SUPPORTING INFORMATION

Al_2O_3-Supported W-V-O bronzes catalysts for oxidative dehydrogenation of ethane

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CONTENTS:

Catalyst Preparation

Reference materials were synthesized and used for characterization purposes and catalytic tests:

a) V-containing *h*-WO_3 bronze with HTB structure were prepared by hydrothermal synthesis according to the preparation procedure described previously [ref. 1]. Finally, the sample was heat-treated at 600ºC/2h in N_2 atmosphere. This sample was named as **WV-HT**.

b) Vanadium oxide supported on alumina**.** This is a benchmark catalyst used for the oxidative dehydrogenation of alkanes [ref. 2]. This material was prepared by the wet-impregnation method of γ-Al_2O_3 using an aqueous solution of ammonium metavanadate. The mixture was rotaevaporated until complete dryness and the material was dried at 110°C overnight. Finally, the sample was calcined at 600ºC for 6 h. The sample is named as **VOx/AL**.

c) Vanadium oxide supported on tungsten hexagonal bronze supported on alumina. It was prepared by the same method than (VOx/AL**)**, i.e. impregnation with an aqueous ammonium metavanadate solution, but using an alumina supported tungsten hexagonal bronze (which was previously prepared by using reflux) rather than pure alumina. This sample was finally heat-treated as 600ºC in N_2. This sample was named as **V/W/AL**.

d) Al_2O_3-supported V-W-O oxide catalysts was prepared by impregnation of alumina with an aqueous solution of ammonium metavanadate and ammonium tungstate. The catalysts was finally heat-treated as 600ºC in N_2. This sample is named as **VW/AL**.

In all cases, the V/W atomic ratio was ca. 0.2.

Table S1. Characteristics of catalysts used as references

Catalyst	Synthesis Procedure	S_{BET} ($m^2\ g^{-1}$)	V/W (XPS)	V/Al (XPS)
WV-HT	Hydrothermal synthesis	19	0.090	0
VOx/AL	Impregnation of γ-Al_2O_3 with aqueous solution of ammonium metavanadate	186	0	0.015
V/W/AL	Impregnation of WOx/γ-Al_2O_3 [(a)] with aqueous solution of ammonium metavanadate	130	0.23	0.023
VW/AL	Impregnation of γ-Al_2O_3 with aqueous solution of ammonium metavanadate and ammonium tungstate	132	0.20	0.015

a) The sample WOx/γ-Al_2O_3 was prepared by impregnation of γ-Al_2O_3 with an aqueous solution of ammonium tungstate and ammonium oxalate and heat-treated at 450ºC for 2h in N_2.

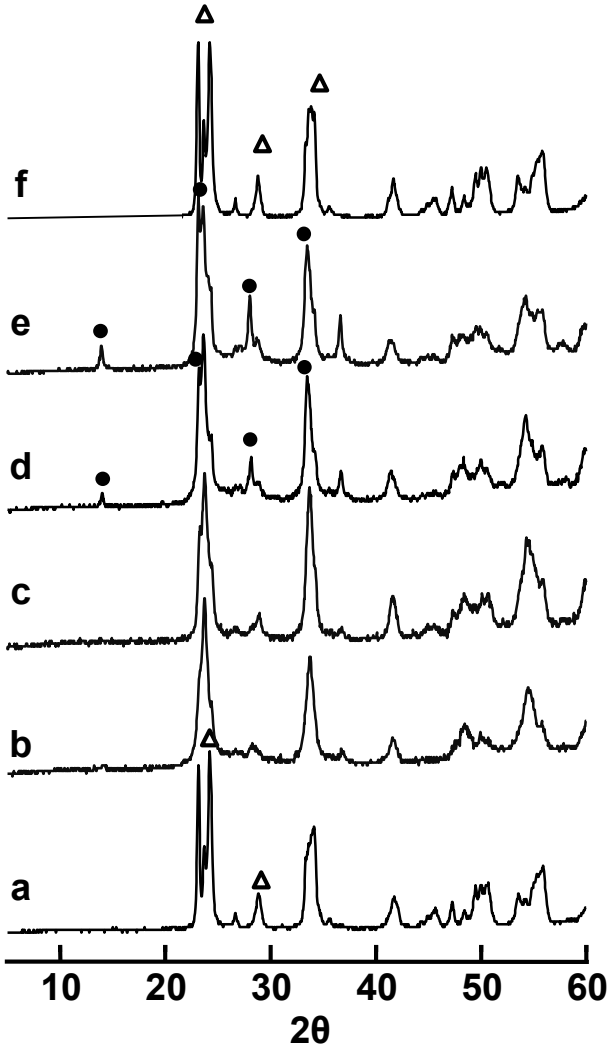

Fig. S1. XRD pattern of $VOSO_4$ + APT, heat-treated under nitrogen at 600 ºC, using different heating rates and hold times: a) 3ºC min^{-1}, hold for 3 h; b) 10ºC min^{-1}, hold for 3 hours; c) 100ºC min^{-1}, hold for 1 hours; d) 100ºC min^{-1}, hold for 2 hours; e) 100ºC min^{-1}, hold for 3 hours; f) 100ºC min^{-1}, hold for 5 hours. Symbols: HTB structure (●); monoclinic WO_3 (Δ).

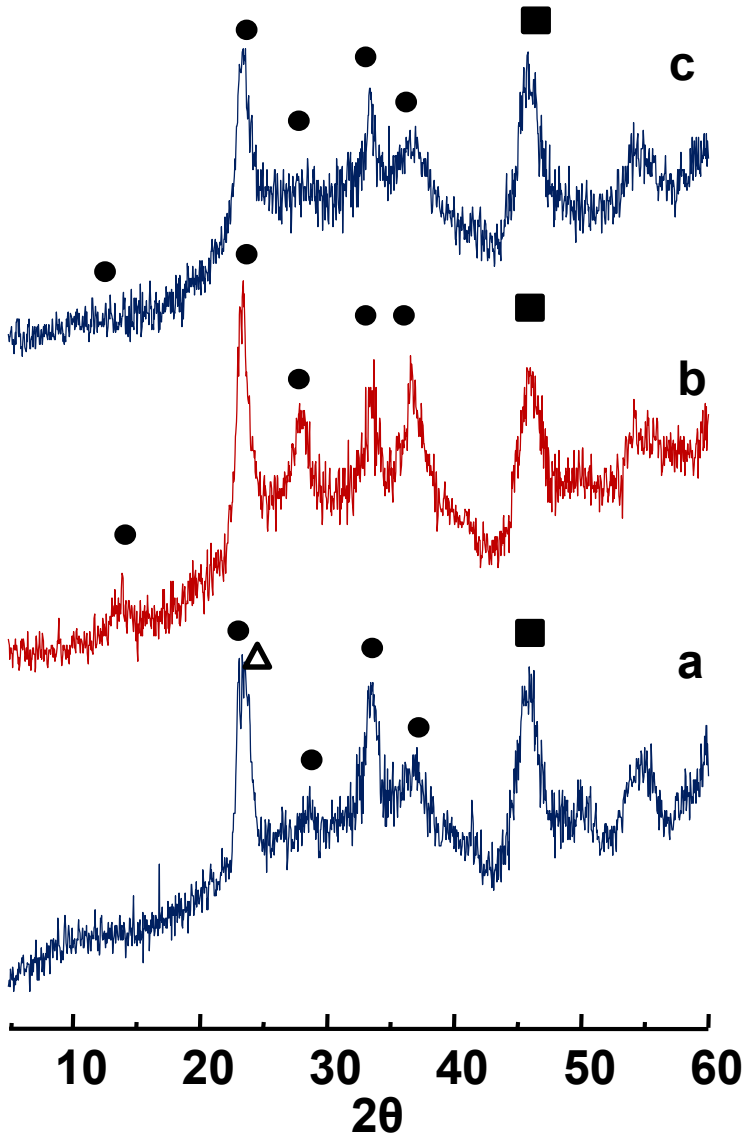

Fig. S2. XRD pattern of Al_2O_3-supported W-V-O oxide bronzes. Catalysts: a) **S-I-1**; b) **S-I-2**; c) **S-I-3.** Details reported in Table 1. Symbols: HTB structure (●); monoclinic WO_3 (Δ); γ-Al_2O_3 (■).

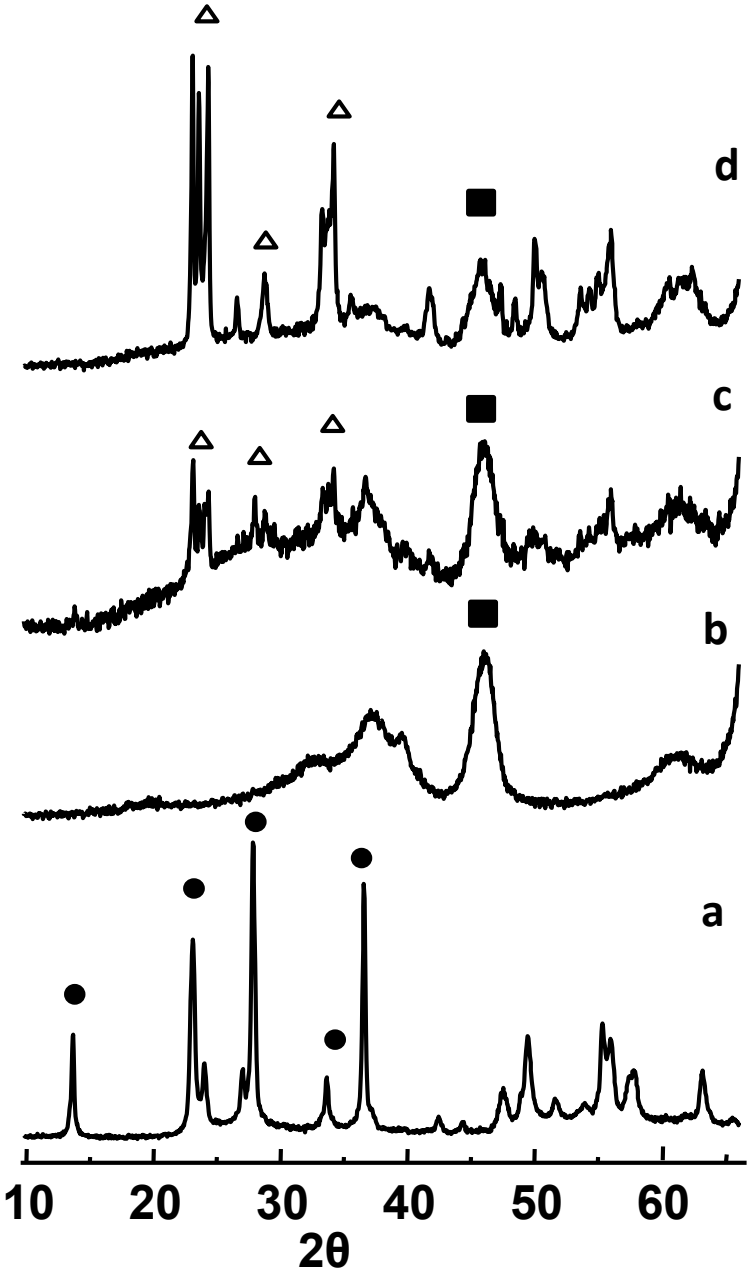

Fig. S3. XRD patterns of reference samples: a) unsupported W-V-O bronze prepared hydrothermally (sample **WV-HT**); b) γ-Al_2O_3-supported vanadium oxide (sample **VOx/AL**); c) vanadium oxide supported on WO_3/Al_2O_3 (sample **V/W/AL**); d) Al_2O_3-supported W-V-O (sample **VW/A**L). Symbols: HTB structure (●); monoclinic WO_3 (Δ); γ-Al_2O_3 (■).

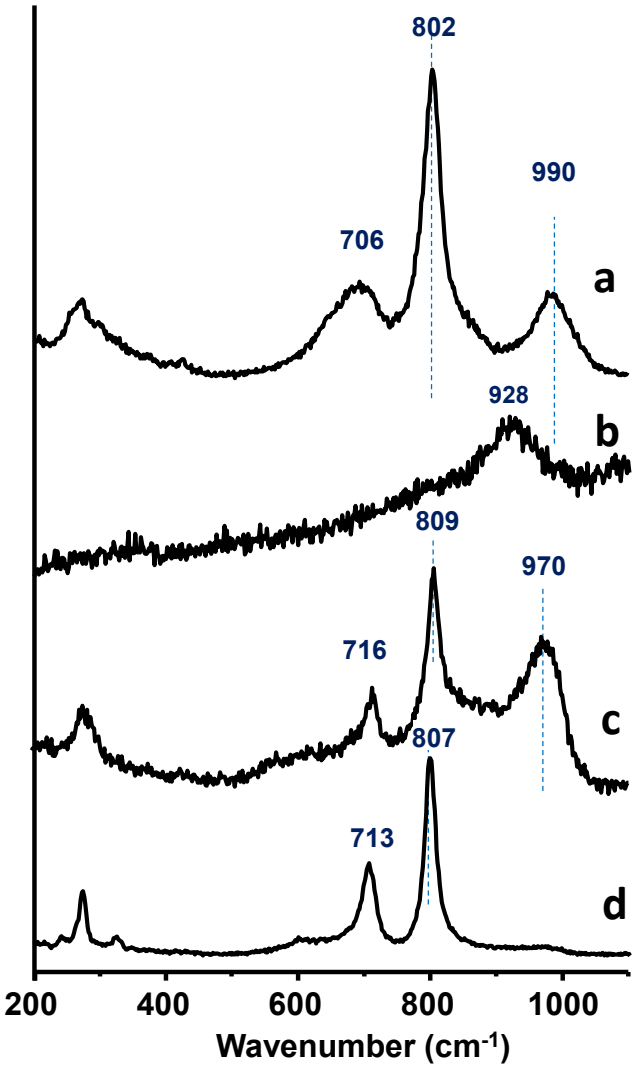

Fig. S4. Raman spectra of reference samples: a) unsupported W-V-O bronze prepared hydrothermally (sample **WV-HT**); b) γ-Al_2O_3-supported vanadium oxide (sample **VOx/AL**); c) vanadium oxide supported on WO_3/Al_2O_3 (sample **V/W/AL**); d) Al_2O_3-supported W-V-O (sample **VW/AL**).

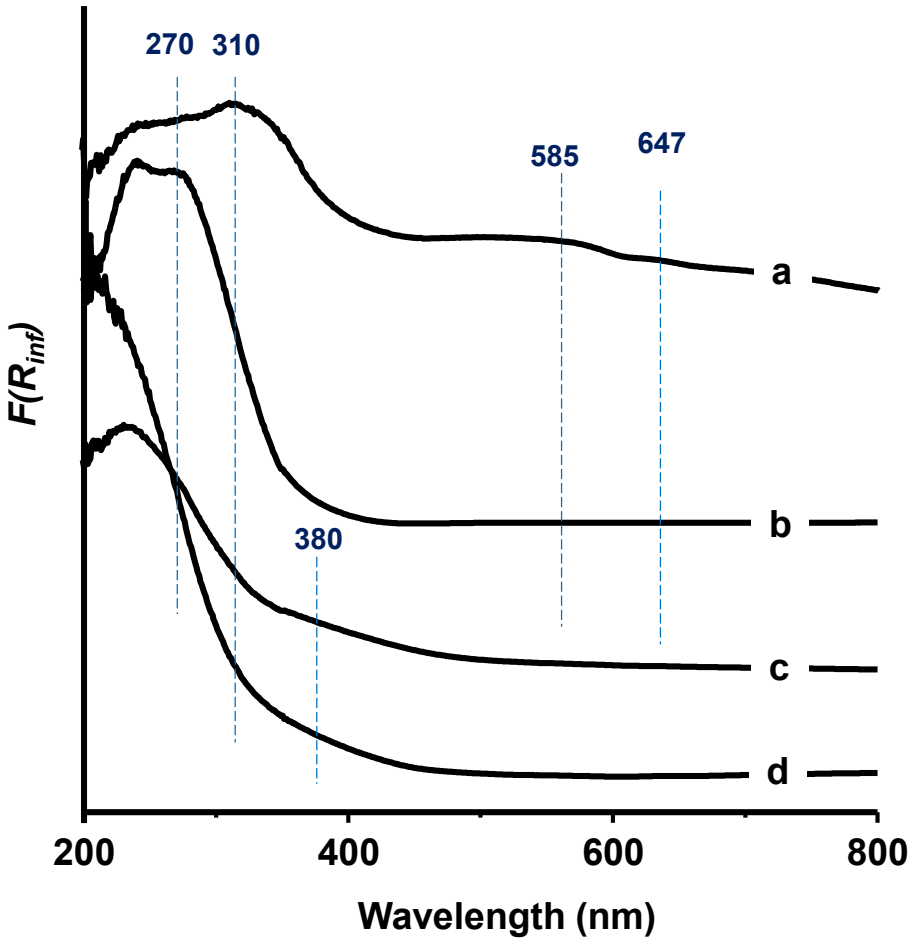

Fig. S5. Diffuse reflectance UV-vis spectra of reference samples: a) unsupported W-V-O bronze prepared hydrothermally (sample **WV-HT**); b) γ-Al_2O_3-supported vanadium oxide (sample **VOx/AL**); c) vanadium oxide supported on WO_3/Al_2O_3 (sample **V/W/AL**); d) Al_2O_3-supported W-V-O (sample **VW/AL**).

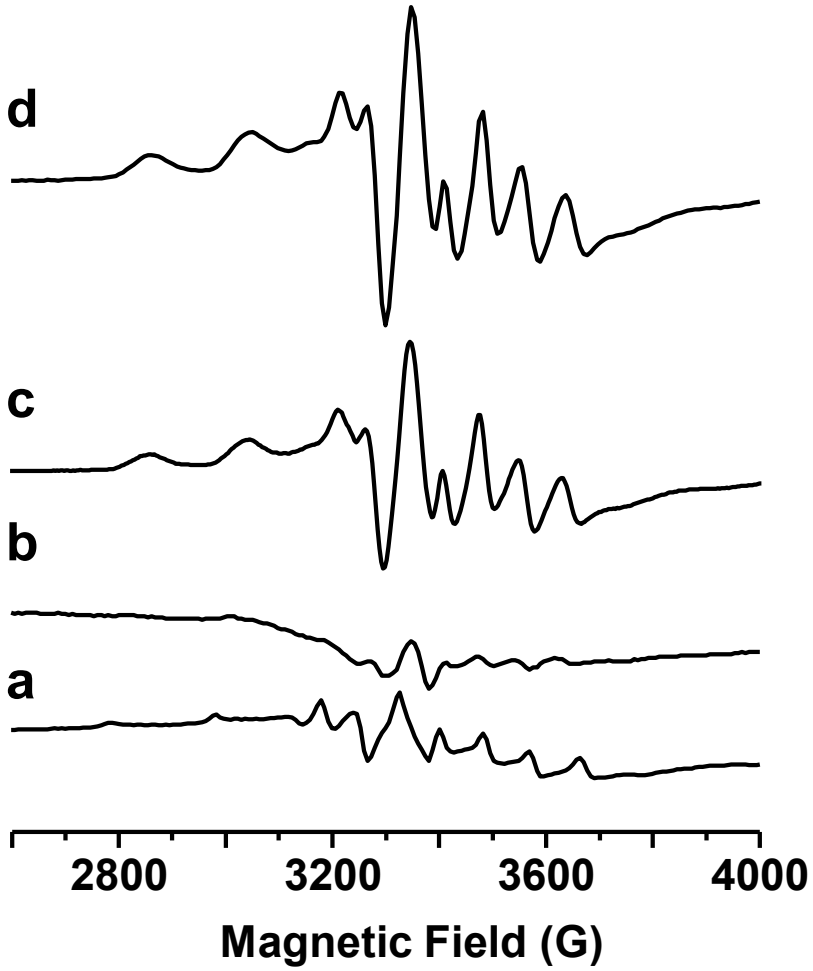

Fig. S6. EPR spectra of references samples: a) unsupported W-V-O bronze prepared hydrothermally (sample **WV-HT**); b) γ-Al_2O_3-supported vanadium oxide (sample **VOx/AL**); c) vanadium oxide supported on **WO_x/Al_2O_3** (sample **V/W/A**L); d) Al_2O_3-supported W-V-O (sample **V-W/AL**).

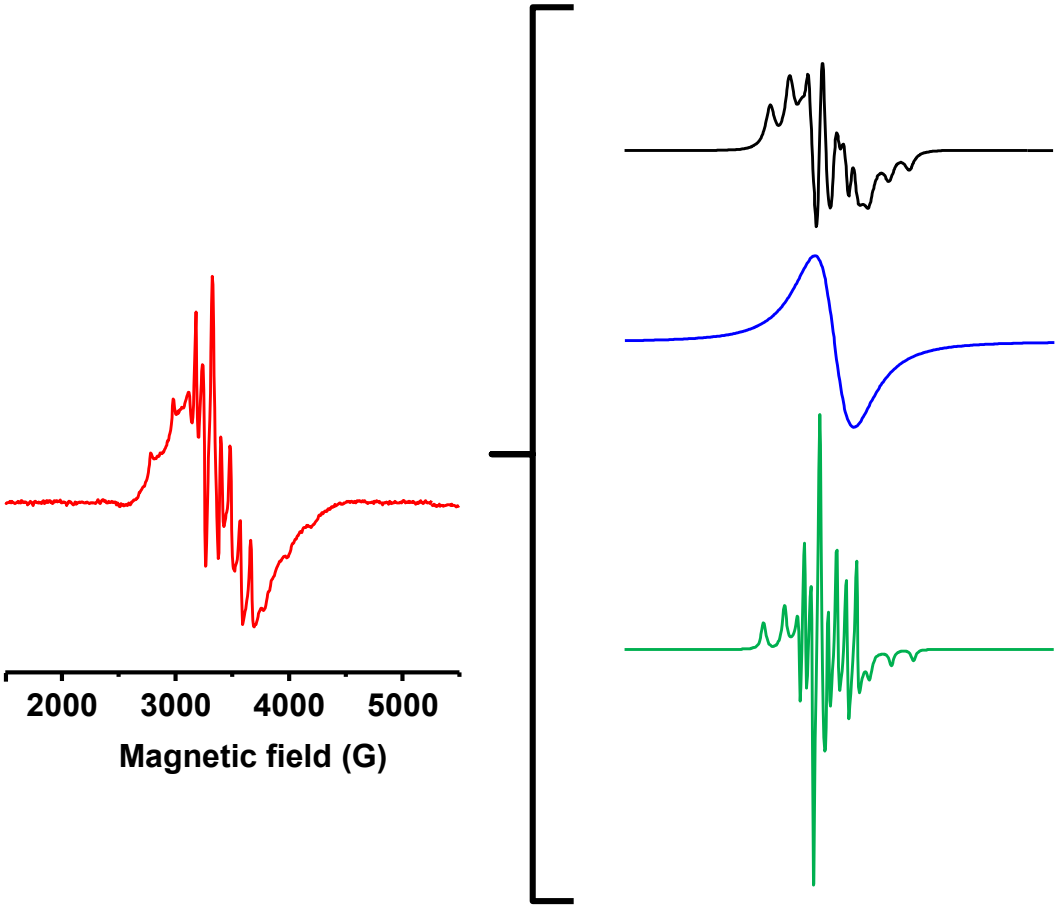

Fig. S7. Simulation of EPR spectrum of a W-V-O oxide bronze sample prepared hydrothermally: **WV-HT**. Original (left) and deconvoluted (right) spectra. The characteristics of each deconvoluted spectrum is also included (right).

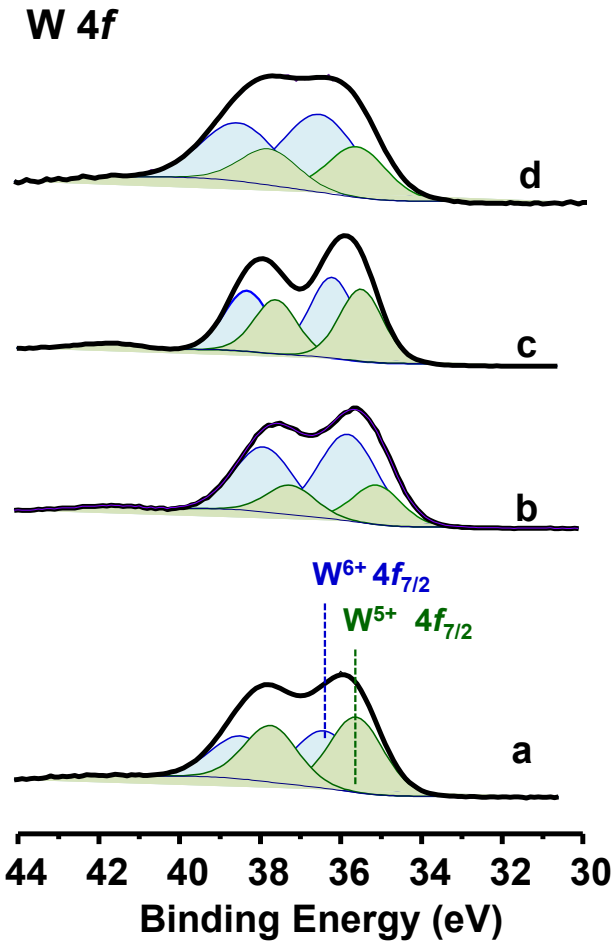

Fig. S8. W 4f core-level XPS spectra of W,V-containing catalysts: a) S-I-2; b) U-I-2; c) WV-HT; d) V/W/AL.

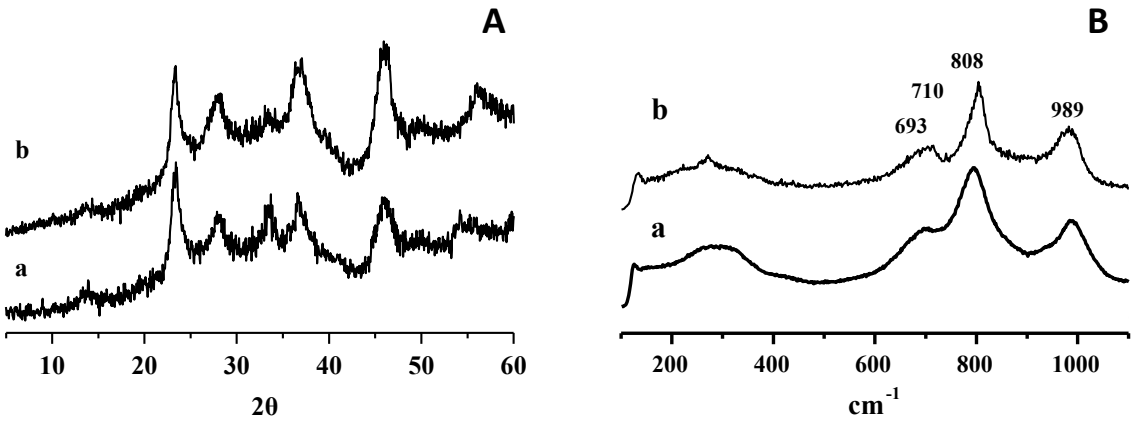

Fig. S9. XRD (A) and Raman (B) spectra of fresh (a) and used (b) **S-I-2** catalyst. Used catalysts catalyst after 70 h time on stream (see Fig. 9).

Table S2. Catalytic performance of catalysts during the oxidative dehydrogenation at 500ºC.[1]

Sample	V-content (wt%)	Temp. (°C)	Conv. (%) (3)	Selectivity C_2H_4 (%)	Yield C_2H_4 (%)	Reaction rate of C_2H_6 conversion[4]	STY-C_2H_4 [5]	C_2H_4 formation per weight of vanadium [6]
S-I-1	0.67	502	13.5	79.6	10.7	13.4	37.5	5.60
S-I-2	2.5	509	24.1	71.4	17.2	21.5	60.2	2.41
S-I-3	4.9	517	45.4	44.9	20.4	25.5	71.4	1.45
U-I-2	9.0	502	1.3	65.9	0.9	1.1	3.1	0.03
S-III-2	2.5	502	15.5	68.0	10.5	13.1	36.7	1.47
WV-HT	9.0	500	7.4	49.8	3.7	4.6	12.9	0.14
VW/AL	3.1	500	22.3	61.8	13.8	17.2	48.2	1.61
V/W/AL	3.1	500	38.0	42.0	15.9	20.0	56.0	1.80
VOx/AL	3.1	506	25.3 [2]	49.6	12.5	7.8	21.8	0.70

1) Ethane/oxygen/nitrogen molar ratio of 4/8/88 and a contact time, W/F, of 80 g_{cat} h $(mol_{C2H6})^{-1}$; Temperature= 500ºC; 2) At a contact time, W/F, of 160 g_{cat} h $(mol_{C2H6})^{-1}$; 3) Conversion of ethane (%); 4) Reaction rate of C_2H_6 conversion in 10^4 mol_{C2H6} g_{cat}^{-1} h^{-1}; 5) Space–time yield, STY_{C2H4}, in g_{C2H4} kg_{cat}^{-1} h^{-1}; 6) C_2H_4 formation per amount of vanadium, in g_{C2H4} g_V^{-1} h^{-1}.

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References

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