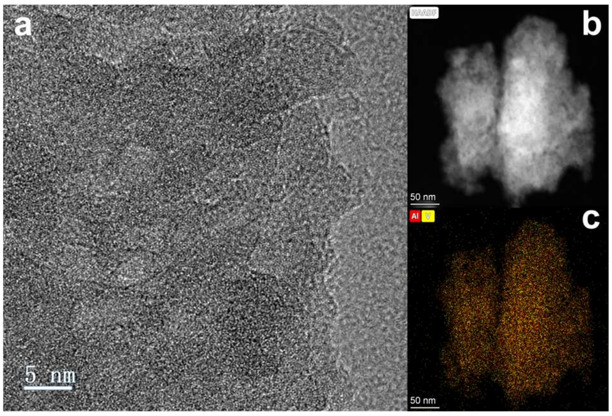

Fig.S3 (a) TEM image of VO_x/Al_2O_3-fresh; (b) The HAADF-STEM imaging of VO_x/Al_2O_3-fresh; (c) EDS mapping of the VO_x/Al_2O_3-fresh shown in b, with the signals attributed to the different elements shown as V and Al.

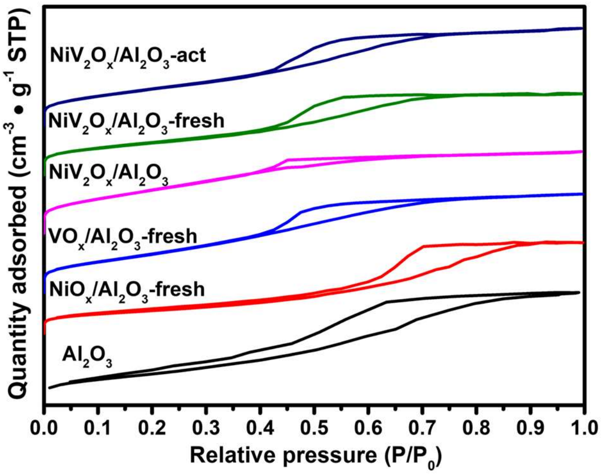

Fig.S4 N_2 adsorption-desorption isotherms of different catalysts

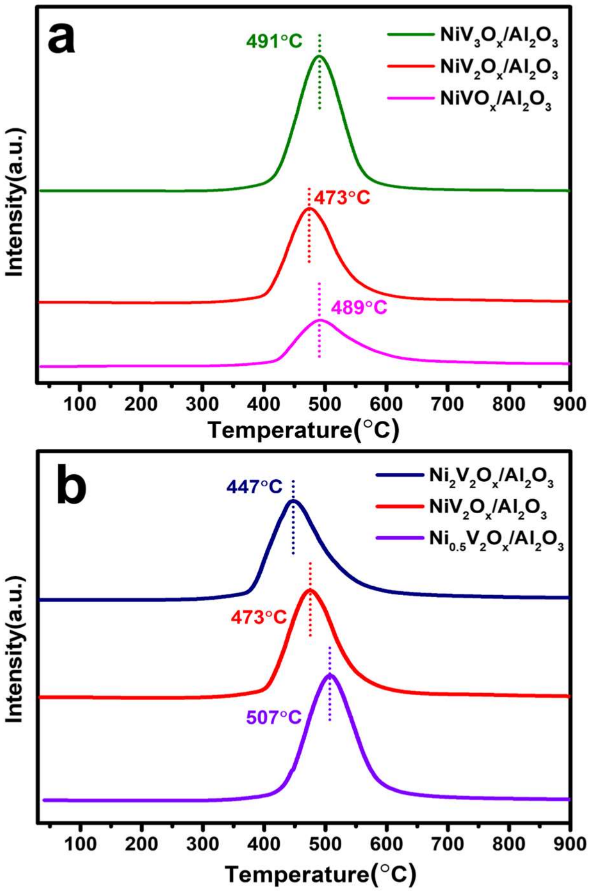

Fig.S5 H_2-TPR spectra of different catalysts: (a) Fixed V loading, changing Ni/V ratio; (b) Fixed Ni loading, changing Ni/V ratio.

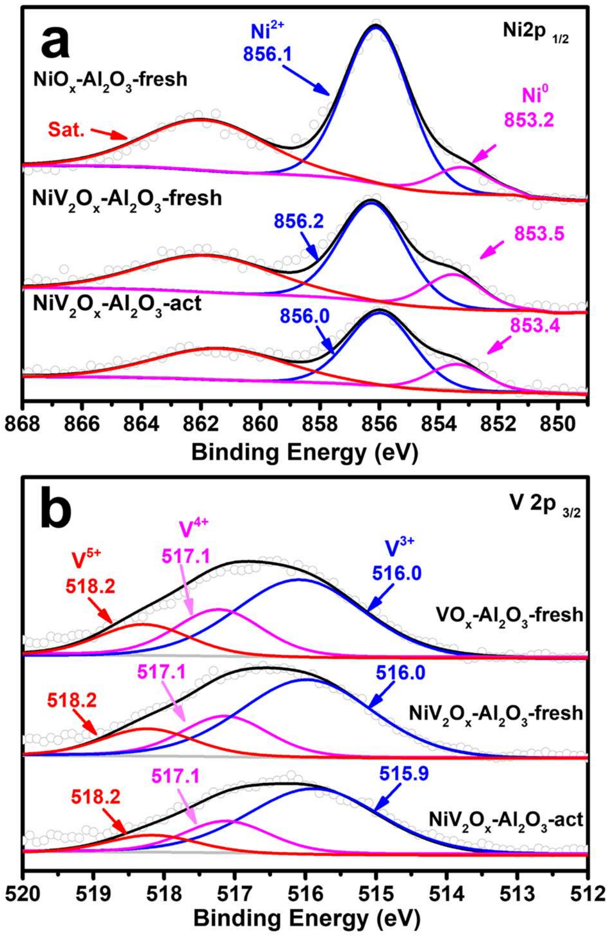

Fig.S6 XPS spectra of (a) Ni2p and (b) V2p with different catalysts.

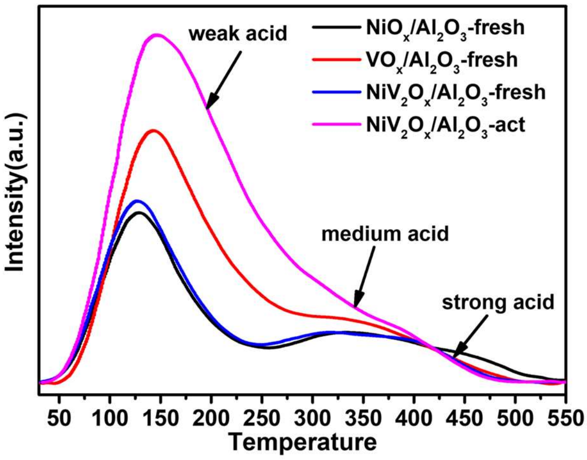

Fig.S7 NH_3-TPD profiles of different catalysts

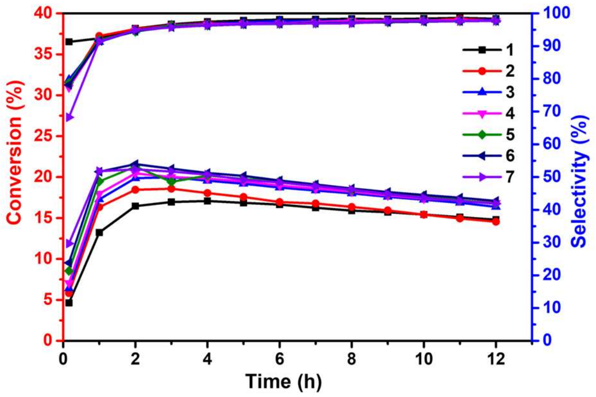

Fig.S8 Regeneration test of NiV_2O_x/Al_2O_3. Reaction conditions:0.5 g catalyst, 3.6ml/min of C_3H_8, 18ml/min of Ar, 500 ^oC. Regeneration condition: air atmosphere, calcination at 500 ^oC for 2 h.

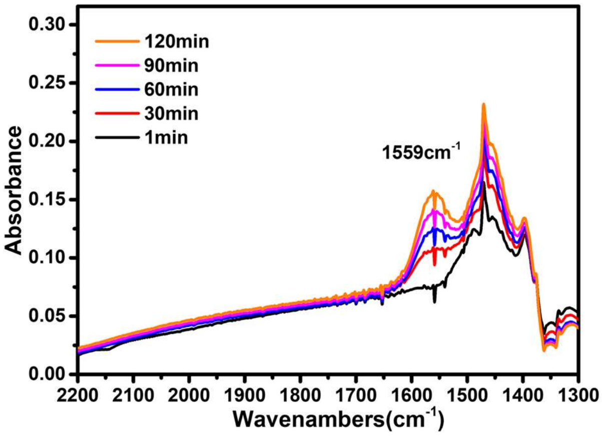

Fig.S9 In-situ FTIR spectra during induction period.

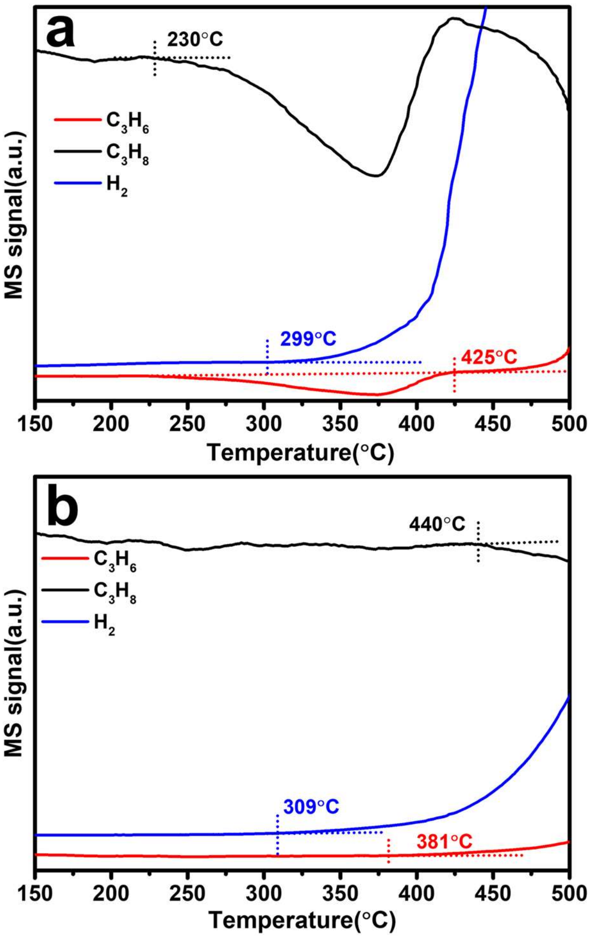

Fig.S10 C_3H_8-TPSR on (a) NiO_x/Al_2O_3-fresh and (b) VO_x/Al_2O_3-act.

Table.S1 Theoretical and actual metal loading of each catalyst and their TOF at 2 h of reaction.

Sample	theoretical loading[a]		actual loading[b]		TOF[c]
	Ni (wt%)	V (wt%)	Ni (wt%)	V (wt%)	($mmol_{C_3H_6}$ * mol_M^{-1} * s^{-1})
NiO_x/Al_2O_3	5.00	-	3.97	-	0.694
VO_x/Al_2O_3	-	8.67	-	3.65	0.270
$NiVO_x/Al_2O_3$	5.00	4.34	3.52	1.88	0.836
NiV_2O_x/Al_2O_3	5.00	8.67	3.37	3.55	0.662
NiV_3O_x/Al_2O_3	5.00	13.01	2.99	4.87	0.618
$Ni_{0.5}V_2O_x/Al_2O_3$	2.50	8.67	1.97	4.26	0.591
$Ni_2V_2O_x/Al_2O_3$	10.00	8.67	6.96	3.73	0.360

a Ideal metal loading based on carrier quality.

b Metal loading measured by ICP based on catalyst quality.

c M represented the total molar of active metals obtained based on ICP results.

Table.S2 The texture property of each catalyst and the proportion of different valence states of V in each catalyst

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	D_{BJH} (nm)	VO_x species proportion		
				V^{3+}(%)	V^{4+}(%)	V^{5+}(%)
Al_2O_3	356.8	0.48	4.41	-	-	-
NiO_x/Al_2O_3-fresh	247.2	0.41	4.19	-	-	-
VO_x/Al_2O_3-fresh	455.8	0.35	3.71	60.61	23.03	16.36
NiV_2O_x/Al_2O_3	514.1	0.42	3.52	-	-	-
NiV_2O_x/Al_2O_3-fresh	349.4	0.31	3.73	64.10	21.15	14.74
NiV_2O_x/Al_2O_3-act	413.5	0.39	4.44	66.67	20.67	12.67