Electronic Supporting Information

Understanding the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate over vanadia/titania catalysts

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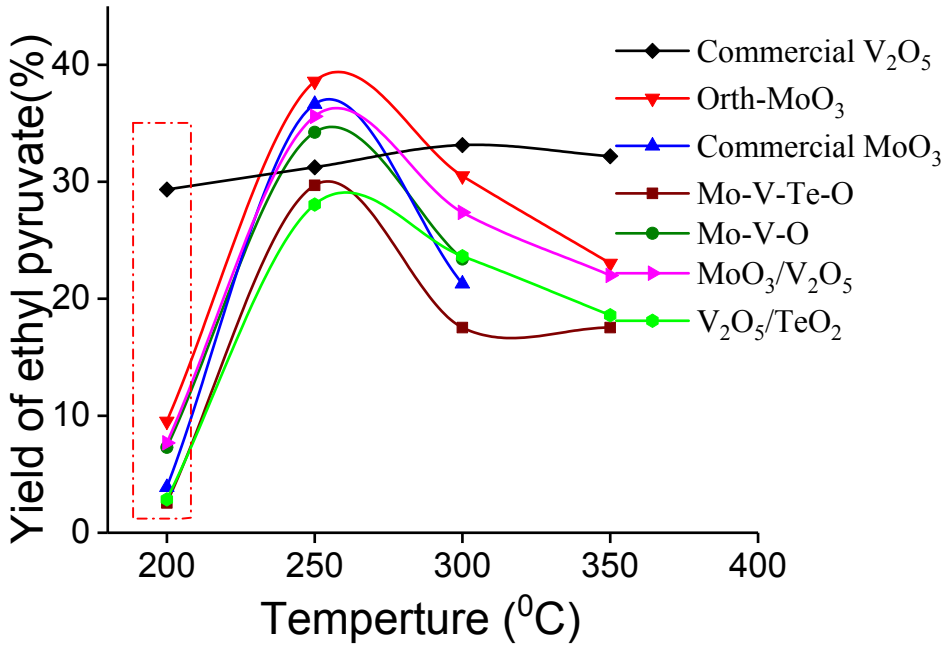

Figure S1. Temperature-resolved yield of ethyl pyruvate over various metal oxides and binary oxides.

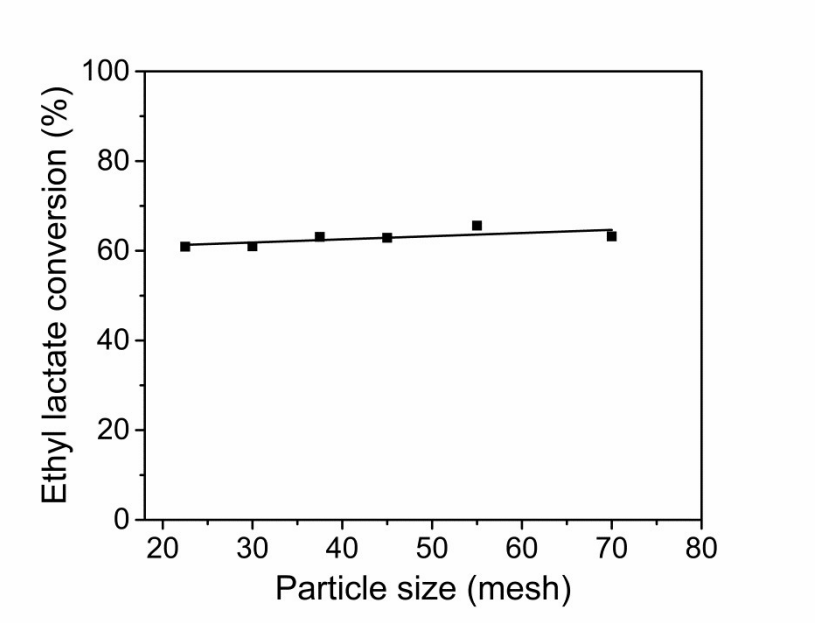

Figure S2. Variation of the ethyl lactate conversion with the different particle sizes over 3-V_2O_5/TiO_2 catalyst (including 20-25, 25-30, 35-40, 40-45, 50-60 and 60-80 mesh). Reaction conditions: 5 ml/h ethyl lactate, 2.25 L/h air flow (molar ratio of ethyl lactate/O_2=2.3), 1.0 g catalyst, 200 °C.

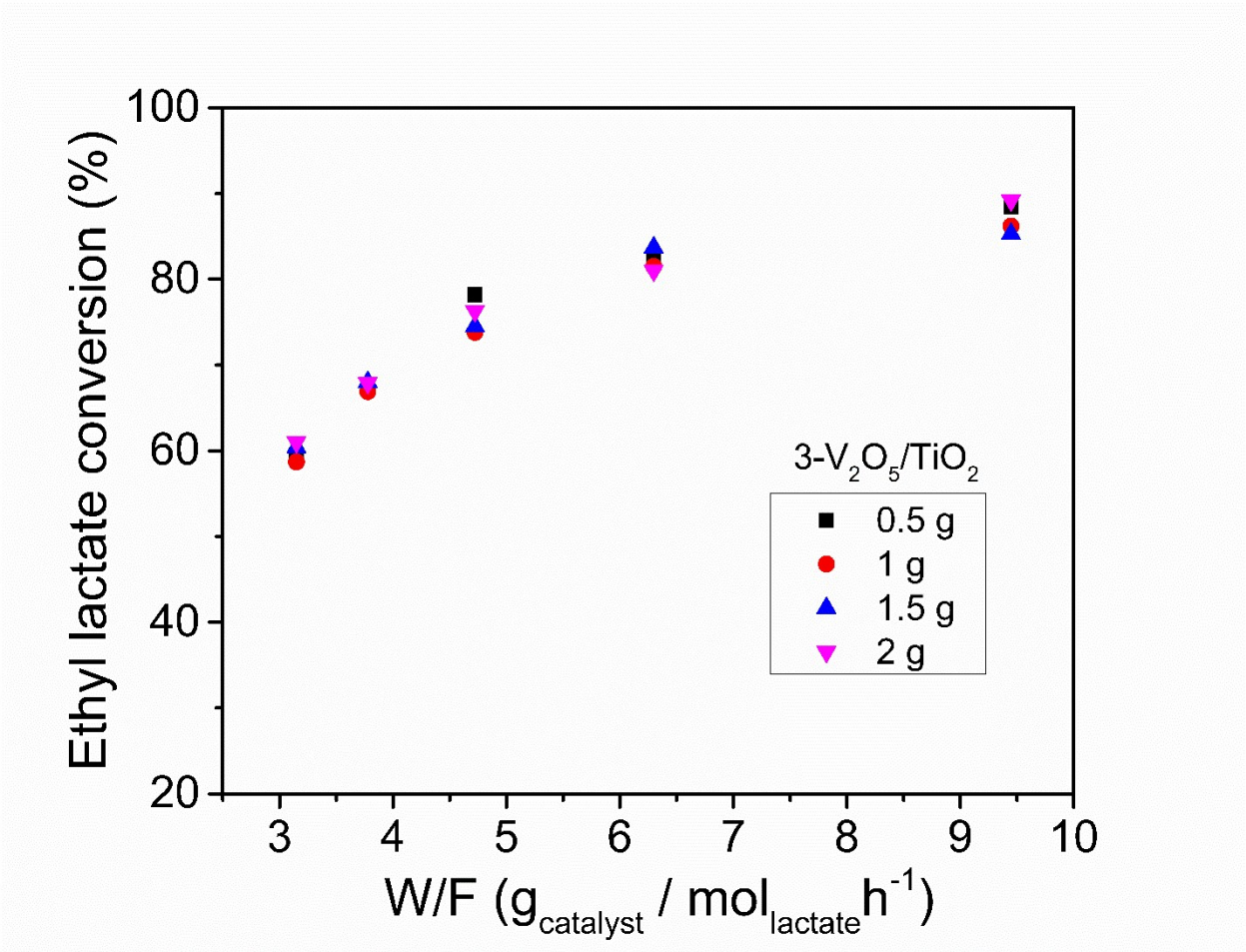

Figure S3. (a) Variation of the ethyl lactate conversion with the reciprocal space velocity (W/F) of ethyl lactate over 3-V_2O_5/TiO_2 catalyst. W (g) is the weight of the catalyst and F (mol/h) is the flow rate of ethyl lactate. Reaction conditions: 2.25 L/h air flow, 200 °C.

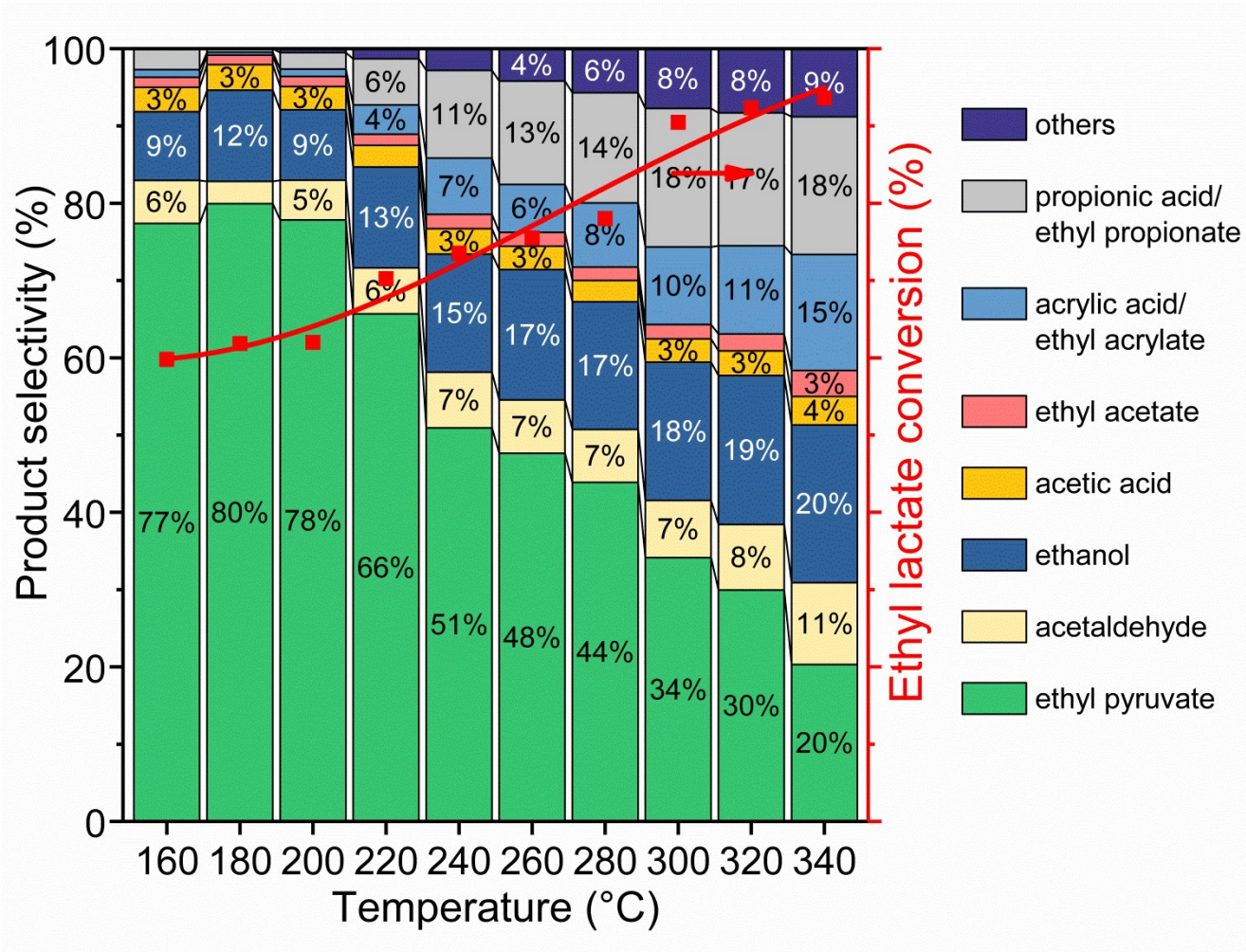

Figure S4. Plots of ethyl lactate conversion and ethyl pyruvate selectivity against reaction temperature over 3-V_2O_5/TiO_2 catalyst; Reaction conditions: 5 ml/h Ethyl lactate, 2.25 L/h air flow (molar ratio of ethyl lactate/O_2=2.3), 1.0 g catalyst.

Table S1. Effect of LHSV on ODH of ethyl lactate to ethyl pyruvate. [a]

LHSV (h^{-1})	Conv. (mol%)	Product selectivity (mol%)							EP Yield (mol %)	Carbon balance
		EP	Acetaldehyde	EtOH	HAc	acrylic acid/ ethyl acrylate	propionic acid/ ethyl propionate	others		
0.5	90	20.1	15.9	22.4	36.6	2.4	2.5	0.1	18.0	87.5
1	84	52.9	7.6	17.3	12.6	4.2	2.9	2.5	44.5	92.6
1.2	82	71.9	5.9	11.5	4.4	1.5	2.8	2.0	58.6	97.2
1.8	73	72.5	5.8	11.0	4.0	1.6	3.4	1.7	53.3	98
2.5	62	80.0	2.9	9.2	3.3	1.2	2.4	1.0	49.5	99
3	50	76.4	3.5	9.3	2.2	1.1	4.8	2.6	38.2	98.4
3.5	45	73.6	4.2	10.2	2.1	1.1	5.1	3.7	33.0	95.5

Reaction conditions: 3-V_2O_5/TiO_2, 2.25 L/h air flow, 1.0 g catalyst, 180 °C.

Table S2. Surface atom ratios of the V_2O_5/TiO_2 calculated from XPS analysis.

Sample	V^{5+} (at%)	V^{4+} (at%)	V^{4+} / ($V^{4+}+V^{5+}$)	O'_{α} (at%)	O_{α} (at%)	O_{β} (at%)
pure TiO_2	–	–	–	2.2	6	52.7
1–V_2O_5/TiO_2	0.3	0.3	0.50	2.1	6.6	49.6
3–V_2O_5/TiO_2	1.3	0.7	0.35	3.5	10.2	43.8
5–V_2O_5/TiO_2	1.9	0.9	0.32	3.4	7.6	51.7
10–V_2O_5/TiO_2	2.4	1.0	0.29	0.8	5	53.6

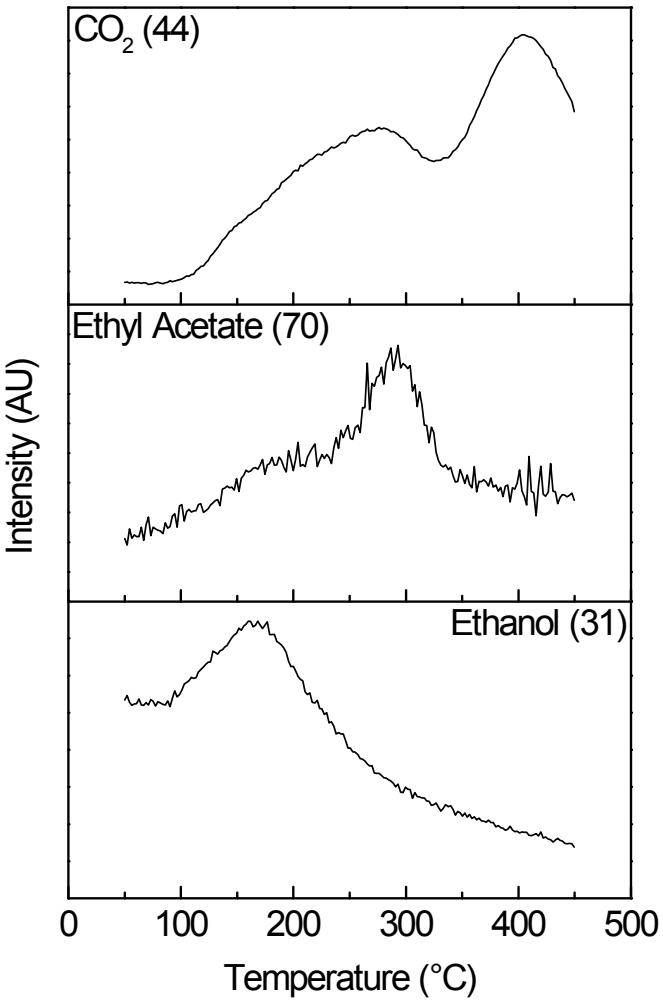

Figure S5. Mass signal for EL adsorption on 3-V_2O_5/TiO_2 in absence of O_2.

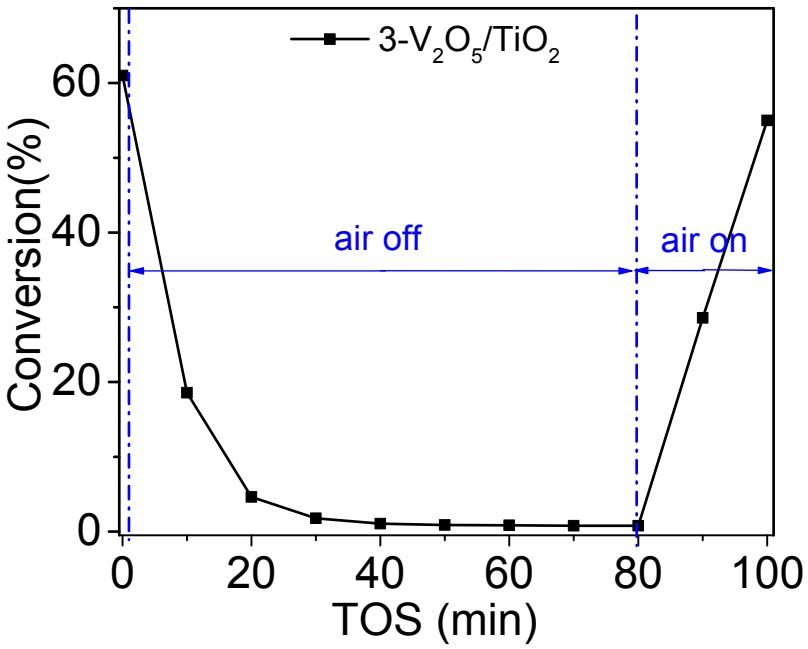

Figure S6. Oxygen on-off experiments over 3-V_2O_5/TiO_2 catalyst. Reaction conditions: 5 ml/h Ethyl lactate, 2.25 L/h air flow (molar ratio of ethyl lactate/O_2=2.3), 1.0 g catalyst, 180 °C.

The conversion decreased and reached a steady-state after 40 min. Without an air stream that can replenish the oxygen, the reaction is limited to oxygen adsorbed on the surface. When air feed was restored, the conversion went up again. The XPS results confirms that the 3–V_2O_5/TiO_2 sample had the highest percentage (10.2%) of surface-chemisorbed oxygen among the supported vanadia catalysts (Table S1). This surface chemisorbed oxygen O_α is considered to be more active and recovered in oxidation reaction due to its high mobility. [1-4]

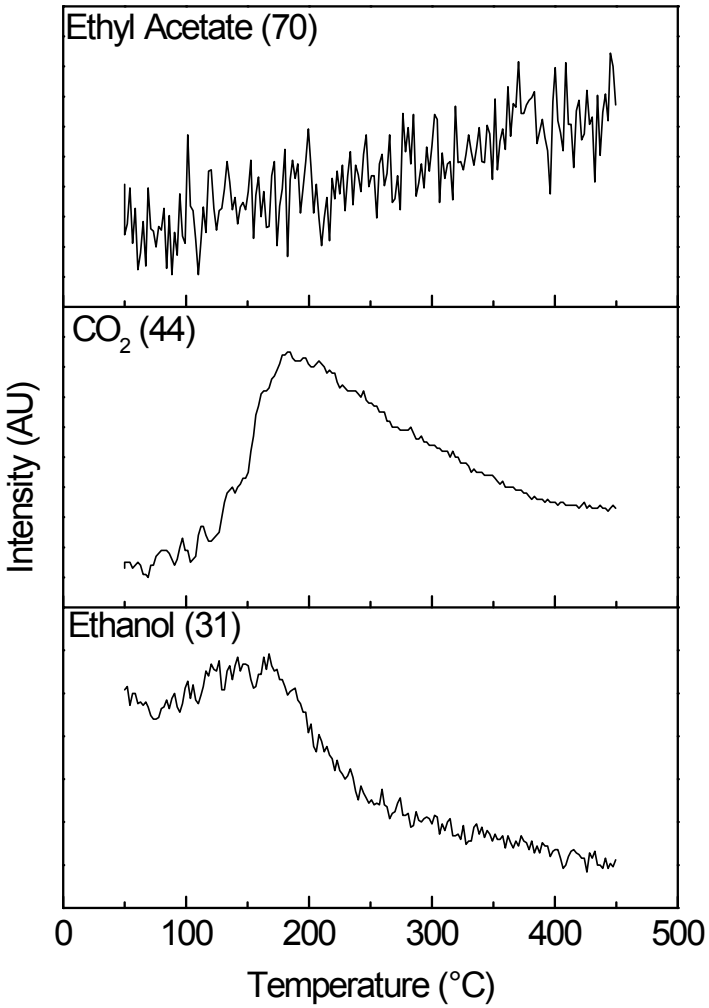

Figure S7. Mass signal for EL adsorption on 3-V_2O_5/TiO_2 in absence of O_2.

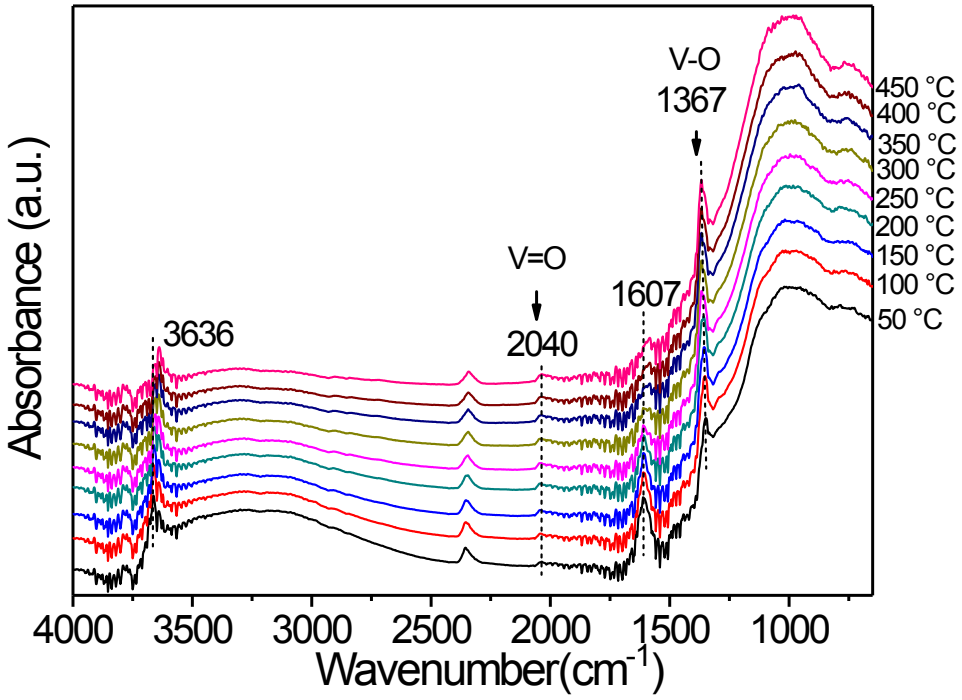

Figure S8. In situ DRIFTS spectra recorded on 3-V_2O_5/TiO_2 catalyst.
It is possible to appreciate three quite defined bands:

- 1367 cm^{-1} this band was attributed by Narayana et al[5] to the anatase phase, by Garcia et al[6] to the interaction of TiO_2 (anatase) with V-O bending modes and by Kantcheva[7] to a combination of the symmetric stretching of the VO_4^{3-} ion with a deformation mode of V-O. Since the bare anatase spectrum, reported in the NIST database[8], does not show any signal in this region; it was reasonable to assign this transition to a combination bands due to V-O bonds;
- 2040 cm^{-1} assigned to the first overtone of V=O bond vibration; [9]
- 1607 cm^{-1} due to the V-O-V bond overtone or the presence of small amount of unreacted hydroxyl groups on the support.[5]

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