Supplementary Material

Mononuclear Gold Species Anchored on TS-1 Framework as Catalyst Precursor for Selective Epoxidation of Propylene

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Experimental Section

Materials

Polyoxyethylene 20-sorbitan monolaurate (Tween 20) and tetrapropylammonium hydroxide (TPAOH, 40 wt.%) were purchased from Fischer Scientific, , tetraethylorthosilicate (TEOS, reagent grade), isopropyl alcohol (IPA), titanium(IV) butoxide (TBOT, 97%), potassium dicyanoaurate(I) (99.98%), caesium hydroxide, caesium carbonate and sodium carbonate were purchased from Sigma-Aldrich. Sodium hydroxide and potassium hydroxide were supplied from Fisher Chemicals. Hydrogen, oxygen, propylene, nitrogen and helium gases were purchased from BOC. All chemicals were used as received without further purification.

Synthesis of titanium silicate-1 (TS-1)

TS-1 with Si/Ti molar ratio = 100 was synthesized according to reported literature method.¹ For a typical synthesis, 3.5 g of Tween20 was mixed with 56 ml MilliQ (18 MΩ.cm resistivity) water under vigorous stirring. Then, 26 ml TPAOH and 66.5 ml TEOS were added respectively. The resultant blurry solution was stirred vigorously for 2-3 h at room temperature (r.t.) until the colour turned into transparent. In a separate flask, 1.08 ml of TBOT was dissolved in 20 ml of IPA which was then added on silica solution while stirring. The final solution was heated to 45 °C and stirred for a minimum of 1h before being placed in a Teflon-lined autoclave. The autoclave was heated to 150°C for 18-20 h. The resulting milky solution was centrifuged at 5000 rpm to separate the solid from the growth liquid. Obtained white solid was then washed with MilliQ water several times and then dried overnight in a vacuum oven at r.t. TS-1 was calcined in air at 550°C for 10-12h before being used.

Preparation of Alkali Promoted Au/TS-1 Catalysts

Sequential impregnation method, adapted from previously reported study², was applied to deposit Au and alkali hydroxides or carbonates on TS-1 support. In a typical experiment, 0.25 wt.% of gold was deposited on calcined TS-1 by incipient wetness impregnation using KAu(CN)₂ as the precursor. Then, Au impregnated TS-1 (Au/TS-1) was dried overnight under vacuum at r.t. before the addition of alkali hydroxides or carbonates (KOH, NaOH, Na₂CO₃, CsOH, Cs₂CO₃, Alkali:Au molar ratio = 10:1) either by solid grinding or incipient wetness impregnation. Alkali promoted Au/TS-1 was further dried under vacuum before being calcined at 300°C with a heating rate of 0.5°C/min under air flow (50 ml/min) for 4h. The prepared samples were stored in dark under dry vacuum before any treatments and tests. The solid grinded and impregnated samples were denoted as “s” and “i” respectively within the text.

Structural properties of synthesized TS-1 and Au/TS-1 catalysts were characterized by powder X-ray, UV-vis and TEM techniques and the results are discussed in the supporting information. The physical properties of TS-1 and Na(OH)_i-Au/TS-1 are given in Table S1.

Catalytic Screening Test

The gas phase propylene epoxidation was performed in a vertical oriented fixed-bed stainless-steel reactor in which 100 mg as-prepared catalyst was packed in the middle using quartz wool. The outlet of the tube was connected to a GC (Shimadzu GC-2014 with methanizer and FID detector) with a stainless-steel tube covered with a heating tape to prevent the condensation of the materials. The GC is then connected to a computer for the

online analysis. For both temperature program and isothermal reactions, the catalysts were heated to desired temperature with a ramping rate of 1.0°C/min under continuous flow of reactant gas mixtures (GHSV=14000 mL.h⁻¹.g_{cat}⁻¹, Propylene: Oxygen: Hydrogen: Helium or Nitrogen = 0.4: 0.4: 0.4: 22.2 mL.min⁻¹). Once the temperature reached to desired value, the GC analysis was started and data points were collected online. For catalytic experiments, the data points were collected every 20 minutes for 1 hour dwell time at 160°C. Similar measurements were taken place for each further temperature: 170, 180, 190, 200 and 210 °C. The average PO production at the selected temperature was calculated and presented in Figure 1 in the main text.

In our controlled experiments, pure TS-1, uncalcined samples or absence of hydrogen gas stream did not contribute any catalytic activity, which were in agreement with the previous observations.^{3,4}

Characterization

The powder X-ray diffraction (PXRD) profile was collected by PANalytical X'pert PRO diffractometer using Cu K α radiation (λ = 1.5418 Å) from a generator operating at 40 kV and 40 mA.

Synchrotron X-ray diffraction (SXR) data were collected on Beamline I11, Diamond Light Source, Harwell, UK. The energy of the incident X-ray flux was set at 15 keV. The wavelength and the 2 θ -zero point were refined using a diffraction pattern obtained from a high quality silicon powder (SRM640c), corresponding to: λ = 0.825575(2) Å and 2 θ ZP = - 0.000753(10)°. High resolution SXR data were obtained from the zeolite samples using the multi-analyser crystals (MAC) detectors. The patterns were collected in the 2 θ range 0-150° with 0.001° data binning. Each MAC pattern was collected for an hour for good statistics. In total, there are 4190 *hkl* reflections measured over the range of 3-55°, of which at least 300 independent *hkl* reflections are observed. From a crystallography perspective, the number of structural variables should not exceed the number of *hkl* reflections in a refinement. In the Rietveld refinements performed in this work, the number of structural parameters has not exceeded 170. Using the TOPAS software, the lattice parameters were refined using Le Bail method, and also the Rietveld refinement analyses of the diffraction patterns were performed. The starting coordinates used were based on the H-ZSM-5 zeolite model by Heo *et al.* for sample refinement.⁵ The background curve was fitted by a Chebyshev polynomial with an average of 20 coefficients. The Thompson-Cox-Hastings pseudo-Voigt peak function proposed by Thompson *et al.* was applied.⁶ The scale factor and lattice parameters were allowed to vary for all the histograms. The refined structural parameters for each data histogram were the fractional coordinates (x,y,z) and isotropic displacement factors (B_{eq}) for all atoms, and the site occupancy factors (SOF). The B_{eq} were constrained in the following way: all the T-sites (T=Ti, Si) share the same value, and the values for the O-sites are twice the B_{eq} for the T-sites. The quality of the Rietveld analyses of the SXR data was confirmed by well-fitted refinement profile, low R-weighted pattern (R_{wp}) values and goodness-of-fit.

Au L3-edge X-ray absorption spectra (XAS) was conducted in fluorescence mode with a 13-Channel Ge detector at the B18 XAS beamline at the Diamond Light Source, UK. To examine the local chemical environment around Au atoms, Extended X-Ray Absorption Fine Structure (EXAFS) data were extracted from XAS spectra. The Demeter ATHENA program was used for XAFS data analysis, where the data were background subtracted, normalised and Fourier transformed. The Demeter ARTEMIS program was used to perform the least-

squares curve fitting analysis of the EXAFS $\chi(k)$ data. The EXAFS Wavelet analysis was performed following the protocol and calculations developed by Marina Chukalina and Harald Funke, where the backscatter atoms are distinguished within the same atomic shell. To confirm the reproducibility of the experimental data, at least 2 scan sets were collected and compared for each sample. The spectra were calibrated with Au foil as reference. The amplitude reduction factor was obtained from analysis of the Au foil, which was used as a fixed input parameter to allow refinement in the coordination number and bond distance of the absorption element.

We are cautious that that X-ray radiation may cause some damage and heating, leading to changes in structure and/or oxidation state of Au (generally photo-reduction), where the latter has previously been shown by Hutchings' group (Malta et. al., Science, 355, 2017, 1399-1403). However, the white line intensity of Au(I) complexes are also sensitive to the ligand attached as well as the oxidation state. For instance, $[\text{AuCl}_2]^-$ has a white line intensity at about 0.7-0.8 whereas for $\text{KAu}(\text{CN})_2$, the white line is at around 1.1. The spectrum that we have measured for $\text{KAu}(\text{CN})_2$ is comparable to the literature (Electrochimica Acta 190 (2016) 997–1006) and the white line intensity is similar to it after the curve is normalised. In addition, a linear combination fitting (using $\text{KAu}(\text{CN})_2$ and Au foil as standards) is performed accordingly with a low R-factor (0.0007336). It is calculated that the ratio of Au(I):Au(0) is 61.7:38.3.

Spherical Aberration Corrected Scanning Transmission Electron Microscopy images of samples using a High Angle Annular Dark Field detector (CS-corrected STEM-HAADF) were taken using a JEOL ARM300F TEM at 200 kV. Energy Dispersive X-ray Spectroscopy of the samples were performed using JEOL ARM200F TEM at 200 kV at ePSIC, Harwell Campus, UK. The sample particles were deposited on an Agar Scientific holey carbon supported copper 400 mesh grid. TEM samples were prepared either by solid deposition or by sonicating a suitable amount of material in 1 mL ethanol for 15 minutes before dropwise addition of the solution onto the copper grid.

BJH and BET analysis was carried out at Materials Department of University of Oxford using Micromeritics Gemini V surface area analyser using Nitrogen as the adsorbate. All samples were degassed at 150°C until a constant weight was achieved prior to analysis.

UV-vis spectra were recorded on a Perkin Elmer Lambda 750S UV/VIS spectrometer using BaSO_4 as the reference.

Physical Properties of As-Prepared Catalysts

The general characterization of the physical properties of synthesized samples was performed by BET, XRD and UV-vis. From Table S1, the BET surface area and pore volume of TS-1 support are $401\text{ m}^2\cdot\text{g}^{-1}$ and $0.237\text{ cm}^3\cdot\text{g}^{-1}$, respectively, in agreement with the literature values¹. Incorporation of Au and NaOH into TS-1 decreased the surface area (401 vs $397\text{ m}^2\cdot\text{g}^{-1}$) and micropore volume (0.142 vs $0.115\text{ cm}^3\cdot\text{g}^{-1}$) which evidence the accommodation of these species inside the TS-1 internal surface.

Table S1 Physical properties of TS-1 and $(\text{NaOH})_i\text{-Au/TS-1}$

	$(\text{NaOH})_i\text{-Au/TS-1}$	TS-1
BET Surface Area (m^2/g)	397	401
Pore Volume (cm^3/g)^a	0.231	0.237
Micropore Volume (cm^3/g)^b	0.115	0.142

^a Single point adsorption total pore volume of pores less than 39.6633 nm diameter at $P/P_0 = 0.949027253$

^b Determined by t-plot method

XRD patterns (Figure S1) of TS-1, Au/TS-1 and alkali treated Au/TS-1 catalysts were collected. The XRD patterns present similar diffraction peaks located at $2\theta = 7.9^\circ, 8.8^\circ, 13.8^\circ, 14.7^\circ, 23.0^\circ, 23.6^\circ$ and 23.8° corresponding to the characteristic Bragg's reflections of *MFI*-type zeolite planes at (011), (200), (012), (301), (501), (151) and (033), respectively.^{7,8} The Bragg's diffraction peaks of Au at $2\theta = 38.2^\circ$ and 44.4° were also identified for all Au loaded TS-1 samples showing the facile conversion of gold precursors to gold nanoparticles (Au NPs) during calcination.^{9,10} We attributed the formation of Au NPs to the poor stabilisation of some precursors without much interaction with the TS-1 internal surface which presumably may have taken place in the voids trapped between TS-1 particles. However, the intensity of these gold peaks were significantly lower in the cases of $(\text{NaOH})_i\text{-Au/TS-1}$ and $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ catalysts, indicating the higher dispersion of Au atoms by the internal surface as compared to other as-prepared catalysts.

Figure S1. Powder X-ray diffraction patterns of TS-1 and as-prepared catalysts. Bottom image is the zoom to the area of $2\theta = 34\text{--}46^\circ$. Dash lines show the diffraction peak positions of bulk Au.

The diffuse reflectance UV-vis spectra (Figure S2) show that samples exhibit a major absorbance band between 210-230 nm which is characteristic of isolated framework Ti(IV) in tetrahedral coordination (T sites). The absence of absorption bands in the 330 nm region indicates there is no formation of extra-framework titanium during the synthesis of TS-1 or after the preparation of catalysts.^{8,11} The absorption bands observed at 280 and 550 nm were attributed to framework Ti(IV) in octahedral coordination, presumably due to water adsorption, and the plasmon resonance of Au nanoparticles, respectively in the as-prepared catalysts. In agreement with XRD results, the intensity of plasmon resonance bands were found to be much lower in (NaOH)_i-Au/TS-1 and (Na₂CO₃)_i-Au/TS-1 catalysts indicating better dispersity of Au atoms within TS-1 structure as opposed to those Au NPs on exterior surface.

Figure S2. Diffuse-reflectance UV-vis spectra of TS-1 and as-prepared catalysts

Selectivity Profiles and Catalytic Activities of As-Prepared Samples

The as-prepared samples were tested in gas phase propylene epoxidation reaction in H_2/O_2 at a temperature range of 160-210°C (Figure S3). The general selectivity of the as-prepared catalysts is optimised at about 180-210°C with >70% towards PO. The catalytic activity and selectivity of the samples were found to be critically dependent on the type of alkali salt and the catalyst preparation method which are discussed in detail in the main manuscript. As evidenced by XRD and UV-vis, Au atoms dispersion was found to be low in as-prepared catalysts, except Na^+ incorporated Au/TS-1 samples prepared by incipient wetness impregnation method (Figure S3d-e). For these catalysts, propionaldehyde was the main side product along with minor amount of CO_2 , CO, ethanal and acrolein. It is known that the formation of isomers of PO (propionaldehyde, acetone) results from the interaction of pre-formed PO with the acidic sites of the catalyst.¹² These acidic sites (Lewis acid sites or surface hydroxyl groups) are expected to be present more on the external surface of TS-1 due to the formation of defects during catalyst preparation. It is therefore high likelihood that PO formed by large size Au nanoparticles supported on the external surface of TS-1 further interacts with surface acid sites and transforms into propionaldehyde. On the other hand, the amount of observed propionaldehyde was much lower on Cs-containing salt deposited Au/TS-1 catalysts. This is attributed to the strong interaction of Cs with Au and Ti, promoting increase in the Au sites for H_2O_2 production and/or increase in the Au-Ti synergetic sites for the PO production.¹ Despite high PO selectivity of CsOH - and Cs_2CO_3 -Au/TS-1 catalysts, propylene conversion stayed as limited, mainly due to the low dispersion of Au atoms, present as large Au nanoparticles on the external surface of TS-1. Similar propylene conversion values of $(\text{KOH})_s$ -Au/TS-1, $(\text{NaOH})_s$ -Au/TS-1, $(\text{CsOH})_i$ -Au/TS-1 and $(\text{Cs}_2\text{CO}_3)_i$ -Au/TS-1 catalysts evidence that number of active sites is alike but nature of alkali salt strongly affects the final product. The boost in propylene conversion and selectivity towards PO with Na^+ -containing salt impregnated Au/TS-1 catalysts is attributed to high dispersion of Au atoms within TS-1 micropores and increase in Au-Ti interface.

Figure S3. Selectivity and conversion profiles of **a)** Au/TS-1, **b)** (KOH)_s- Au/TS-1, **c)** (NaOH)_s-Au/TS-1, **d)** (NaOH)_i- Au/TS-1, **e)** (Na₂CO₃)_i- Au/TS-1, **f)** (CsOH)_i-Au/TS-1, **g)** (Cs₂CO₃)_i- Au/TS-1; CO₂=Carbon dioxide, CO= Carbon monoxide, Et=Ethanal, An= Acrolein, PA=Propionaldehyde, PO=Propylene oxide

CS-STEM/HAADF/BF Images of As-prepared $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ and $(\text{NaOH})_i\text{-Au/TS-1}$

Figure S4 shows Spherical Aberration Corrected Scanning Transmission Electron Microscopy (CS-STEM) images of as-prepared $(\text{NaOH})_i\text{-Au/TS-1}$ and $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ samples using a High Angle Annular Dark Field detector (HAADF) where primary TS-1 particles of around 200 nm are clearly seen. The presence of Au nanoparticles of ca. 3-11 nm with inter-planar distance of $2.4\text{\AA}$ corresponding to fcc Au (111), is distinguished in small extent on both samples. We attributed the formation of these Au nanoparticles to the poor stabilisation of some precursors without much interaction with the TS-1 internal surface which presumably may have taken place in the voids trapped between TS-1 particles. These particles appeared to be weakly attached to TS-1 surface from which they started to migrate and sinter under the electron beam illumination.

Figure S4. CS-STEM/HAADF images of as-prepared (a-b) $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ and (c-d) $(\text{NaOH})_i\text{-Au/TS-1}$ samples before reaction. The inset of image b is the zoom to the area labelled by red frame

The presence of Au atoms within the selected nanoparticle (Figure S5a) and on nanoparticle free area (Figure S5b) was confirmed by Energy Dispersive X-ray Spectroscopy (EDS) analysis. Atomic resolution CS-STEM/HAADF/BF (Figure S6) was also used to identify mononuclear Au inside TS-1 but individual Au atoms could not be differentiated unambiguously which is presumably due to high dispersion of Au atoms within the internal micropores of TS-1 masked by multilayer framework atoms (atomic resolution images can only be taken at the edge of the particles where TS-1 crystal has a thin layer).

Figure S5. a) CS-STEM/HAADF image of as-prepared (NaOH)_x-Au/TS-1 at high magnification and corresponding EDS spectrum of the selected point, b) CS-STEM/HAADF image of as-prepared (NaOH)_x-Au/TS-1 catalyst at low magnification and corresponding EDS mapping of the selected area shown by rectangular frame.

Figure S6. Atomic resolution (a-b) CS-STEM/BF (c,d) Cs-STEM/HAADF images of as-prepared (NaOH)_i-Au/TS-1 before reaction

XAS Studies

The chemical state and local structures surrounding the Au species were probed by using X-ray Absorption Spectroscopy (XAS). Figure S7 shows the X-ray absorption near edge spectra (XANES) of as-prepared and spent $(\text{NaOH})_i\text{-Au/TS-1}$ catalyst together with $\text{KAu}(\text{CN})_2$ and Au foil as references. Apart from the large Au NPs as spectators, the extremely dispersive nature of the precursor (nuclei) on the inner surface of TS-1 in as-prepared catalyst before the catalytic test is evident while the spent catalyst contains larger gold clusters. The significant reduction in the relative intensity of absorption peak (white line) and slight shift in the energy of absorption edge and long range fine structure oscillation of the as-prepared catalyst compared to $\text{KAu}(\text{CN})_2$ approaching to Au foil can be attributed to the change of cationic $\text{Au}(\text{I})$ to immobilised Au likely with δ^+ character together with $\text{Au}(0)$ NPs in the same sample. These results are consistent with our STEM observations and strongly suggest that dispersed anchored Au species on inner surface, invisible by STEM, are present in addition to the Au NPs within the as-prepared samples.

The extended X-ray absorption fine structure (EXAFS) functions of as-prepared and spent catalysts after Fourier Transform presented some detailed information about the local environment of Au. However, it is rather challenging for typical EXAFS data fitting to separate the contributions of anchored Au-O species from Au-Au of the exterior Au NPs without mixing them up in the same sample. In order to differentiate the close distances of Au-Au from Au-O, EXAFS spectra treated with wavelet transform analysis were therefore performed. In simplified terms, the wavelet transform is a 3D image that combines the EXAFS-spectra in k-space and r-space (FT transform) where the back-scattering of the elements appear with high intensity. Depending on the weight of the back-scatterer the maximum intensity appears at different k-values. As shown in Figure S8, a 2D contour plot derived from Fourier transformation of EXAFS spectra allows differentiation of heavy (Au) from light back-scatterer (O), which gives the short-range distances (R) ($<4\text{\AA}$) and coordination numbers (CN) of Au in the as-prepared samples while spent catalyst presents higher Au-Au CN (see Table 1 in the main manuscript). It should be noted that all XAS plots, including Fourier and wavelet transformed, are represented without phase correction. Therefore, the radial distances observed in the EXAFS plots are $\sim 0.4\text{--}0.5\text{ \AA}$ below their actual value.

Figure S7. XANES spectra for Au LIII edge of as-prepared and spent (NaOH)_i-Au/TS-1 catalyst together with KAu(CN)₂ and Au foil as references

From the white light intensity above, it is clear that spent catalyst has Au(0) character. Small differences (slight shift of peak maxima to higher energies and lower intensity peaks) are consistence with previously reported XANES spectra of reduced average coordination number of Au atoms (clusters/nanoparticles) compared to bulk Au. In addition, it is known in the literature that features of XANES spectra might slightly change based on cluster size and shape (please refer to Top Catal (2017), 60, 283–288). Therefore, we attribute the small changes in XANES features to different size and shape of Au clusters within TS-1 support.

Figure S8a. Upper: The k^3 -weighted EXAFS function and fitting of (NaOH)_i-Au/TS-1 as-prepared catalyst. $k^3\chi$ experimental and fitted data with and without Fourier transformation; **Bottom:** The k^3 -weighted EXAFS function and fitting of (NaOH)_i-Au/TS-1 spent catalyst. $k^3\chi$ experimental and fitted data with and without Fourier transformation (see summary in Table 1 in the main text).

Figure S8b. Upper: The k^3 -weighted EXAFS function and fitting of (NaOH)_i-Au/TS-1 as-prepared catalyst. Its Fourier transform and Central: corresponding Morlet wavelet transform analysis; **Bottom:** The k^3 -weighted EXAFS function and fitting of (NaOH)_i-Au/TS-1 spent catalyst. Its Fourier transform and Central: corresponding Morlet wavelet transform analysis. Parameters used in Morlet wavelet: Kappa = 4, Sigma = 1

With the background information collected such as XAS and microscopic studies, SXRD combined with Rietveld refinement can be used to elucidate both organic and inorganic adsorbate structures in zeolites.^{13,14} The alteration in scattering parameters of modified framework atoms by the host species enables the probing of adsorption geometries and interactions on the inner zeolitic surface.^{15,16} SXRD patterns of calcined TS-1 and (NaOH)_i-Au/TS-1 are presented in Figure S9. As discussed in the main text, the incorporation of Au into TS-1 did not alter the space group of TS-1; on the other hand, the relative intensities of the peaks were different for the two samples without any observable peak broadening. For instance, compared to the XRD pattern of pure TS-1, the intensities of the peaks around 12-14° increased in the as-prepared catalyst. Generally, the peak around 12.33° is related to the d-spacing of the (5 0 1) plane as shown in the Figure S9b. The rise in the intensity of the 12.33° peak indicated that some atoms or molecules (such as Au, NaOH, etc.) have successfully diffused into the periodic place of TS-1. Based on this, the refinement procedures of the TS-1 or Au TS-1 were performed as follows: Firstly, the Pawley method was used to check the space group and structure parameters. Secondly, the suitable TS-1 crystal information files were input into the TOPAS software to fit the observed data. The refined structural parameters for each data histogram were the fractional coordinates (x,y,z) and isotropic displacement factors (B_{eq}) for all atoms, and the site occupancy factors (SOF). To fit the Au TS-1 data, the Au atom and NaOH were added one by one. Also, the refined structural parameters for each data histogram were the fractional coordinates (x,y,z) and isotropic displacement factors (B_{eq}) for all atoms, and the site occupancy factors (SOF). Notice that any free species of amorphous nature or crystalline species with different space group from the crystalline zeolite framework such as Au NPs will not create the corresponding intensity changes in the parent diffraction peaks of zeolite hence will not affect the elucidation of the adsorbate structure on this zeolite framework. As stated in experimental details in SI, more than 4000 independent hkl reflections were used for the Rietveld refinement, which allowed for a greater number of structural variables to be refined in a satisfactory manner. The quality of the Rietveld analyses of the SXRD data was confirmed by well-fitted refinement profile, low R-weighted pattern (R_{wp}) values and goodness-of-fit (Tables S2, S3).

Based on refinement results, we determined the crystal structure of anchored mononuclear Au species as $K^+Au(OH)_2Na^+(O_f)_3$, in which f signifies the framework oxygens of TS-1 (see the main text for further discussions). According to the kinetic stable gas phase Au clusters with magic numbers, the first or inner shell around the central Au atom should compose of 12 atoms if equal size Au atoms are coordinated.¹⁷ Using XAS and modelling calculations, a range of alkali hydroxide (Na^+ or K^+) stabilised but isolated $Au-O(OH)_x$ species supported on internal surface of MCM-41 as the active catalytic centres for water gas shift reaction have previously been proposed by Yang *et. al.*² Considering their proposed larger but the structurally undefined mononuclear anchored $AuO_x(OH)_y(Na,K)_{9-11}$ clusters within the mesoporous MCM-41, the formation of such single gold atom species stabilised by 9-11 of Na^+ or K^+ OH^- groups is unlikely to take place in our catalyst precursor due to the much smaller pores of TS-1. Particularly, in our case, only two Na^+/K^+OH^- ion pairs are found to stabilise the three-surface rigid oxygens anchored mononuclear Au alongside with the sinusoidal channel, without any alkali hydroxide ion pair accommodated across the cross-sectional channel (5.3×5.6 Å). This can be appreciated since the additional ca. 3.35 Å $NaO(H) \cdots Au$ interaction for the bulky anchored Au species in this narrow and congested small channel cross section is sterically unfavourable, leaving this immobilised but lesser

coordinated Au active for catalysis or as precursor for the formation of encapsulated clusters. Thus, the crystalline TS-1 zeolite offers the formation of structurally more defined adsorbed single mononuclear Au on its internal surface. It is also noted that the structural elucidation from SXRD can give unique information beyond those from XAS and microscopic techniques, which could especially offer the precise structure and location of the anchored species in the 3-D channels of TS-1 structure.

Figure S9. SXRD and Rietveld refinement profiles of a) TS-1 ($R_{wp} = 6.31\%$) with the corresponding crystal structure (Atoms are presented in sticks with O = red, Si/Ti = grey) b) as-prepared $(NaOH)_x$ -Au/TS-1 catalyst ($R_{wp} = 7.36\%$) with the corresponding refined crystal structure along $\langle 501 \rangle$ plane. (Atoms are presented in balls with Au = light orange, Na = yellow, O = red, Si/Ti = blue)

Table S2. Crystallographic data and details of as-prepared (NaOH)_i-Au/TS-1

Sample	(NaOH) _i -Au/TS-1
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Chemical formula	AuO ₃ (ONa)(OK)
<i>a</i> (Å)	20.07719(3)
<i>b</i> (Å)	19.90199(5)
<i>c</i> (Å)	13.38260(3)
<i>V</i> (Å ³)	5347.366 (45)
<i>R</i> _{wp} / <i>R</i> _p / <i>R</i> _{exp} (%)	7.36/5.73/2.65
Wavelength (Å)	0.825634(2)
Zero point	-0.000753
Gof	2.77

*R*_{wp}: the weighted profile factor.
Gof: goodness-of-fit.

Table S3. Atomic parameters from the Rietveld refinement of (NaOH)_i-Au/TS-1 at room temperature

Species	Atom	X	Y	z	SOF	B _{eq} (Å ²)	Wyckoff
Zeolite framework	O1	0.3771(4)	0.0468(4)	0.7573(5)	1	2.06(2)	8d
	O2	0.3060(4)	0.0600(3)	0.9179(4)	1	2.06(2)	8d
	O3	0.1975(3)	0.0618(3)	0.0263(3)	1	2.06(2)	8d
	O4	0.0930(3)	0.0644(4)	0.9169(5)	1	2.06(2)	8d
	O5	0.1205(3)	0.0584(5)	0.7290(4)	1	2.06(2)	8d
	O6	0.2502(3)	0.0449(5)	0.7509(5)	1	2.06(2)	8d
	O7	0.3764(4)	0.8393(4)	0.7610(5)	1	2.06(2)	8d
	O8	0.3014(4)	0.8440(3)	0.9307(5)	1	2.06(2)	8d
	O9	0.2011(3)	0.8459(2)	0.0356(4)	1	2.06(2)	8d
	O10	0.0892(3)	0.8403(3)	0.9197(6)	1	2.06(2)	8d
	O11	0.1188(4)	0.8555(3)	0.7324(5)	1	2.06(2)	8d
	O12	0.2476(4)	0.8364(4)	0.7693(5)	1	2.06(2)	8d
	O13	0.3162(3)	0.9509(3)	0.8225(3)	1	2.06(2)	8d
	O14	0.0840(2)	0.9525(4)	0.8285(4)	1	2.06(2)	8d
	O15	0.4194(3)	0.1288(3)	0.6120(6)	1	2.06(2)	8d
	O16	0.4071(4)	1.0035(4)	0.5814(6)	1	2.06(2)	8d
	O17	0.3995(3)	0.8658(3)	0.5686(6)	1	2.06(2)	8d

	O18	0.1928(5)	0.1245(3)	0.6199(5)	1	2.06(2)	8d
	O19	0.2063(4)	0.0013(3)	0.6017(5)	1	2.06(2)	8d
	O20	0.1976(4)	0.8743(3)	0.5882(4)	1	2.06(2)	8d
	O21	0.9990(4)	0.0555(5)	0.7922(4)	1	2.06(2)	8d
	O22	0.9999(4)	0.8593(3)	0.8004(4)	1	2.06(2)	8d
	O23	0.4227(6)	0.75	0.6426(7)	1	2.06(2)	4c
	O24	0.1951(6)	0.75	0.6607(6)	1	2.06(2)	4c
	O25	0.2848(4)	0.75	0.0570(7)	1	2.06(2)	4c
	O26	0.1134(5)	0.75	0.0780(7)	1	2.06(2)	4c
	Si1	0.4214(1)	0.0577(2)	0.6635(2)	1	1.36(1)	8d
	Si2	0.2801(1)	0.0596(2)	1.0302(2)	1	1.36(1)	8d
	Si3	0.3079(2)	0.0300(1)	-0.1862(2)	1	1.36(1)	8d
	Si4	0.1199(1)	0.0602(2)	0.0338(2)	1	1.36(1)	8d
	Si5	0.0700(2)	0.0272(1)	0.8166(3)	1	1.36(1)	8d
	Si6	0.1854(2)	0.0593(2)	0.6767(2)	1	1.36(1)	8d
	Si7	0.4269(2)	0.8268(1)	0.6754(3)	1	1.36(1)	8d
	Si8	0.3106(2)	0.8697(1)	0.8161(2)	1	1.36(1)	8d
	Si9	0.2727(1)	0.8274(1)	0.0353(2)	1	1.36(1)	8d
	Si10	0.1191(2)	0.8256(1)	0.0277(3)	1	1.36(1)	8d
	Si11	0.0727(2)	0.8695(2)	0.8159(3)	1	1.36(1)	8d
	Si12	0.1907(2)	0.8269(1)	0.6783(3)	1	1.36(1)	8d
AuO3(ONa)(OK)	Au	0.8590(8)	0.7018(6)	0.3142(3)	0.009(1)	2	8d
	K/Na1	0.0102(5)	0.2049(5)	0.9031(7)	0.009/0.178(2)	5	8d
	OK1	0.1095(8)	0.2974(8)	0.9316(13)	0.187(2)	2	8d
	Na2	0.3449(12)	0.2863(12)	-0.0552(18)	0.126(3)	5	8d
	ONa2	0.2769(17)	0.2130(18)	-0.1706(24)	0.126(3)	2	8d

SOF, site occupation factor;
B_{eq}, isotropic temperature factor (thermal parameter).

Table S4. Atom distances of the refined Au structure

	Atom	Nº	d [Å]
1.	O18	34	2.057
2.	O25	49	2.471
3.	O5	13	2.941
4.	ONa2	54	3.347
5.	OK1	53	3.351

Catalytic activity of pre-activated sample has also been run. The as-prepared sample $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ was reduced slowly under hydrogen over 10 hours and then the catalytic propylene oxidation was then started. The catalytic performance of pre-activated catalyst was followed by GC, results of which can be seen in Figure S10. There is no induction period observed which is in agreeable with our other experimental results and conclusion.

Figure S10. Catalytic performance of pre-activated $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ in propylene epoxidation reaction. (STY= space time yield. Reaction conditions: $\text{C}_3\text{H}_6:\text{O}_2:\text{H}_2:\text{He}=0.4:0.4:0.4:22.2 \text{ mL}\cdot\text{min}^{-1}$, $\text{GHSV}=14000 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$, 0.1 g catalyst)

We did not study the stabilization time for each temperature range for all the catalysts during catalyst screening. Instead, we selected two temperatures, 180 and 210°C for $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ catalyst at which the highest PO selectivity and yield were observed, respectively, before and after reaching steady-state so induction period can be observed (Figure S11). The catalysts were heated to desired temperatures with 1°C/min of ramp and then, their catalytic activity was monitored by online GC analysis. PO selectivity was found to be 95% at 210°C and 97% at 180°C, in agreement with the previous catalytic screening results. In addition, an activation period was clearly observed at both temperatures. While the steady state conditions could be achieved in 6h at 210°C, much longer time (10h) was necessary at 180°C. These results strongly suggest that an induction period of time is required for the formation of catalytically active species which is quicker at high temperatures as expected. It is also worthy to note that the maximum PO yield (STY) was found to be much higher than the av. STY observed during the catalysis screening test (20 vs 14 $\text{g}_{\text{PO}}\cdot\text{h}^{-1}\cdot\text{kg}_{\text{cat}}^{-1}$) at 180 °C, while the situation was reverse at 210 °C (35 vs 22 $\text{g}_{\text{PO}}\cdot\text{h}^{-1}\cdot\text{kg}_{\text{cat}}^{-1}$). The loss in catalytic activity at 210°C was attributed to the formation of larger size particles (lower surface area), which was evident by TEM analyses, due to a more rapid nucleation and growth of atoms used at higher temperature and at shorter time. Finally, $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ catalyst exhibited excellent catalytic stability during 18h under steady state conditions at 210°C; however, a drastic drop in its catalytic activity was observed 6h after reaching steady state condition at 180°C. As the decrease in propylene conversion was more severe than the slight decay in PO selectivity, it is evident that some of the PO active sites were blocked by bidentate species or carbon deposition and further sintering of particles did not generate active sites for partial and/or total oxidation products since otherwise, the propylene conversion would not be decreasing as the reaction proceeded. On the other hand, adsorption/desorption of reactants/products at 210°C is expected to be thermodynamically much easier than at 180°C; thus, allowing accessibility to active metal surface. Based on these results, we think that

high temperature ($>190\text{ }^{\circ}\text{C}$) is preferable for continuous propylene oxidation without catalyst deactivation.

Figure S11. Catalytic performance of $(\text{Na}_2\text{CO}_3)_i\text{-Au/TS-1}$ catalyst under isothermal conditions at a) 180°C and b) 210°C .

As evidenced by UV-vis and PXRD, less active catalysts have already formed large Au nanoparticles during calcination period (the decomposition of $\text{KAu}(\text{CN})_2$ under air results in self-reduction of $\text{Au}(\text{I})$ to $\text{Au}(0)$, leading to large Au agglomerates in the absence of stabilization). Therefore, we did not observe any significant induction period for these catalysts during catalytic transformation. The slight increase in PO production with temperature is attributed to increase in reaction kinetics as propylene oxidation is thermodynamically more favourable at high temperatures.

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