Thermally stable single atom Pt/m-Al₂O₃ for selective hydrogenation and CO oxidation

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Single-atom metal catalysts offer a promising way to utilize precious noble metal elements more effectively, provided that they are catalytically active and sufficiently stable. Herein, we report a synthetic strategy for Pt single-atom catalysts with outstanding stability in several reactions under demanding conditions. The Pt atoms are firmly anchored in the internal surface of mesoporous Al₂O₃, likely stabilized by coordinatively unsaturated pentahedral Al³⁺ centres. The catalyst keeps its structural integrity and excellent performance for the selective hydrogenation of 1,3-butadiene after exposure to a reductive atmosphere at 200 °C for 24 h. Compared to commercial Pt nanoparticle catalyst on Al₂O₃ and control samples, this system exhibits significantly enhanced stability and performance for n-hexane hydro-reforming at 550 °C for 48 h, although agglomeration of Pt single-atoms into clusters is observed after reaction. In CO oxidation, the Pt single-atom identity was fully maintained after 60 cycles between 100 and 400 °C over a one-month period.
Element sustainability has become a global issue. Maintaining current consumption rate, there are 22 elements facing depletion within the coming 50 years, including almost all Platinum Group metals that are crucial catalyst components. Despite the critical role of Pt in catalysis, it is rare, in short supply in recent years and has no adequate alternatives. In this regard, single-atom catalysts (or atomically dispersed catalysts), in which all the metal atoms are exposed on the support available for catalytic reactions, could help to address the problem. The electronic properties of isolated metal atoms may be distinctly different from the active sites in bulk materials and nanoparticles, potentially triggering innovative applications and enabling more effective usage of noble metal elements.

A challenge in the development of single-atom catalysts is the increasing difficulty to stabilize single-atom species under drastic reaction conditions. Many industrially important catalytic processes involving Pt catalysts, such as reforming of hydrocarbons in petroleum refineries, are operated at several hundred degrees under oxidative or reductive atmosphere. In this context, single-atom catalysts that are able to withstand harsh reaction conditions are highly desirable. Very recently, Datye and co-workers have illustrated the trapping of atomic Pt species leached from alumina onto the defect sites in rod or polyhedral shaped ceria at 800°C (ref. 31). Corma et al. reported subnанometric Pt species finely confined within the internal framework cavities of MCM-22, which withstands thermal treatment in air up to 540°C, and is more stable in propane dehydrogenation than catalysts prepared via the conventional wet-impregnation method. Flytzani-Stephanopoulos and Sykes et al. developed single-atom alloy catalysts, in which isolated Pt atoms substituted into the Cu(111) surface, that are stable for butadiene dehydrogenation at 160°C for more than 46 h (ref. 33). These examples highlight the importance of manipulating the interactions between metal atoms and the host support to achieve high stability without losing reactivity in single-atom catalysis.

Herein, we report a highly stable, atomically dispersed Pt catalyst supported on mesoporous Al2O3. The Pt – Al – O system is chosen because Al2O3 is a common support for Pt in industrial and environmental applications. The catalyst was prepared by a modified sol-gel solvent vaporization self-assembly method, followed by calcination in air and reduction with H2. Encouragingly, the catalyst maintained the catalytic activity as well as structural integrity when scrutinized in a series of reactions under drastic conditions with long durations.

Results

Catalyst synthesis and characterization. In the first step, C9H21AlO3 (EO)20(PO)70(EO)20 triblock copolymer (P123) and H2PtCl6 were mixed and dissolved in ethanol. With continued evaporation of the solvent, the amphiphilic P123 macromolecules associated with C9H21AlO3 spontaneously assembled into a rigid, highly ordered, hexagonally arranged mesoporous structure with the presence of nitrogen (0.97 wt%) and carbon (0.79 wt%) in 0.2Pt/m-Al2O3-O2 whereas the content of these elements became negligible in 0.2Pt/m-Al2O3-H2 (Supplementary Table 2).

The samples were subsequently investigated by scanning transmission electron microscope (STEM) with high-angle annular dark-field (HAADF), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area analysis, H2-O2 and CO titration, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Al magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) to probe the characteristics of the support and the Pt species. These materials exhibit similar surface areas (200.6 to 227.3 m2 g−1), pore volumes (0.51 to 0.56 ml g−1), and a diffraction peak at around 0.8° in the small-angle XRD pattern, unambiguously proving the mesoporous structure (Supplementary Figs 4 and 5, Supplementary Table 3). No Pt peaks are detected from XRD patterns in 0.2Pt/m-Al2O3-O2, 0.2Pt/m-Al2O3-H2, 0.5Pt/m-Al2O3-O2 and 0.5Pt/m-Al2O3-H2, suggesting that most Pt species are present in small nanoclusters and/or isolated atoms. Weak diffraction peaks for Pt are found on 2.0Pt/m-Al2O3-O2 and 2.0Pt/m-Al2O3-H2, indicating the formation of Pt nanoparticles (Supplementary Fig. 6).

Consistent with BET and XRD analysis, the TEM images of 0.2Pt/m-Al2O3-O2 and 0.2Pt/m-Al2O3-H2 show well-aligned, mesoporous Al2O3 without any Pt nanoparticles (Fig. 2a,b, Supplementary Fig. 7a–d), and TEM-EDS images reveal that Pt is uniformly dispersed throughout the sample (Fig. 2c, Supplementary Fig. 7e). Indeed, HAADF-STEM technique clearly demonstrates the existence of isolated Pt atoms with high number density in 0.2Pt/m-Al2O3-H2 (Fig. 2d) and 0.2Pt/m-Al2O3-O2 (Fig. 2f). This is remarkable, since 0.2Pt/m-Al2O3-H2 was even treated at 400°C in the presence of H2. Apart from the dominant amount of isolated atoms, a few small clusters that exhibit considerable structural dynamics under electron beam were also observed. A snapshot image (Fig. 2g,h) shows that the cluster has loosely packed atoms with the interatomic distances longer than those observed in metallic Pt. However, it is difficult to affirm whether these small clusters are formed by loose packing of single Pt atoms, or by electron beam-induced fragmentation of the close packed structure. More images and intensity profiles of Pt species in these samples can be found in Supplementary Figs 8 and 9. The numbers of atoms for the nearest neighbour distance from 525 single atoms identified on 0.2Pt/m-Al2O3-O2 and 532 single atoms identified on 0.2Pt/m-Al2O3-H2 were analysed (Fig. 2e, Supplementary Fig. 9c), showing that a vast majority of Pt atoms are well separated from each other (distance ≥ 0.5 nm). Not surprisingly, Pt nanoclusters and nanoparticles are observed in samples with 0.5 and 2.0 wt% Pt loading. In addition, the enhanced Pt content is detrimental to the formation of high quality hexagonally arranged mesoporous Al2O3 (Supplementary Figs 10 and 11).

The pre-catalysts and catalysts were labeled in the following manner: Pt weight percentage, nature of the support (for example, m-Al2O3, referring to mesoporous Al2O3), and treatment atmosphere. For instance, 0.2Pt/m-Al2O3-O2 refers to 0.2 wt% Pt supported on mesoporous Al2O3 which was calcined in air at 400°C without reduction, whereas 0.5Pt/m-Al2O3-H2 refers to 0.5 wt% of Pt on mesoporous Al2O3, consecutively calcined in air and reduced with H2 at 400°C. FT-IR spectra (Supplementary Fig. 2) suggest complete removal of the P123 triblock copolymer and the ligand of aluminium isopropoxide in all samples. Supplementary Fig. 3 provides a photo of the aforementioned samples: 0.2Pt/m-Al2O3-O2 and 0.2Pt/m-Al2O3-H2 are grey, while the others are black. This contrasts with pure m-Al2O3 which is light yellow. Organic elemental analysis suggested
Figure 1 | Schematic illustration of the 0.2Pt/m-Al2O3-H2 synthesis process. Aluminum isopropoxide, P123, and H2PtCl6 mixture ethanolic solution self-assembled into a gel after ethanol evaporation at 60 °C. The gel was calcined at 400 °C and reduced in 5% H2/N2 at 400 °C, forming the single atom catalyst 0.2Pt/m-Al2O3-H2.

Figure 2 | Characterization of single-atom Pt materials. For 0.2Pt/m-Al2O3-H2, (a,b) TEM, (c) TEM-EDS elemental mapping, (d) HAADF-STEM image, (e) the number of atoms for the nearest neighbour distance from 532 single atoms (representative images were shown in Supplementary Fig. 8). For 0.2Pt/m-Al2O3-O2, (f) an HAADF-STEM image, (g) the circle and square regions with the same colour and shape from f, (h) line-scanning intensity profiles obtained on the two zoomed areas in g. Scale bar, 200 nm (a), 20 nm (b), 100 nm (c), 2 nm (d), 2 nm (f).
Extended X-ray absorption fine structure spectroscopy (EXAFS) provides important evidence on the dispersion of Pt species on m-Al₂O₃. The Pt–Pt contribution at about 2.7 Å is absent in the \( k^3 \)-weighted EXAFS at the Pt L₃-edge for either 0.2Pt/m-Al₂O₃-H₂ or 0.2Pt/m-Al₂O₃-O₂ (Fig. 3a), strongly indicating that Pt exists predominantly as isolated atoms. The only prominent shell located at approximately 1.7 Å arises from Pt–O contribution, which is consistent with HAADF-STEM observation. At increased Pt loading (0.5 and 2.0 wt%), both Pt–O and Pt–Pt shells are present (Supplementary Fig. 12). The FT-EXAFS curves and the fitting results are summarized in Fig. 3d, Supplementary Fig. 13, Supplementary Table 4. The fitted Pt–O coordination number for both 0.2Pt/m-Al₂O₃-O₂ and 0.2Pt/m-Al₂O₃-H₂ is 3.8–4.0, implying that each Pt atom coordinates with four oxygen atoms on the support regardless of whether the sample has been reduced or not³⁶. Notably, the four-coordination mode is inherently preferred by zero or low valent Pt complexes, which partially explains the high stability of the Pt single-atom catalyst in the system. The electronic state of Pt species was investigated by X-ray absorption near edge structure analysis (Fig. 3b). The spectra exhibit a decreasing trend in the white-line intensities at 11,568 eV following this order: PtO₂ (2.20) \( \succcurlyeq \) H₂PtCl₆ (2.08) \( \succcurlyeq \) 0.2Pt/m-Al₂O₃-O₂ (1.66) \( \succcurlyeq \) 0.2Pt/m-Al₂O₃-H₂ (1.65) \( \succcurlyeq \) Pt foil (1.25) (Supplementary Fig. 14)³⁷,³⁸. This observation confirms that Pt species in these catalysts are positively charged by charge transfer from Pt to Al₂O₃, in excellent agreement with EXAFS fitting results where one Pt atom is anchored on the surface of m-Al₂O₃ by coordinating with four oxygen, as illustrated in Fig. 3c.

H₂–O₂ titration was applied to probe the available Pt atoms on the surface, involving treatment of the freshly prepared sample with air, followed by titration with H₂. Pure m-Al₂O₃ could not absorb H₂ (Supplementary Fig. 15a), suggesting that any H₂ uptake is due to the presence of Pt. During titration, 0.2Pt/m-Al₂O₃-H₂- exp. and 0.2Pt/m-Al₂O₃-H₂- ref. showed a decrease in the absorbance at 2,084 cm⁻¹, which is assigned to CO adsorbed on Pt (Fig. 3f). The 27Al MAS-NMR spectra of 0.2Pt/m-Al₂O₃-O₂ and 0.2Pt/m-Al₂O₃-H₂, and commercial Pt/Al₂O₃ show relative intensity changes of tetra-, penta- and octa-coordinated Al₂O₃ with recovery time for a spin-lattice relaxation measurement of Al₂O₃ for 0.2Pt/m-Al₂O₃-H₂ (Fig. 3g). Photographs of 0.2Pt/m-Al₂O₃-H₂ and 0.2Pt/p-Al₂O₃-H₂ under visible light and UV light (365 nm) show the different colors due to the presence of Pt.
m-Al₂O₃-O₂ and 0.2Pt/m-Al₂O₃-H₂ (Fig. 3e, Supplementary Fig. 15b) consumed 2.7 equivalent H₂ per mole of Pt, much higher than the samples with 0.5 and 2.0 wt% Pt loading (0.8–1.3 equivalent H₂ per mole of Pt) (Supplementary Fig. 15c–f), demonstrating the excellent dispersion and reactivity of Pt atoms towards O₂ and H₂ at 0.2 wt% Pt loading. The CO adsorption behaviour of the samples using DRIFTS was also investigated. For 0.2Pt/m-Al₂O₃-O₂ and 0.2Pt/m-Al₂O₃-H₂ (Fig. 3f, Supplementary Fig. 16a), a narrow, quasi-symmetrical band at around 2,087 cm⁻¹ is observed, which can be rationally ascribed as linearly adsorbed CO on Pt₃⁹,⁴₀. For Pt nanoparticles supported on α-Al₂O₃, CO stretching frequencies below 2,100 cm⁻¹ have been rigorously assigned to metallic adsorption sites on nanoparticle surfaces at either well-coordinated (∼2,090 cm⁻¹) or undercoordinated (∼2,070 cm⁻¹) Pt sites⁴¹, but CO adsorbed on Pt⁶⁺ single-site atoms may also exhibit a peak in this region. In fact, the adsorption strength and DRIFT-IR peak of CO on Pt sites are highly dependent on the system. While Pt/γ-ZSM-5 prepared by atomic layer deposition and Pt/CeO₂ prepared by atomic vapour trapping exhibited strong CO adsorption, Pt/C₉H₂₁AlO₃ with peak positioned at 2,095–2,115 cm⁻¹, Pt/FeOₓ synthesized via sol-gel method showed much weaker CO binding strength at 2,080 cm⁻¹, which is similar to our catalyst. CO readily desorbed from 0.2Pt/m-Al₂O₃-H₂ even at room temperature, with 3 cm⁻¹ red shift observed, which reflects the atomically dispersed Pt species may have non-identical coordination environments. For samples 0.5Pt/m-Al₂O₃-O₂, 0.5Pt/m-Al₂O₃-H₂, 2.0Pt/m-Al₂O₃-O₂ and 2.0Pt/m-Al₂O₃-H₂ (Supplementary Fig. 16b–e), two bands belonging to linearly bonded CO on Pt⁶⁺ nanoparticles (2,058 cm⁻¹) and on Pt⁶⁺ single-atoms (2,087 cm⁻¹) are observed. The CO absorption band dropped to ca. 1/3 of its original height after 30 min purging with N₂ at room temperature, and disappeared after heating at 100 °C for 2 min. This suggests weak interaction between adsorbed CO and Pt species, which is consistent with the CO titration experiment where CO adsorption and desorption were found in equilibrium (Supplementary Fig. 17). All these characterizations combined provide compelling evidence that our protocol affords 0.2 wt% Pt (Supplementary Fig. 17). All these characterizations combined provide compelling evidence that our protocol affords 0.2 wt% Pt (Supplementary Fig. 17). All these characterizations combined provide compelling evidence that our protocol affords 0.2 wt% Pt (Supplementary Fig. 17). All these characterizations combined provide compelling evidence that our protocol affords 0.2 wt% Pt (Supplementary Fig. 17). All these characterizations combined provide compelling evidence that our protocol affords 0.2 wt% Pt (Supplementary Fig. 17).

The strong interaction between Pt single-atoms and the support matrix is mainly attributed to the complex effect of metallic Pt centres and collapsed porous structure after high temperature calcination and reduction processes (Supplementary Fig. 22a). As such, the presence of a high concentration of pentahedrally coordinated Al⁵⁺ species mainly form in calcination and reduction processes (Supplementary Fig. 22a). As such, the presence of a high concentration of pentahedrally coordinated Al⁵⁺ species mainly form in calcination and reduction processes (Supplementary Fig. 22a). As such, the presence of a high concentration of pentahedrally coordinated Al⁵⁺ species mainly form in calcination and reduction processes (Supplementary Fig. 22a). As such, the presence of a high concentration of pentahedrally coordinated Al⁵⁺ species mainly form in calcination and reduction processes (Supplementary Fig. 22a). As such, the presence of a high concentration of pentahedrally coordinated Al⁵⁺ species mainly form in calcination and reduction processes (Supplementary Fig. 22a).

The thermal stability of 0.2 wt% Pt supported on m-Al₂O₃ and p-Al₂O₃ was further investigated by calcination at 600 and 800 °C in air for 4 h. XRD patterns, BET analysis and their pore size distribution curves (Supplementary Fig. 26), TEM images (Supplementary Fig. 27)⁴⁷, Al MAS-NMR spectra and IR spectra of CO absorption (Supplementary Fig. 28) indicate that m-Al₂O₃ preserved its mesoporous structure and surface area, with a majority of Pt species maintaining single-atom identities. Noteworthy, Pt can be emitted as volatile PtO₂ at 800 °C under oxidative conditions⁴¹. However, the Pt content remained at around 0.2 wt% after thermal treatments at 600 and 800 °C (Supplementary Table 1), highlighting Pt is strongly anchored in m-Al₂O₃ in the material. On the other hand, p-Al₂O₃ exhibited decreased surface area, diminished pentahedrally unsaturated Al⁵⁺ centres and collapsed porous structure after high temperature treatment. Meanwhile, the Pt species in p-Al₂O₃ was largely transformed into nanoparticles. These control experiments indicate that the mesoporous structure and the unique interior surface framework of m-Al₂O₃ play a decisive role for efficient stabilization of atomically dispersed Pt.

**Catalytic activity: Selective hydrogenation reactions.** The activity and selectivity of single-atom Pt catalysts were investigated over a series of reactions in the presence of H₂, including the hydrogenation of nitrobenzene⁴³, acetonitrile⁴⁴, benzylideneamine⁴⁵, benzylic alcohols⁴⁶, phenylacetylene⁴⁶ and 1,3-butadiene⁴³ (Supplementary Fig. 30 and Supplementary Tables 5–7). In all cases, excellent yields of desired products were obtained. For instance, 98.7% selectivity to 1-phenylethanol in the hydrogenation of acetophenone was achieved over Pt/m-Al₂O₃-H₂, which is higher than 0.2Pt/p-Al₂O₃-H₂ (78.9%) and commercial Pt/Al₂O₃ (68.3%) (Supplementary Table 5). The excellent activity and selectivity not only highlight the applicability of the catalyst for hydrogenation reactions, but are encouraging testimonies of the single-atom identity and the positively charged nature of Pt species on m-Al₂O₃ (ref. 36). Aromatic ring normally coordinates...
to multiple metal atoms before undergoing hydrogenation, and remain to interact with metal surface during step-wise hydrogenation. This mechanism is not possible over single-atom catalysts, which satisfactorily explains why ring hydrogenation on 0.2Pt/m-Al2O3-H2 was almost fully suppressed. In contrast, positively charged Pt species favours C=C bond adsorption and activation forming an η1(O) configuration, as previously established on Pt nanoparticle catalysts. In our system, η1(O) acetophenone adsorbed on Pt single-atom site plausibly reacts with spilled-over hydrogen to form 1-phenylethanol. Afterwards the product transfers to Al2O3 support where it is more strongly adsorbed before finally diffuses into the solution phase, leading to regeneration of the Pt site for a new cycle.

Next, selective hydrogenation of 1,3-butadiene were studied in detail to investigate the stability of our single-atom Pt catalysts in reductive atmosphere at elevated temperatures. 0.2Pt/m-Al2O3-H2 transformed 1,3-butadiene into butanes with >99% selectivity at 50°C, without affecting the co-feed propylene molecule. The TOF for butane formation is 0.034 h⁻¹, a few times higher than earlier reported PtCu catalyst under comparable condition (Supplementary Table 8). 0.2Pt/p-Al2O3-H2 and commercial Pt/Al2O3 catalysts, on the other hand, exhibited much lower selectivity (77 and 29%, respectively) (Fig. 4a, Supplementary Figs 31 and 32). To evaluate the long-term stability of these catalysts under H2 atmosphere at high temperature, the three catalysts were exposed to the mixture of gas reagents at 200°C for 24 h (Fig. 4b, Supplementary Figs 33–35). Afterwards, their catalytic performances were re-evaluated at 30°C for 12 h. Remarkably, 0.2Pt/m-Al2O3-H2 even exhibited slightly increased activity and near-quantitative selectivity towards butanes, confirming the preservation of Pt active sites after high temperature treatment (Fig. 4c, Supplementary Figs 33–35), whereas 0.2Pt/p-Al2O3-H2 and commercial Pt/Al2O3 dropped in activity and selectivity. To our delight, a number of well-separated Pt atoms are clearly identified by HAADF-STEM on spent 0.2Pt/m-Al2O3-H2 catalyst, with no visible Pt atom aggregation being observed (Fig. 4d, Supplementary Figs 36 and 37). The IR spectrum of CO adsorption on 0.2Pt/m-Al2O3-H2 shows a single sharp peak at 2,090 cm⁻¹, substantiating HAADF-STEM finding that Pt species remain predominantly isolated. The major CO absorption peak on spent 0.2Pt/p-Al2O3-H2 catalyst, on the other hand, shifts to 2,064 cm⁻¹ suggesting significant formation of Pt nanoparticles (Fig. 4e).

**Catalytic activity: n-hexane reforming.** Most Pt catalysts for high temperature applications under reductive conditions are related to oil refining. The hydro-refining of n-hexane provides a good model reaction to understand the catalytic conversion of linear hydrocarbons into branched isomers under H2 which is a vital reaction for fuel and chemical production from naphtha. Typically, n-hexane reacts via four major pathways: cracking to shorter chain hydrocarbons; isomerization to 2-methylpentane, 3-methylpentane and multi-branched isomers; cyclization to methylcyclopentane or cyclohexane; and aromatization to benzene (Supplementary Fig. 38). One critical requirement in this process is to achieve long duration against deactivation via preventing carbon deposition. Previous studies were focused on Pt nanoparticles, whereas little attention has yet been paid to single-atom catalysts. We compared the performance of 0.2Pt/m-Al2O3-H2, 0.2Pt/p-Al2O3-H2, and commercial Pt/Al2O3 catalysts for n-hexane reforming at 400 and 550°C. The conversion of n-hexane was maintained below 30% in all cases to ensure that the reaction is under kinetic control. While the initial activities (reflected by n-hexane conversion) of the three catalysts at both 400 and 550°C were similar, the selectivity of 0.2Pt/m-Al2O3-H2 towards desired isomeric products was the highest among the three (ca. 50%), in particular at 550°C (Fig. 4f, Supplementary Figs 39 and 40). The superior selectivity of 0.2Pt/m-Al2O3-H2 catalyst for branched products is likely due to the strong interaction between Pt and support, which is known to be critical for n-hexane isomerization.

0.2Pt/m-Al2O3-H2, 0.2Pt/p-Al2O3-H2 and commercial Pt/Al2O3 catalysts were subjected to long-term stability tests. Under both 400 and 550°C, the stability of the 0.2Pt/m-Al2O3-H2 catalyst, reflected by the substrate conversion, was superior than other catalysts. Its final activity merely dropped to 88% compared to the activity of the fresh catalyst after reacting at 550°C for 48 h. In contrast, a staggering decrease of activity to 50% for 0.2Pt/p-Al2O3-H2 after 48 h and to 38% for commercial Pt/Al2O3 after 24 h was observed (Fig. 4g). The deactivation rates of the three catalysts were generated by curve fitting the conversion as a function of time, followed by differentiation. 0.2Pt/m-Al2O3-H2 exhibited a horizontal line suggesting negligible deactivation whereas 0.2Pt/p-Al2O3-H2 and commercial Pt/Al2O3 catalysts continued to drop in activity (Fig. 4g). The selectivity for isomeric products remained relatively constant for all samples, with 0.2Pt/m-Al2O3-H2 being the most selective (Fig. 4h).

There are no detectable Pt nanoparticles in the TEM images for 0.2Pt/m-Al2O3-H2 after reacting for 48 h at 400 and 550°C (Supplementary Fig. 41), but a number of Pt nanoparticles were identified on 0.2Pt/p-Al2O3-H2 (Supplementary Fig. 42) and commercial Pt/Al2O3 (Supplementary Figs 29 and 43) after the reaction. In addition, 0.2Pt/p-Al2O3-H2 had more carbon deposition than 0.2Pt/m-Al2O3-H2 from TEM images, thermogravimetry (TG) measurements (Supplementary Fig. 44) and visual inspection (Supplementary Fig. 45). BET analysis and 27Al MAS-NMR spectroscopy reveal insignificant changes of mesopores as well as Al species on 0.2Pt/m-Al2O3-H2. Serious damage of the porous structure on 0.2Pt/p-Al2O3-H2 was however observed after reaction (BET analysis in Supplementary Fig. 46, 27Al MAS-NMR spectra in Supplementary Fig. 47). Nevertheless, obvious changes in CO adsorption IR spectra are found for all samples. The CO absorption band broadened on 0.2Pt/m-Al2O3-H2, with the main peak shifting from 2,089 to 2,084 cm⁻¹, together with a shoulder peak at 2,060 cm⁻¹ (Supplementary Fig. 48). Meanwhile, there is a significant drop of Pt–O coordination number from 3.6 to 1.1 (after reaction at 400°C) and 1.4 (after reaction at 550°C), with concurrent increase of Pt–Pt coordination number to around 6 (Supplementary Fig. 49) and 1.1 (after reaction at 400°C) and 1.4 (after reaction at 550°C), with concurrent increase of Pt–Pt coordination number to around 6 (Supplementary Fig. 49) and 1.1 (after reaction at 400°C) and 1.4 (after reaction at 550°C), with concurrent increase of Pt–Pt coordination number to around 6 (Supplementary Fig. 49). 0.2Pt/m-Al2O3-H2 after reaction, but there is still a substantial amount of isolated Pt atoms in the catalyst. On the other hand, only a single band at 2,060 cm⁻¹ can be observed for commercial Pt/Al2O3 and 0.2Pt/p-Al2O3-H2 catalysts, ascribed to linearly bonded CO on Pt⁰ sites on nanoparticles (Supplementary Fig. 50).

**Catalytic activity: CO oxidation.** CO oxidation. To evaluate the catalyst stability under oxidative conditions, CO oxidation between 100 and 400°C was conducted. While thermally stable Pt nanoparticle catalysts for CO oxidation have been developed, high temperature Pt single-atom catalysts have been much less studied. A feed gas containing 2.5 vol% CO, 2.5 vol% O2 and balance Ar was passed through the reactor at a flow rate of 80 ml min⁻¹ (corresponding to a space velocity of 4.8 × 10³ ml g⁻¹ h⁻¹, Supplementary Figs 51 and 52). The TOF was 0.023 s⁻¹ at 200°C and steadily increased to 0.175 s⁻¹ at 250°C (Supplementary Table 9). These numbers well match...
Butenes selectivity

0.1 ml h⁻¹

and maintained for 70 h (Fig. 5d). No appreciable drop in CO selectivity of butenes and conversion of propene at 30 °C the activity of 0.2Pt/m-Al₂O₃-H₂ increased slightly in the first 13 rounds, and then became very stable in the subsequent 37 cycles (Fig. 5a, Supplementary Fig. 5a). The temperature of the reactor was set at 400 °C for 220 h, during which 100% CO conversion was maintained for the entire period (Fig. 5b). Afterwards, the 0.2Pt/m-Al₂O₃-H₂ spent catalyst was inspected—coated on an incomplete CO conversion—by a series of instrumental analyses. No Pt nanoparticles can be detected from the TEM image and TEM-EDS elemental mapping, indicating that Pt species is uniformly dispersed on spent 0.2Pt/m-Al₂O₃-H₂. The CO absorption peak remains sharp and quasi-symmetrical, centred at 2,090 cm⁻¹ (Fig. 5e). In the EXAFS spectrum, Pt–O contribution located at 2,064 cm⁻¹, and Pt–O coordination number (3.6) remain almost identical after reaction, an increase in Debye–Waller factor was observed, reflecting some degree of evolution of catalyst active centre (Supplementary Table 4). BET analysis and the ²⁷Al MAS-NMR spectrum confirm the integrity of the mesoporous structure, and the preservation of a majority of unsaturated pentahedral Al³⁺ species (Supplementary Figs 53f and 54).

Similar recycling results were observed over 0.2Pt/m-Al₂O₃-H₂ catalyst under dilute conditions (100 mg 0.2Pt/m-Al₂O₃-H₂, mixed with 1.0 g commercial Al₂O₃, Supplementary Fig. 55).
0.2Pt/m-Al₂O₃-O₂, too, was highly stable in CO oxidation despite a slightly lower activity (Supplementary Fig. 56). Moreover, after calcined at 600 °C the catalyst remained high stability over 14 cycles (0.2Pt/m-Al₂O₃-O₂-600) (Supplementary Fig. 28e).

In comparison, the catalytic activity of commercial Pt/Al₂O₃, 0.2Pt/p-Al₂O₃-H₂ and 0.2Pt/m-Al₂O₃-imp decreased only after several cycles (100–400 °C) (Fig. 5g, Supplementary Figs 57 and 58). The Pt species underwent agglomeration in these control samples to form larger particles as shown in TEM images (Supplementary Fig. 59). BET and TEM analysis also suggest decreased surface area with collapsed porous structures.

The CO adsorption experiment on spent commercial Pt/Al₂O₃ and 0.2Pt/p-Al₂O₃-H₂ reveals the relative decrease of the peak at 2,090 cm⁻¹ with increase of the peak at about 2,064 cm⁻¹, corroborating TEM findings (Fig. 5e).

Discussion

The metal–support interactions often play a pivotal role in shaping the stability and reactivity of supported metal catalysts. Considering isolated metal atoms are in sole contact with the support. Strong interactions between the metal atom and the support are conceived to be the key to preventing metal atom aggregation, while an overly strong interaction may lead to catalytically inactive species acting as spectators. In some earlier works, atomically dispersed Pt catalysts were obtained at low-temperature reduction conditions, and could be used in mild hydrogenation reactions. Unfortunately, atom aggregation into clusters and nanoparticles could occur when the catalysts are exposed to increased reduction temperature, or employed in harsher reaction conditions, plausibly due to insufficient anchoring effect of the support to Pt atoms.

In the current work, we have developed an atomically dispersed Pt catalyst supported on mesoporous Al₂O₃ exhibiting astounding catalytic activity and stability under both oxidative and reductive atmospheres at high temperatures. The complex effect between the metal and support precursors enables the Pt cation to be strongly anchored in the inner surface of the support, staying in a four oxygen coordination mode that is intrinsically favoured by low valent Pt atoms. Additionally, the P123 template facilitates the formation of highly stable mesoporous structures.
enriched with unsaturated pentahedral Al\(^{3+}\) centres, further enhancing metal–support interactions. As a result, the single-atom catalyst can survive for long durations in a series of reactions under demanding conditions. An apparent limitation of the system is that the single-atom identity of Pt was achieved only at a low loading (0.2 wt%), plausibly due to the low abundance of Al\(^{3+}\) species on surface. Nevertheless, our work adds solid proof that the single-atom catalyst may not be necessarily more vulnerable than nanocluster and nanoparticle catalysts under harsh reaction conditions. Rational control of the structure and surface property of the support, and fine-tuning of the synthetic procedure, are two key factors to achieve desirable metal–support interactions in atomically dispersed Pt catalysts for high temperature operations with superior activity and stability. For the current system, future work should be directed to enriching Al\(^{3+}\) species on the surface by tuning the synthetic procedure, and/or incorporate other metal oxides such as silica and titania to the alumina support.

**Methods**

**Catalysts synthesis.** In a typical synthesis, Pluronic P123 (2.1 g) was dissolved in ethanol (20 ml) at room temperature. Then, 67% nitric acid (2 ml) was added and stirred for 30 min. The Pt precursor [Pt(OAc)\(_2\)] was added and stirred for 1 h. After cooling to room temperature, the catalyst was collected by filtration and washed with ethanol and acetone. The catalysts were stored in ethanol for further use.

**Catalysts characterization.** Wide-angle XRD analysis was carried out using a Bruker D8 Advance X-Ray Diffractometer, at a scan rate of 2° min\(^{-1}\). It was operated at 40 kV applying a potential current of 30 mA. The XRD pattern was collected on the Bruker D8 Advance diffractometer equipped with a Cu-K\(_{α}\) radiation source operating at 40 kV and 40 mA. The XRD patterns were recorded in the range of 20° to 80° 2θ.

**Data availability.** The data that support the findings of this study are available from the authors on reasonable request.

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Author contributions

N.Y. and Z.Z. conceived the idea, designed the experiments, analysed the data and wrote the manuscript. Z.Z. carried out the catalyst synthesis, evaluated their catalytic performances and conducted some characterizations. Y.H. and Y.Z carried out HAADE-STEM characterizations. T.Z., A.W. and M.Z. arranged and conducted 27Al MAS NMR characterizations and DFT simulation. T.T. and H.A. carried out the XAS measurements. B.Z. and J.Z. participated in material characterizations and catalytic reaction evaluation. All authors discussed the results and edited the manuscript.

Additional information

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