catalysts

MDPI

Supplementary Materials

Vanadium Supported on Alumina and/or Zirconia Catalysts for the Selective Transformation of Ethane and Methanol

Souhila Benomar [1,2], Amada Massó [1], Benjamín Solsona [3], Rachid Issaadi [2] and Jose M. López Nieto [1,*]

[1] Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain; benosouh06@yahoo.fr (S.B.); masso.amada@gmail.com (A.M.)

[2] Laboratoire des Applications Energétiques de l'Hydrogène, Faculté de Technologie, Université Saad Dahlab, Blida 1, Blida 09000, Algeria; rachidissaadi@yahoo.fr

[3] Department of Chemical Engineering, Universitat de València, Av. Universitat s/n, 46100 Burjassot, Spain; bensoles@yahoo.es

* Correspondence: jmlopez@itq.upv.es; Tel.: +34-96-387-7808

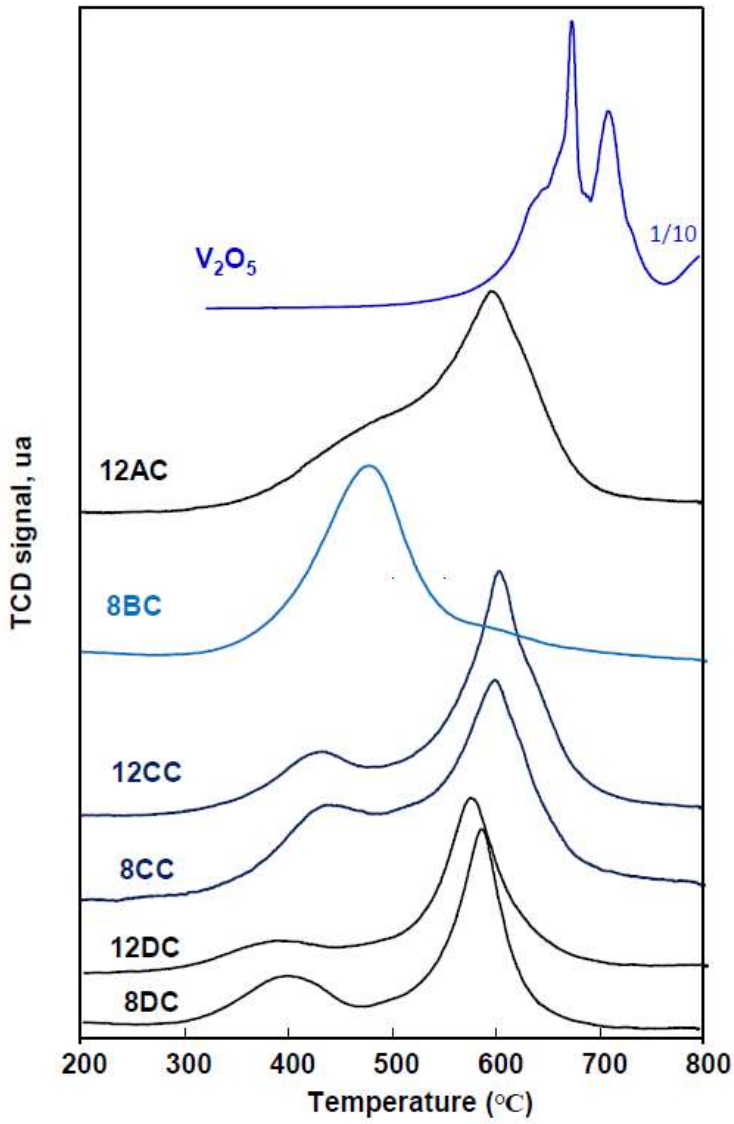

Figure S1. TPR-H_2 results of supported catalysts. For comparison it has been also included the results for a pure V_2O_5. Characteristics of catalysts in Table 1.

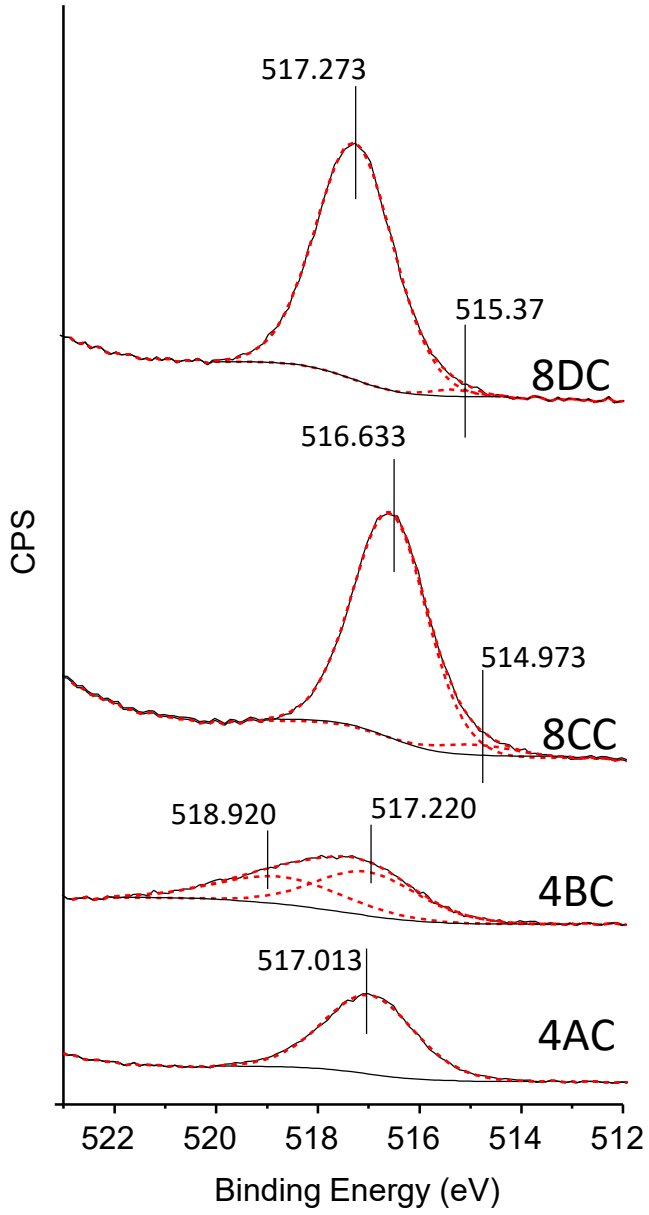

Figure S2. V $2p_{3/2}$ photoelectron spectra of catalysts with a V-loading of 4 or 8 wt% of V-atoms. Characteristics of catalysts in Table 1.

The XPS peak at 517.5 eV can be assigned to V^{5+} whereas the peak at 516.4 eV can be related to V^{4+} species [Silversmit, G.; Depla, D.; Poelman, H.; Marin, G.B.; De Gryse, R. Determination of the V2p XPS binding energies for different vanadium oxidation states ($V^{5+}$to V^{0+}). J. Electron Spectrosc. 2004, 135, 167-175]. In the case of sample 4BC it can be also observed a peak at ca. 518.9 eV which is characteristic of highly dispersed V^{5+} species in supported vanadium oxide catalysts as proposed previously by Hess et al. [Hess C, Tzolova-Müller G, Herbert R. The influence of water on the dispersion of vanadia supported on silica SBA-15, a combined XPS and Raman study, J. Phys Chem C 2007, 111, 9471-71-9479].

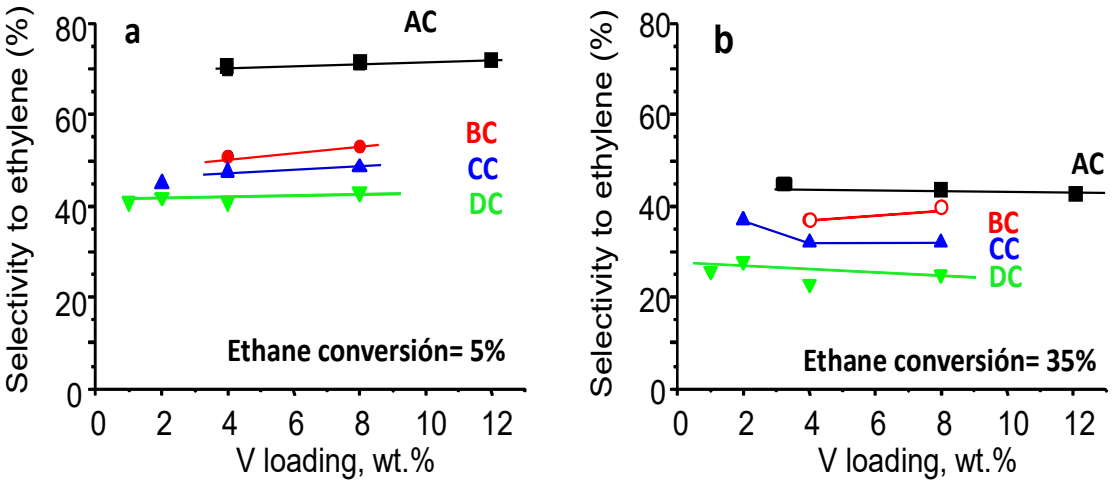

Figure S3. Variation of the selectivity to ethylene with V-loading during the ODH of ethane over supported vanadium oxide catalysts (AC, BC, CC and DC series) at ethane conversion of: a) 5%; b) 35 %. Reaction conditions: T=500 °C; ethane/oxygen/helium with a molar ratio of 4/8/88.

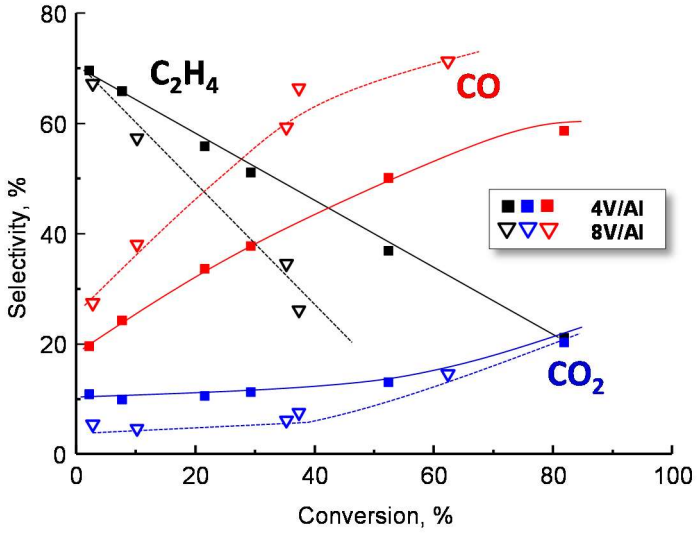

Figure S4. Variation of the selectivity ethylene, CO and CO_2 with ethane conversion during the ODH of ethane over Al_2O_3-supported vanadium oxide catalysts (V/Al series, prepared over commercial Al_2O_3 support). Reaction conditions: T=500 °C; ethane/oxygen/helium with a molar ratio of 4/8/88.

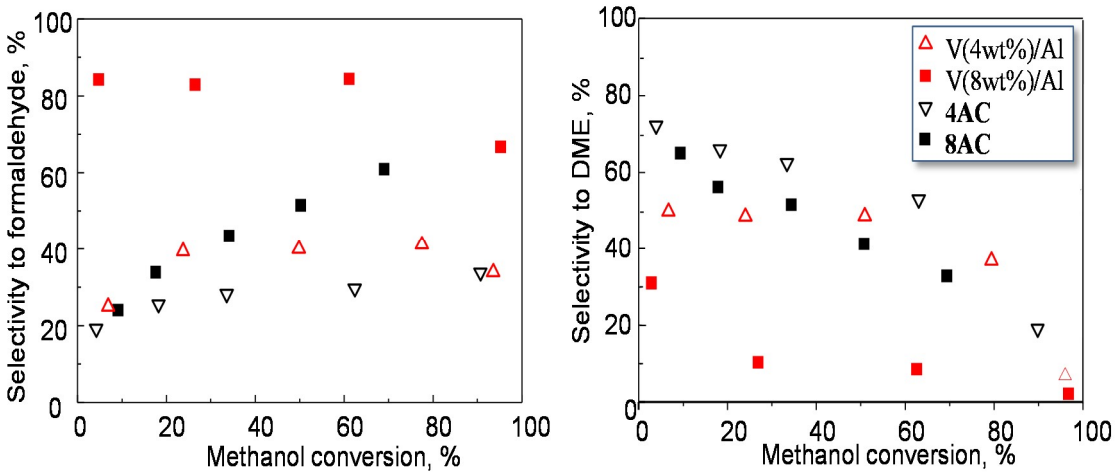

Figure S5. Variation of the selectivity to formaldehyde (or Formaldehyde + DMM) (left) and to DME (right) with methanol conversion during the aerobic transformation of methanol over Al_2O_3-supported vanadium oxide catalysts (V/Al series: V(4wt%)/Al and V(8wt%)/Al), prepared over commercial Al_2O_3 support). For comparison it has been also included the catalytic results for samples **4AC** and **8AC**.

Table S1. XPS results of supported catalysts.

Sample	Surface composition			$V^{4+}/(V^{4+}+V^{5+})$ (%)
	Al	Zr	V	
4AC	94.99	0	5.01	0
4BC	77.50	16.15	6.35	0
8CC	48.75	32.75	18.50	5.6
8DC	0	84.34	15.66	1.6

Table S2. Catalytic results during the ethane ODH over catalysts of AC-series.[1]

Catalyst	W/F	T (ºC)	Conv.(%)	S_{C2H4} (%)	S_{CO2} (%)	S_{CO} (%)
4AC	25.6	502	6.45	68.0	5.4	26.6
	25.6	528	11.3	65.0	5. 6	29.5
	50.0	525	19.6	59.6	6.2	34.2
8AC	25.6	506	6.9	68.0	5.1	26.8
	25.6	519	9.4	66.3	5.3	28.3
	25.6	530	11.9	64.6	5.5	29.9
	50.0	505	11.9	60.7	5.9	33.3
	50.0	517	15.6	58.5	6.2	35.3
	50.0	529	19.3	56.2	6.5	37.3
	100.0	505	21.0	59.5	6.3	34.2
	100.0	516	31.4	49.9	7.9	42.2
12AC	25.6	517	10.5	65.5	5.2	29.3
	50.0	505	13.7	62.4	5.2	32.5
	50.0	517	26.8	50.7	6.3	43.0

[1] Contact time W/F in g_{cat} h $(mol_{C2H6})^{-1}$; Conversion of ethane (Conv.); Selectivity to ethylene (S_{C2H4}), CO_2 (S_{CO2}) and CO (S_{CO}).

Table S3. Catalytic results during the ethane ODH over catalysts of BC-series.[1]

Catalyst	W/F	T (ºC)	Conv. (%)	S_{C2H4} (%)	S_{CO2} (%)	S_{CO} (%)
4BC	25.6	502	7.8	40.2	10.2	49.6
	25.6	516	10.0	41.0	10.1	48.9
	50	505	12.2	41.8	10.0	48.2
	50	517	19.2	42.7	10.3	47.0
8BC	25.6	500	11.3	50.8	8.6	40.6
	25.6	510	14.6	50.4	8.7	40.9
	25.6	517	16.2	50.2	8.7	41.1
	25.6	524	17.9	50.0	8.7	41.2
	50	525	29.4	46.4	9.9	43.7

[1] Contact time W/F in g_{cat} h $(mol_{C2H6})^{-1}$; Conversion of ethane (Conv.); Selectivity to ethylene (S_{C2H4}), CO_2 (S_{CO2}) and CO (S_{CO}).

Table S4. Catalytic results during the ethane ODH over catalysts of CC-series. [1]

Catalyst	W/F	T (ºC)	Conv. (%)	S_{C2H4} (%)	S_{CO2} (%)	S_{CO} (%)
2CC	25.6	500	4.4	42.8	10.1	47.1
	25.6	519	6.5	44.3	9.9	45.8
	50	500	7.3	44.8	9.8	45.4
	50	519	12.7	43.5	10.2	46.3
4CC	25.6	500	6.0	45.9	8.6	45.5
	25.6	515	10.3	42.4	9.4	48.1
	50	500	12.4	41.0	9.9	49.1
	50	512	18.7	36.7	11.4	51.9
8CC	25.6	505	7.3	48.2	9.2	42.6
	25.6	518	9.6	47.7	9.3	43.0
	50	507	15.6	34.5	11.8	53.8
	50	533	25.7	27.7	14.6	57.7
12CC	25.6	507	8.1	47.8	8.9	43.2
	25.6	520	10.5	47.8	9.1	43.1
	50	502	13.0	47.9	9.2	42.9
	50	519	20.4	44.9	10.6	44.6

[1] Contact time W/F in g_{cat} h $(mol_{C2H6})^{-1}$; Conversion of ethane (Conv.); Selectivity to ethylene (S_{C2H4}), CO_2 (S_{CO2}) and CO (S_{CO}).

Table S5. Catalytic results during the ethane ODH over catalysts of DC-series. [1]

Catalyst	W/F	T (ºC)	Conv. (%)	S_{C2H4} (%)	S_{CO2} (%)	S_{CO} (%)
1DC	25.6	500	7.8	39.8	20.3	39.9
	25.6	520	12.4	38.0	22.9	39.1
	50	521	21.5	33.3	27.0	39.7
2DC	10	500	10.6	39.5	15.8	44.7
	25.6	520	34.0	27.3	21.8	51.0
4DC	10	500	12.0	36.5	13.8	49.8
	25.6	519	32.4	24.8	17.2	58.0
	50	500	39.1	21.9	16.8	61.3
8DC	10	500	8.6	38.9	13.6	47.5
	25.6	508	21.5	30.8	15.2	54.0
	25.6	522	26.4	28.0	15.8	56.2
	25.6	500	13.9	30.0	18.0	52.0
	50	509	32.4	22.2	22.7	55.1
	50	516	36.1	20.8	24.1	55.1
12DC	10	500	9.9	38.8	13.6	47.7
	25.6	512	24.8	29.6	15.8	54.6
	25.6	500	27.2	28.3	15.8	55.8
	50	501	34.3	24.6	15.9	59.5

[1] Contact time W/F in g_{cat} h $(mol_{C2H6})^{-1}$; Conversion of ethane (Conv.); Selectivity to ethylene (S_{C2H4}), CO_2 (S_{CO2}) and CO (S_{CO}).