Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information of

Catalyst sites and active species in the early stages of the MTO conversion over Cobalt AlPO-18 followed by IR spectroscopy

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Ex-situ DR-UV-visible spectroscopy

Table S 1. Average frequency of principal absorption maxima identified in the DR-UV-visible spectra of CoAPO-18u and CoAPO-18c in air and upon ex situ high temperature O_2 and H_2 treatments.

Spectral Region	**CoAPO-18u**			**CoAPO-18c**		
	Air	**O_2**	**H_2**	**Air**	**O_2**	**H_2**
UV	50000		50000	50000 41500	50000	50000
Uv-vis		30600 24600	30600 24600	30600 24600	30600 24600	30600 24600
Visible	18500 17200 16000	17000 15200	19 723 17 000 15 200	18700 17250 16000	19400 17000 15200	19400 17000 15200
NIR	7500-5800	8800-5000	7900-5500	From 7800	8800-5000	8000-5000

Ex-situ FT-IR Spectroscopy

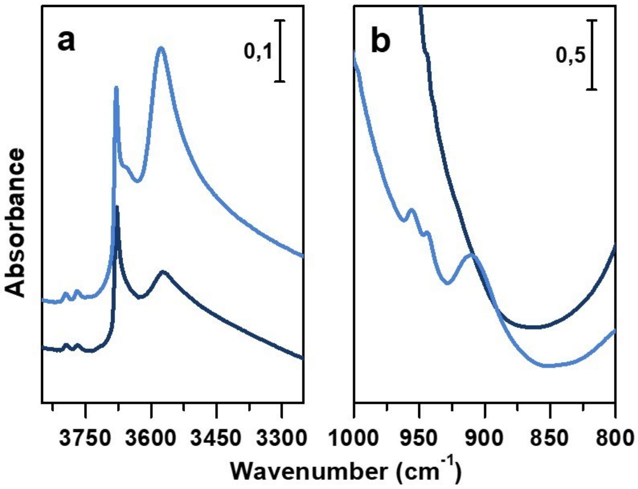

Figure S 1. The OH stretching region (a) and "transparent window region" (b) of IR spectra of CoAPO-18u (light blue line) and CoAPO-18c (dark blue line). The spectra are normalized to the overtone's intensity for sake of comparison.

Table S 2. Fundamental vibrational modes of activated CoAPO-18 CoAPO-18u and CoAPO-18c.

Vibrational mode attribution	**Frequency (cm^{-1})**	
	CoAPO-18u	**CoAPO-18c**
$\boldsymbol{v}$ Al-(OH)	3793 3768	3793 3768
$\boldsymbol{v}$ P-(OH)	3678	3678
$\boldsymbol{v}$ P-(OH)-Co	3578	3578
$\boldsymbol{v}_{asym}$(TO$_4$)	1200-1100	1200-900
$\boldsymbol{\delta}$ (P-OH)	955	/
$\boldsymbol{v}$ (TO$_3$-Co)	945	/
$\boldsymbol{\delta}$ (P-OH-Co)	905	/
$\boldsymbol{v}_{sym}$(TO$_4$)	770-600	770-600

In-situ FT-IR Spectroscopy

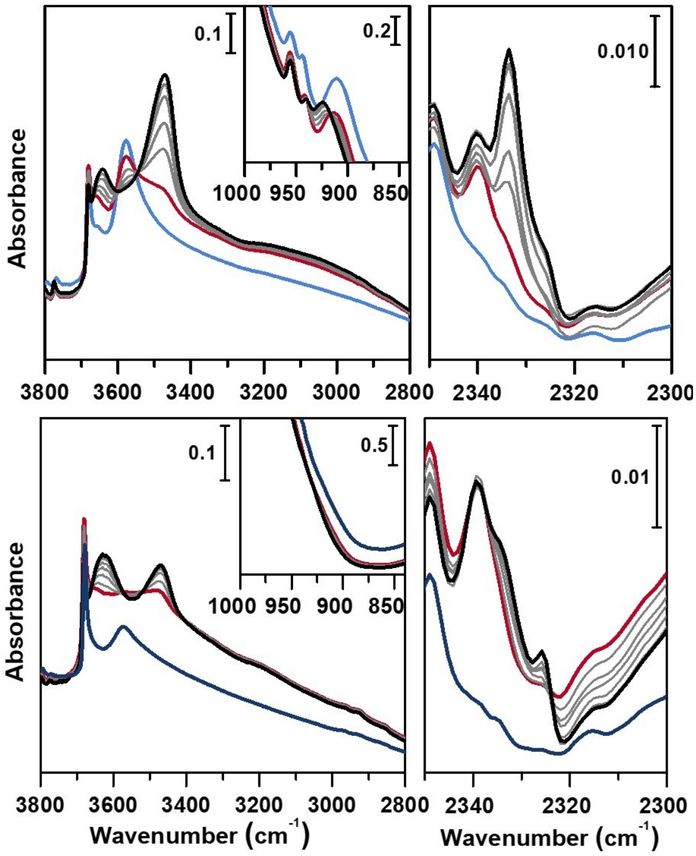

Figure S 2. IR spectra of a) CoAPO-18u and b) CoAPO-18c in presence of adsorbed N_2 at LNT in the OH stretching region (left panels), N≡N stretching region (right panels) and transparent window region (Insets). Blue lines are the activated sample spectra, red lines correspond to the first interaction with the probe, grey lines to the increasing of the adsorption and black to the maximum of coverage.

The very weak nature of the interaction of N_2 with CoAPO makes this molecule suitable as probe, [1,2] ensuring any modification of the system. In the left panels of Figure S2 the perturbation of hydroxyl groups of CoAPO-18u (a) and CoAPO-18c (b) in presence of N_2 is observed. Similar effects can be reported for the two samples. The Al-OH groups vibration is unaffected by the interaction, while the P-OH and bridged P-OH-Co components are suddenly eroded by the formation of the H-bonding. At the same time the perturbation of these two oscillators generates two components at lower frequencies, at 3653 cm^{-1} and 3475 cm^{-1} respectively (red spectra). In case of CoAPO-18u, the erosion involves also the δ(P-OH-Co) mode (Figure S2 a, Inset). At the same stage of adsorption, the appearance of a new component in the ν(N≡N) region is also recorded at 2339 cm^{-1} (Figure S2 a-b, right panels). When the interaction with N_2 is enhanced by increasing cooling of the system (from grey to black spectra) the shifted components are stabilized and intensified, while adjunctive signals appear in the ν(N≡N) region (Figure S2 a-b, right panels). These are a less intense signal at 2325 cm^{-1} due to N_2 in interaction with P-(OH) and one at 2234 cm^{-1} due to N_2 interacting with the BAS, more intense for CoAPO-18u.[3] The component at 2339 cm^{-1} is persistent in all spectra and is significantly more pronounced in the case of CoAPO-18c. It is compatible with the N_2 perturbed by the electronic density of a coordinatively unsaturated metal centre, reasonably an extraframework Co(II) which represent a Lewis acidic site (LAS). The δ(P-OH-Co) in CoAPO-18u at low temperature is upward shifted, consistently with a strong acidic site.

In continuo FT-IR Spectroscopy

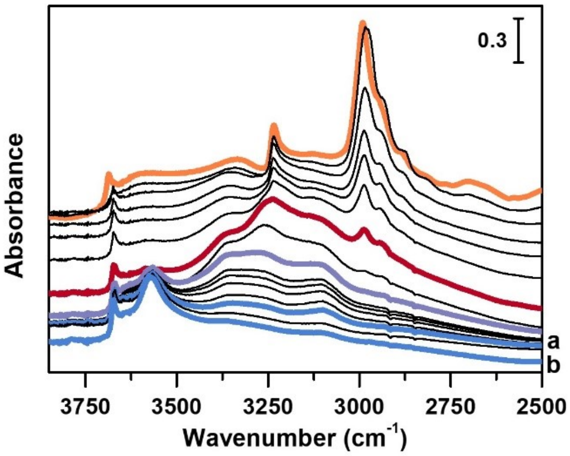

*Figure S 3. IR spectra of CoAPO-18u between 3850 and 2500 cm^{-1} (OH, NH, CH stretching regions) collected in N_2/O_2 mixture flux at rising temperature. Selected spectra are highlighted with different colour remarking the most significant changes in the profile due to temperature (orange spectrum at 180°C, red spectrum at 280°C, violet spectrum at 550°C) or prolonged heating treatment (blue spectrum **a** at 550°C for 4 hours and blue spectrum **b** after 24 hours). The spectra are shifted along the y axis for sake of clarity.*

The evolution of the decomposition of the templating agent (N,N-Diisopropylethyl amine) has been previously studied step by step by Marchese et al.[4] through a series of *ex situ* IR acquisitions and finds correspondence with what is reported in Figure S3. In the figure the initial steps of desorption of atmospheric water that saturates the OH zone due to the strong H-bonding on the surface, are omitted. Starting from a temperature at which the material is considered free from adsorbed species (180°C orange spectrum) it is possible to clearly distinguish the characteristic signals of the organic template, i.e. the ν (C-H) of the isopropyl and ethyl functionalities between 3000 and 2700 cm^{-1} and the ν (N-H) of the interacting amine at 3235 cm^{-1}. Also, regarding the CoAPO-18 profile, the ν P(O-H) signal emerges at 3678 cm^{-1}, while the Brønsted site signal is not yet distinguishable. Increasing the temperature, the decrease of ν (CH) signals intensity and the enlargement of ν (NH) signals are observed, indicating that alkyl functionalities decompose first, releasing the amine that start to establish intermolecular H-bonds (red spectrum, recorded at 280°C). Once 550°C is reached (temperature commonly used for calcination of this type of materials, violet spectrum) the total removal of the carbonaceous fraction is observed, while the N-H signals of the amine persist, indicating a rather strong interaction of this species with the surface of CoAPO-18. N-H signals undergo a noticeable decrease as the duration of treatment increases. In the violet spectrum, the appearance of the 3578 cm^{-1} signal of the BAS is recorded for the first time, as it is gradually released as a free oscillator while the concentration of the H-bonding acceptors decreases. In fact, the signal increases in intensity from the blue spectrum **a** to the spectrum blue **b**. The two blue spectra are further investigated in the "Methanol conversion over SAPO-18 and CoAPO-18" section of the main text. The first one corresponds to the result of a standard calcination treatment (comparable to that undergone by CoAPO-18c, 4 hours at 550°C)[5] while the second corresponds to the moment in which no more amine signals are recorded, i.e. a calcination treatment of 4 hours followed by a synthetic air flow overnight at RT and a second activation at 400°C just before the catalytic reaction. It is relevant to note that, despite undergoing oxidative treatment, H-CoAPO-18 exhibits its characteristic Brønsted site-related signal, indicating the presence of Co(II) in the framework. This suggests that the metal oxidation in framework is not a particularly favoured process and requires rather drastic conditions such as prolonged pure oxygen atmosphere treatments to occur.

The Brønsted acidity of SAPO-18

The differences in the acidic strength of the BAS in CoAPO-18 (P-(OH)-Co) and SAPO-18 (P-(OH)-Si) can be appreciated comparing the data of Tables S3 and S4. As first indication, the frequency of the fundamental ν(OH) vibrational mode must be considered. This is 3578 cm^{-1} for CoAPO-18 and 3613 cm^{-1} for SAPO-18. It is known that the vibration frequency of the OH group associated with a BAS is lower as the acid strength of the site increases, because it corresponds to a shorter O-H bond. This suggests that the acidity of P-OH-Co site is stronger. Furthermore, comparing the shifts of the same bands induced by the interaction with the basic probe molecules N_2 (the spectra are shown in Figure S4) and CO (the spectra of Ref. 29 are considered), this trend can be observed more clearly. In particular, CO induces a shift of 518 cm^{-1} in CoAPO-18 and 253 cm^{-1} in SAPO-18, again underlining how the former has a higher acidic strength. The difference can be explained by the greater polarisation induced in Co(II) compared to Si. This induces a more negative charge to the bound O and consequently makes the bond with the proton stronger.

Table S 3. Δν of the fundamental vibrational modes of CoAPO-18u after probe molecules interaction.

Vibrational mode	Frequency (cm^{-1})	Δν (cm^{-1})

attribution				
		N_2 (LNT)	**CO** (RT)	**CO** (LNT)
ν Al-(OH)	3793 3768	/	/	/
ν P-(OH)	3678	-25	/	-256
ν P-(OH)-Co	3578	-103	-518	-518
δ (P-OH)	955	/	/	/
ν (TO_3-Co)	945	/	-7	-7
δ (P-OH-Co)	905	+30	Partially eroded	+90

Table S 4. Δv of the fundamental vibrational modes of SAPO-18 after probe molecules interaction

Vibrational mode attribution	**Frequency (cm^{-1})**	**Δv (cm^{-1})**	
		N_2 (LNT)[a]	**CO** (LNT)[b]
ν Al-(OH)	3793 3768	/	/
ν Si-(OH)	3745	/	/
ν P-(OH)	3678	-25	-255
ν P-(OH)-Si	3613	-84	-253
δ (P-OH)	955	/	/
δ (P-OH-Si)	/	/	/
[a] Δv calculated from Figure S4; [b] Δv calculated from Ref.29 data			

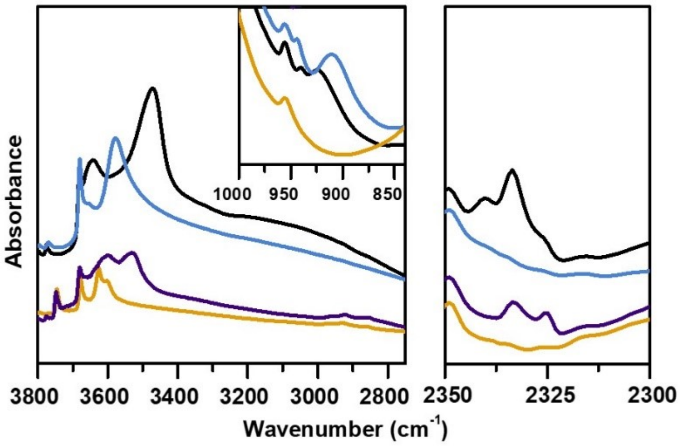

Figure S 4. IR spectra of CoAPO-18u (blue) and SAPO-18 (yellow) in presence of adsorbed N_2 at LNT (black and violet respectively) in the OH stretching region (left panel), N≡N stretching region (right panel) and transparent window region (Inset).

Bibliography

1 C. Pazé, S. Bordiga, C. Lamberti, M. Salvalaggio, A. Zecchina and G. Bellussi, *J. Phys. Chem. B*, 1997, **101**, 4740–4751.

2 F. Giordanino, P. N. R. Vennestrøm, L. F. Lundegaard, F. N. Stappen, S. Mossin, P. Beato, S. Bordiga and C. Lamberti, *Dalt. Trans.*, 2013, **42**, 12741.

3 L. Marchese, E. Gianotti, N. Damilano, S. Coluccia and J. M. Thomas, *Catal. Letters*, 1996, **37**, 107–111.

4 L. Marchese, G. Martra, N. Damilano, S. Coluccia and J. M. Thomas, *Stud. Surf. Sci. Catal.*, 1996, **101 B**, 861–870.

5 J. Xie, D. S. Firth, T. Cordero-lanzac, A. Airi, C. Negri, S. Øien-ødegaard, K. P. Lillerud, S. Bordiga and U. Olsbye, , DOI:10.1021/acscatal.1c04694.