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

Supporting Information

Synthesis and Molecular Structure of Model Silica-supported Tungsten oxide Catalysts for Oxidative Coupling of Methane (OCM)

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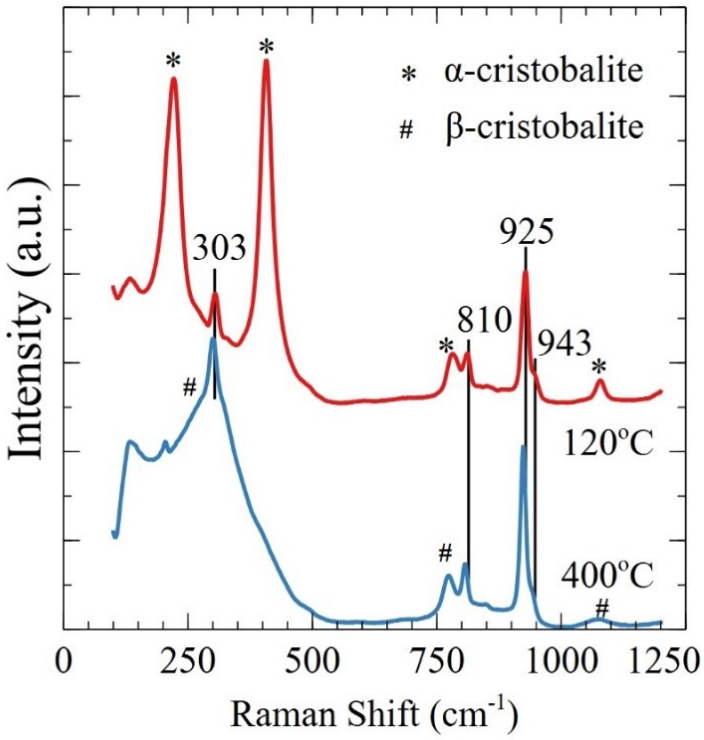

Figure S1. *In situ* Raman spectra of the temperature-dependent transformation of crystalline α↔β cristobalite phases of the SiO_2 support for 5%Na_2WO_4/SiO_2 prepared using the $Na_2WO_4{\cdot}2H_2O$ precursor after dehydration at 400°C under flowing 10%O_2/Ar (~30 cc/min) for 1 hour.

The *in situ* Raman spectra of the supported 5%Na_2WO_4/SiO_2 catalyst prepared using $Na_2WO_4{\cdot}2H_2O$ are shown in **Figure S1** at 120 and 400°C. Each spectrum shows vibrations from Na_2WO_4 crystalline NPs (925, 810 and 303 cm^{-1}) and surface Na-coordinated WO_x species (943 cm^{-1}). For the 120°C spectrum, the vibrations marked with "*" at 220, 407, 780 and 1076 cm^{-1} are from the crystalline α-cristobalite phase of SiO_2 support.[1] This phase has been reported by almost all studies in OCM literature for supported Mn-Na_2WO_4/SiO_2 catalysts.[2,3] Increasing the temperature to 400°C transforms the crystalline α-cristobalite phase to the crystalline β-cristobalite phase, with its Raman bands indicated with "#" (288 cm^{-1} (weak shoulder of 303 cm^{-1} band), 770 and 1074 cm^{-1}).[1] The crystalline α↔β phase transformation of SiO_2 support was also observed during OCM with *in situ* XRD measurement.[4,5] More importantly, these findings demonstrate that the crystalline α-cristobalite phase of the SiO_2 support is not present under OCM catalytic reaction conditions.

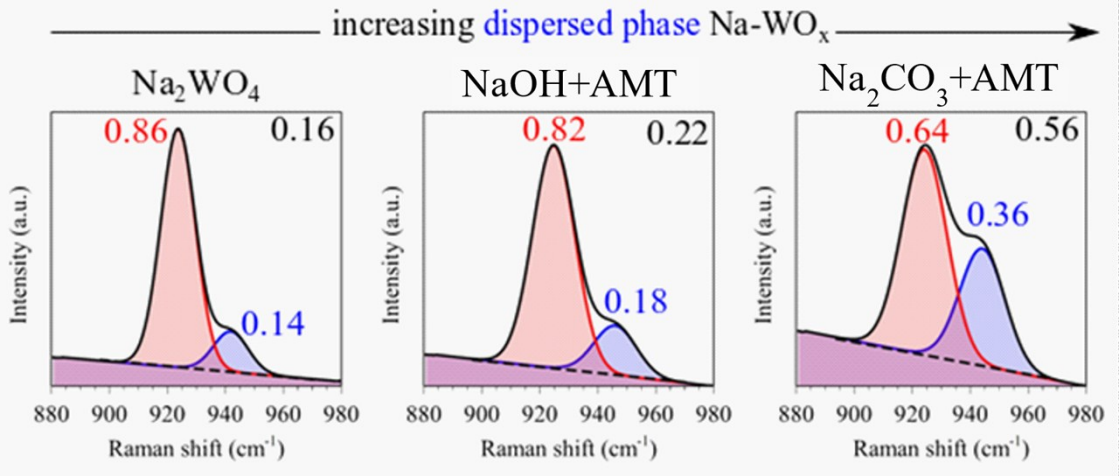

Figure S2. Deconvolution of *in situ* Raman spectra yielding the spectral ratio of surface Na-WO_x sites to the crystalline Na_2WO_4 phase for the supported 5%Na_2WO_4/SiO_2 catalysts prepared using different Na- and W-oxide precursors. The red curve is for the crystalline Na_2WO_4 NPs, the blue curve is for the surface Na-WO_x species and the black curve is the original measured *in situ* Raman spectrum. The numeric values indicated in each plot is the percentage of surface of each phase, calculated by finding the area under the respective deconvoluted curves for each catalyst.

Table S1. *In situ* UV-Vis DR data of stoichiometric (Na/W=2) Na_2WO_4/SiO_2 dehydrated catalysts. The reader is directed to **Figure 3** for a brief analysis of UV-Vis data of the aqueous precursor solutions that corroborate UV-Vis DRS data summarized herein.

5% Na_2WO_4/SiO_2 from different precursors	**Eg (eV)**	**LMCT (nm)**
$Na_2WO_4.2H_2O$	4.6	214 (s); 257 (w)
AMT, NaOH	4.8	214 (s); 257 (m)
AMT, Na_2CO_3	4.6	214 (w), 237(s)
AMT, $NaNO_3$	4.6	240(s)

s= strong, m=moderate and w= weak

Table S2. *In situ* UV-VisDR data of non-stoichiometric (Na/W<2)dehydrated supported Na-WO_x/SiO_2 catalysts prepared from the AMT+NaOH precursors.

Na/W ratio (sample composition)	**Eg (eV)**	**LMCT (nm)**
0.00 ($5WO_x$/0.0 Na))	3.9	248
0.32 (5 WO_x/0.2 Na)	4.1	240
0.64 (5 WO_x/0.4 Na)	4.3	235
~1.00 (5 WO_x/0.8Na)	4.5	232
0.40 (8 WO_x/0.4Na)	4.1	243

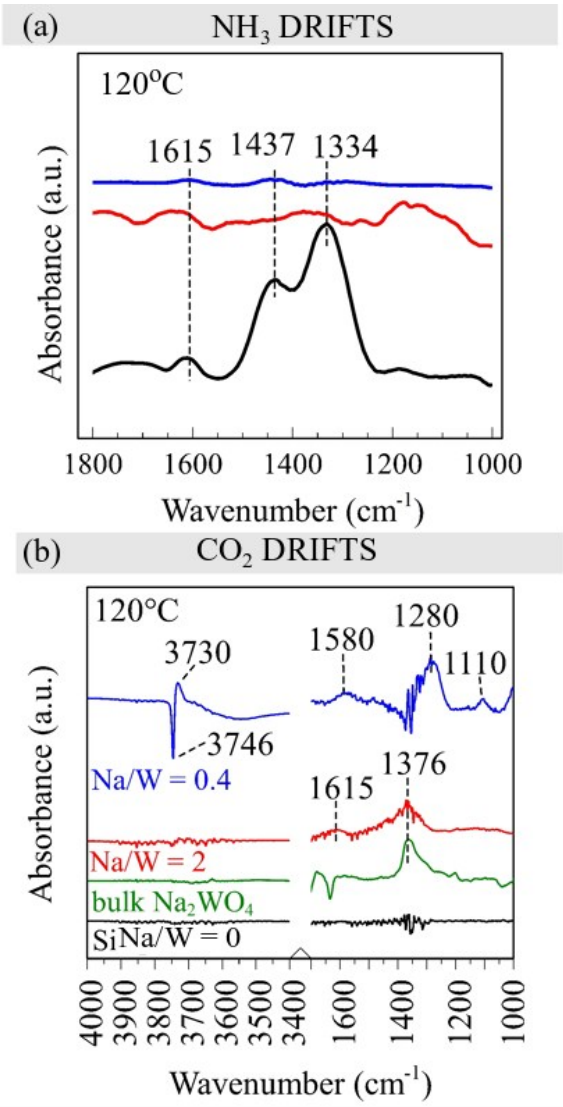

Figure S3. (a)NH_3-DRIFT, (b)CO_2-DRIFT spectra at 120°C, highlighting the absence of acidity in Na-containing samples (red, blue) in (a) and absence of basicity in undoped WO_x/SiO_2 sample (black) in (b)

Table S3. Ratio of the contribution of dispersed Na-WO_x species to crytalline Na_2WO_4 phase towards the H_2-temperature-programmed reduction profiles of various 5%Na_2WO_4/SiO_2 catalysts.

Precursor Used	Na-WO_x/Na_2WO_4 contribution ratio
$Na_2WO_4 \cdot 2H_2O$	1.89
AMT+NaOH	1.96
AMT+Na_2CO_3	2.68

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