Electronic Supplementary Information for

Towards efficient catalysts for the oxidative dehydrogenation of propane in the presence of CO₂: Cr/SiO₂ systems prepared by direct hydrothermal synthesis

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Formulae for the calculation of conversion, selectivity

The paraffin conversion (x) was calculated using the equation:

$$x = \frac{p_c}{P_{C_3H_8}^0} \times \frac{1}{1 - p_c}$$
(1)

where $P_{C_3H_8}^0$ is the initial propane partial pressure and p_c is the partial pressure of any reaction product in equilibrium conditions, derived from the following equation:

$$K_{p} = \frac{p_{c}^{3}}{\left(d \times P_{CO_{2}}^{0} - p_{c}\right)\left(d \times P_{C_{3}H_{8}}^{0} - p_{c}\right)}$$
(2)

where: $d = \frac{p_t - p_c}{p_t} = \frac{V_0}{V_{eq}}$ is the parameter that consider the change of the volume during the reaction (V_0 and V_{eq} are the volumes of the reaction mixture in initial and equilibrium conditions, respectively), $P_{CO_2}^0$ is the initial partial pressure of CO₂ and p_t is the total pressure.

The selectivity to the reaction products (S) was calculated as:

$$S = \frac{p_c}{P_{C_3H_8}^0 - P_{C_3H_8}}$$
(3)

The product yield (Y) was calculated as:

$$y = \frac{x \times S}{100} \tag{4}$$

Table S1: Codes, composition and textural properties of the Cr/DHS catalysts regenerated after use in propane ODH.

entry	Catalyst	Specific surface area (m²/g)	Total pore volume (cm³/g)	Pore volume 2-3 nm (cm³/g)	Pore diameter (nm)
1	0.25-Cr/DHS	971	0.58	0.55	2.6
2	0.5-Cr/DHS	942	0.55	0.53	2.6
3	1.0-Cr/DHS	847	0.50	0.39	2.7
4	2.0-Cr/DHS	617	0.35	0.26	2.9



Fig. S1: C_3H_8 conversion vs. chromium loading for ODH of propane on the Cr/DHS catalysts $(C_3H_8:CO_2:N_2=15:30:55, T=873 \text{ K}, w=200 \text{ h}^{-1}).$



Fig.S2: XRD patterns of the used catalysts: a) MCM-41, b) 0.25-Cr/DHS, c) 0.5-Cr/DHS, d) 1.0-Cr/DHS, e) 2.0-Cr/DHS.



Fig. S3: DR UV-Vis spectra of the dehydrated/oxidized (see Experimental section in the main text): a) MCM-41, b) 0.25-Cr/DHS, c) 0.5-Cr/DHS, d) 1.0-Cr/DHS, e) 2.0-Cr/DHS.



Fig. S4: DR UV-Vis spectra of catalysts in the dehydrated/oxidized state (dotted lines) and in the dehydrated/reduced state (see Experimental section in the main text) in the presence of CO (solid lines): a,a') 0.25-Cr/DHS , b,b') 0.5-Cr/DHS, c,c') 1.0-Cr/DHS, d,d') 2.0-Cr/DHS.



Fig. S5: IR spectra of NH₃ irreversible adsorbed at 298 K on catalysts in the dehydrated/oxidized state (see Experimental section in the main text): a) MCM-41, b) 0.25-Cr/DHS, c) 0.5-Cr/DHS, d) 1.0-Cr/DHS, e) 2.0-Cr/DHS.

Comment to the figure

The figure shows IR spectra of species irreversibly adsorbed at room temperature in the wavenumber region where absorption bands due to the deformation modes of adsorbed NH_3 and NH_4^+ species.

After outgassing, the IR spectrum of NH₃ adsorbed on the bare MCM-41 (curve a) shows only a very weak δ_{asym} (NH₃) absorption band at ca. 1600 cm⁻¹, which is assigned to some residual NH₃ adsorbed on defects. A significantly more intense band at ca. 1613 cm⁻¹, due to ammonia molecules adsorbed on surface Cr centres, dominated the spectra obtained for the various catalysts. Additionally, a broad absorption band with maximum at ca. 1445 cm⁻¹ and a shoulder at ca. 1410 cm⁻¹ is observed, due to the antisymmetric bending modes of adsorbed ammonium ions.^{S1, S2} The deviation of the NH₄⁺ ion from the tetrahedral symmetry because of the interaction with the surface rendered partly IR active also the symmetric bending mode, producing the very weak band at ca. 1700 cm⁻¹.

Finally, the spectra are characterized by a weak band at 1552 cm⁻¹, that can be attributed to the $\delta(NH_2)$ mode of Si–NH₂ species formed by reaction of NH₃ with strained Si–O–Si (and/or Si-O-Cr) bridges.^{53,54} The other product of this reaction should be Si-OH (and/or Cr-OH) species, likely contributing to the broad and complex band in the v_{OH} region. On pure silicas, such strained bridges are usually expected to be formed by outgassing at higher temperature^{S5} and then, as for the Brønsted acid sites, their formation was favoured by the presence of supported metal ions, as observed also in the case of Ti⁴⁺/MCM-41 prepared by the DHS method.^{S4} The intensity of the 1552 cm⁻¹ band reached a maximum for the 0.50-Cr/DHS and 1.0-Cr/DHS catalysts and then declined, following a trend different from both the 1613 and 1445 cm⁻¹ bands, and not simply related neither to the chromium loading nor to the relative abundance of ordered or disordered porosity in the silica matrix (see Fig. 1A and Table 1 in the main text). It is then proposed that the formation of strained siloxane bridges occurred only in the neighborhood of a limited amount of Cr species.

References

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Fig. S6: C₃H₈ conversion vs. reaction time for ODH of propane on the Cr/DHS catalysts (C₃H₈:CO₂:O₂:N₂=15:30:3:52, T=873 K, w=200 h⁻¹) in the as-prepared state (open symbols) and after reaction and subsequent treatment in flowing O₂ at 873 K for 6h (full symbols): a) 0.25-Cr/DHS, b) 0.5-Cr/DHS, c) 1.0-Cr/DHS, d) 2.0-Cr/DHS.



Fig. S7: Selectivity to C₃H₆, C₂H₄ and total olefin vs. reaction time for ODH of propane on the 2.0-Cr /DHS catalyst (T=873 K, w= 200 h⁻¹). Left panel: selectivity to C₃H₆ (curves a1,b1) and C₂H₄ (curves a2,b2). Right panel: selectivity to total olefins (curves a3,b3). Blue curves: reaction mixture with only CO₂ as oxidant (C₃H₈:CO₂:N₂=15:30:55, curves a1,a2 and a3). Orange curves: reaction mixture as CO₂+O₂ as oxidant (C₃H₈:CO₂:N₂=15:30:3:52, curves b1,b2,b3).



Fig. S8: Yields of C_3H_6 , C_2H_4 and total olefin vs. reaction time for ODH of propane on the 2.0-Cr /DHS catalyst (T=873 K, w= 200 h⁻¹). Left panel: yield of C_3H_6 (curves a1,b1) and C_2H_4 (curves a2,b2). Right panel: yield of total olefins (curves a3,b3). Blue curves: reaction mixture with only CO₂ as oxidant (C_3H_8 :CO₂:N₂=15:30:55, curves a1,a2 and a3). Orange curves: reaction mixture as CO₂+O₂ as oxidant (C_3H_8 :CO₂:N₂=15:30:3:52, curves b1,b2,b3).