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Engineering Sodium-decorated Bifunctional Au-Ti Sites to Boost Molecular Transfer for Propene Epoxidation with H_2 and O_2

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Abstract: Regulating the microenvironment of active sites is crucial to boost the performance of direct propene epoxidation with H_2 and O_2. Herein, the enhanced surface transfer of H_2O_2 intermediates was first achieved by sodium-decorated Au-Ti bifunctional active sites. Combined with multi-techniques (e.g., operando UV-vis-NIR system, DFT studies and quantitative model calculations), it is found that the sodium-decorated silanols (Si-ONa species) on the TS-1 support enhance the formation of Ti-OOH intermediates by restraining H_2O_2 decomposition. In addition, sodium-decorated silanols improves the desorption of propylene oxide, suppressing its ring-opening and formation for the carbonaceous deposits. Moreover, the sodium-decorated Au nanoparticles with smaller diameter and higher electron density further strengthen O_2 adsorption and boost the H_2O_2 formation. This work not only provides fundamental understandings on the microenvironment of Au-Ti bifunctional catalysts but also sheds new light on enhancing the performance by boosting the surface molecular transfer.

Keywords: Microenvironment, Sodium decoration, Surface molecular transfer, Bifunctional catalyst, Propene epoxidation.

1. Introduction

Propylene oxide (PO) as one of the key intermediates of the chemical industry has widespread applications in automobiles, food, cosmetics, and architecture et al[1-3]. The PO could be widely used to synthesize polyether polyols and propylene glycol[4, 5]. However, the major industrial process for propylene oxide production is the chlorohydrin method[6], which uses the harmful chlorine gas as raw materials and causes great environmental pollution and potential safety hazards[4, 7, 8]. Other industrial methods include the Halkon method (the alkyl hydroperoxide as the oxidant) and the HPPO method (the hydrogen peroxide as the oxidant). The Halkon method usually involves a complicated production process and heavy capital investment[7, 8]. The HPPO method normally requires the transport of explosive hydrogen peroxide and additional separation of the catalysts[4, 5]. Therefore, great need is required to develop a novel green method to synthesize PO.

As an environmental-friendly and easy-operating process, the direct propene epoxidation with gaseous hydrogen and oxygen has attracted more attention from both academia and industry[9-15]. Since Haruta et al.[16] reported that the Au/TiO_2 could catalyze this reaction in 1998, it is found that the Au nanoparticles are used to synthesize the H_2O_2 and the isolated Ti active sites on support further react with H_2O_2 to form Ti-OOH intermediates, which catalyze the epoxidation reaction[17]. In order to enhance the synergy between the Au active site and Ti active site, the deposition precipitation (DP) method was developed to locate Au nanoparticles near Ti sites by adjusting the pH, thus enhancing the surface transfer of H_2O_2 which is easy to decompose at high reaction

temperatures[2, 18, 19]. However, there are few reports on developing a new strategy to enhance the surface transfer of H_2O_2 from Au sites to Ti sites, which is highly desired for direct propene epoxidation with H_2 and O_2.

Besides the improvement of performance by regulating the properties of support, measures were also taken to improve the physico-chemical properties of Au nanoparticles. Delgass et al. first prove that small gold clusters in TS-1 channels are active for the propene epoxidation[20]. In our previous work,[21] we developed a strategy to manipulate the Au particle size by tuning the Au spatial location. The manipulated composition of Au complexes by regulating Au hydrolysis process could result in more Au clusters in the channel to decrease the size of Au nanoparticles and further improves epoxidation reaction performance. Nijhuis et al.[11] synthesized the sub-nanometer Au clusters (~0.8 nm) stabilized by the phosphine ligands and shows enhanced stability and selectivity for direct propene epoxidation. Moreover, improving the electron transfer of Au nanoparticles was used to enhance O_2 adsorption and further H_2O_2 formation[14]. In our previous work[22], Ag atom was added to synthesize electron-riched Au atom and further enhance the electron transfer with O_2 molecules to boost the formation of H_2O_2. Therefore, there is great need to develop novel strategy to simultaneously improve the geometry and electron structure of Au nanoparticles in the propene epoxidation.

In this work, the catalyst microenvironment was regulated by constructing sodium-decorated Au-Ti bifunctional sites to enhance the surface molecular transfer. Different from the traditional Au/TS-1 by deposition-precipitation method, a novel alkalis-

strengthened wet-chemistry method was proposed. By multi-techniques (e.g., operando UV-vis-NIR system, DFT studies and quantitative model calculations), it is found that the TS-1 support decorated with Si-ONa species improves the surface transfer of H_2O_2 by inhibiting its decomposition, thus enhancing the formation of Ti-OOH sites and subsequent epoxidation reaction. The Si-ONa species could also restrain the ring-opening reaction of PO and formation for aromatic carbonaceous deposits, thus improving the catalytic stability. Moreover, the adsorption of oxygen was improved due to smaller diameter and higher electron density of sodium-decorated Au nanoparticles, enhancing the formation of H_2O_2 species. This work provides guiding significance to regulate the catalyst microenvironment in order to boost surface molecular transfer for propene epoxidation.

2. Experimental Section

2.1 Synthesis of titanium silicalite-1 (TS-1)

The fast synthesis of TS-1 was based on our reversed-oligomerization synthetic approach[23]. In a typical process, 21.50 g of H_2O (18.2 MΩ•cm), 17.00 g of a solution containing tetrapropylammonium hydroxide (TPAOH, 25 wt%, Sinopharm Chemical Reagent Co., Ltd), 0.25 g of tetrabutyl titanate (TBOT, 99.0 wt%, Shanghai Aladdin Biochemical Technology Co., Ltd) and 30.48 g of tetraethyl orthosilicate (TEOS, 98.5 wt%, Sinopharm Chemical Reagent Co., Ltd) were directly mixed under magnetic stirring. After that, the mixed solution containing template, Si source, and Ti source was irradiated by the ultraviolet lamp (mercury lamp, 500w) for 1 h. Subsequently, the clear gel was crystallized at 170 ºC for 72 h. Then the as-synthesized product was washed

three times and dried at 90 °C for 8 h. The white power was further calcined at 550 °C for 6h to get the support which is denoted as TS-1.

2.2 Synthesis of the Au/TS-1 catalysts

The Au/TS-1 was prepared by the alkalis-strengthened wet-chemistry method rather than the deposition-precipitation method. The 0.009 g of chloroauric acid ($HAuCl_4•4H_2O$, 99.9 wt %, Sinopharm Chemical Reagent Co., Ltd) was mixed with 4.5 g of deionized H_2O (18.2 MΩ•cm). Subsequently, the pH of the mixed solution was regulated by the NH_4HCO_3 or Na_2CO_3 to reach 7.3-7.6. Then the deionized H_2O was added into this solution dropwise until the volume of this solution reached 5 ml. After that, 0.4 ml of the mixed solution was impregnated on the 0.5 g TS-1. The sample was dried in the vacuum oven at 30 °C overnight. The obtained catalyst was referred to as NH_4-Au/TS-1 or 0.04Na-Au/TS-1 with a Na loading of 0.04 wt%, respectively. The 0.23Na-Au/TS-1 and 0.48Na-Au/TS-1 were synthesized by further increasing the loading of Na element to 0.23 and 0.48 wt%, respectively. In order to keep the pH constant, a specific amount of neutral $NaNO_3$ was added to the solution instead of basic Na_2CO_3. In the Na-Au/TS-1 catalysts, the Na content is all higher than the Cl content.

2.3 Characterizations

The crystal structure was determined by X-ray diffraction with a scanning speed of 10 °/min (XRD, Cu K_α radiation, X'pert PRO MPD). The chemical environment of the Ti atom was characterized by ultraviolet-visible spectroscopy (UV-vis, UV-2700). The pure solid $BaSO_4$ was used as the background. The Fourier transform infrared spectroscopy of catalyst was recorded by the Fourier infrared spectrum instrument (FT-

IR, Thermo Scientific Nicolet spectrometer, IS30), and the pure KBr solid was used as the reference. As for the spectroscopy of Si-OH, the samples were pretreated at 773 K under vacuum for 1 h. The sample mass was strictly controlled to 25 mg and the sample was tested at 773 K under vacuum to avoid the effect of air. The pore structure of catalysts was obtained at 77 K by the volumetric adsorption analyzer (Micromeritics ASAP 2460). The thermogravimetry analysis combined with differential scanning calorimetry (TG-DSC, Netzsch) was used to reveal the coke content and coke species of the catalyst with a heating speed of 10ºC/min from 30 to 1000ºC. The chemical state of Au species was determined by the X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) and the 284.6 eV of C1 binding energy was taken as the reference. The morphology and size of Au nanoparticles were characterized by the high-resolution transmission electron microscope (HRTEM, JEM-2100UHR). The reaction intermediate of Ti-OOH at different temperatures was revealed by operando UV-vis-NIR spectroscopy (AvaSpec-ULS4096CL-EVO, AVANTES).

2.4 Catalytic testing

The bifunctional Na-Au/TS-1 catalysts were prepared by the alkalis-strengthened wet-chemistry method and were tested in the direct propene epoxidation with H_2 and O_2 in a fixed-bed reactor. The catalysts (0.15 g) were loaded in the quartz tubular reactor with a diameter of 8 mm. The reaction temperature was 200 ^{o}C and the space velocity of the reaction was 14000 $mL{\cdot}h^{-1}{\cdot}g_{Cat}^{-1}$. The reaction mixture includes oxygen (3.5 ml/min), hydrogen (3.5 ml/min), propene (3.5 ml/min) and nitrogen (24.5 ml/min).

The online analysis results of reactants and products were recorded on the gas

chromatography. The Porapak Q column and 5A column were equipped for the FID and TCD detectors, respectively. Due to the low conversion of propene in the direct propene epoxidation with H_2 and O_2 (typically < 5%), the conversation of propene was calculated based on the products[18]. The calculations of conversion, selectivity, and hydrogen efficiency are based on the following formulas:

Propene conversion:

$$= \frac{C_3 \text{ moles} + (\text{acetaldehyde moles} \times 2)/3 + (\text{carbon dioxide moles})/3}{\text{propene moles}}$$

Propylene epoxide selectivity:

$$= \frac{\text{propylene oxide moles}}{C_3 \text{ moles} + (\text{acetaldehyde moles} \times 2)/3 + (\text{carbon dioxide moles})/3}$$

Hydrogen efficiency:

$$= \frac{\text{propylene oxide moles}}{H_2 \text{ moles in the feed} - H_2 \text{ moles in the product}}$$

2.5 The stability test of H_2O_2 over different catalysts

The stability test of H_2O_2 was tested at 60 ºC for 2 h with 0.05 g catalyst under atmospheric pressure. The relative decomposition rate of H_2O_2 was calculated based on the following formula:

$$= \frac{(\text{content of } H_2O_2 \text{ with the specific catalyst-content of } H_2O_2 \text{ without catalysts})}{(\text{content of } H_2O_2 \text{ with the catalyst of } NH_4\text{-TS-1-content of } H_2O_2 \text{ without catalysts}) \times 2 \text{ h}}$$

2.6 Density functional theory calculation

The VASP (Vienna Ab-initio Simulation Package) was used to perform the density functional theory (DFT) calculation with the exchange-correlation energy function of GGA-PBE and cutoff energy of 400 eV. The interaction between the valence electron and core was described by the projected augmented wave potentials. In order to avoid the pseudo-interactions, the vacuum slab of 15 Å was used. The Kohn-Sham orbitals

were expanded based on the plane-wave basis. The K points were set to be 4×4×1 in the Brillouin zones. The optimization of the structure was stopped until the force was less than 0.03 eV/Å in ion relaxation steps and the difference of energy was less than 1×10^{-5} eV in adjacent electronic relaxation steps.

In order to get the atomic charges, the Bader charge analysis was performed by a fast algorithm. The VESTA software was used to visualize the differences in charge density. The calculation was based on the following formula: $\triangle\rho(r) = \rho_{total}(r) - \rho_{NaCl}(r) - \rho_{support}(r)$. The ρ_{total} represents the total electron densities, ρ_{NaCl} represents the electron densities of NaCl, and $\rho_{support}$ represents the electron densities of support.

3. Results and Discussion

3.1 Enhanced performance of sodium-decorated Au-Ti bifunctional sites

In the direct propene epoxidation with H_2 and O_2, It is found that the NH_4-Au/TS-1 without alkalis shows the lowest propene conversion of ca. 0.3% with a PO selectivity of 75% in Figure 1a. After adopting the alkalis-strengthened wet-chemistry method, the propene conversion was significantly increased from 0.3% to 6% and 7% over 0.04Na-Au/TS-1 and 0.23Na-Au/TS-1 catalysts, respectively (Figures 1b-1c). However, the conversion decreased to 4% over the 0.48Na-Au/TS-1 catalyst in Figure 1d, demonstrating that the catalysts by the alkalis-strengthened wet-chemistry method show a volcano curve of propene conversion in the propene epoxidation. It showed that the excessive amount of sodium could restrain the propene epoxidation with H_2 and O_2. With the increase of Na loading from 0.04 to 0.48 wt%, the selectivity of propylene

oxide was gradually increased from 70 to 90% over Na-Au/TS-1 catalysts.

The catalytic stability is shown in Figure 1e. Although the 0.04Na-Au/TS-1 catalyst has a relatively high initial PO formation rate (~190 $g_{PO}h^{-1}kg_{Cat}^{-1}$), it quickly decreased by ca. 26% during the first 3 hours. Compared with the 0.04Na-Au/TS-1 catalyst, the 0.23Na-Au/TS-1 catalyst not only shows the highest PO formation rate (~210 $g_{PO}h^{-1}kg_{Cat}^{-1}$) which is superior to the reported catalysts shown in the table S1, but also exhibits better stability for direct propene epoxidation with H_2 and O_2. Moreover, it can be seen from Figure 1f that the 0.23Na-Au/TS-1 catalyst also shows the highest initial gold atom efficiency (~310 $g_{PO}h^{-1}g_{Au}^{-1}$) which is ca. 20 times higher than that of NH_4-Au/TS-1 without the alkalis-strengthened wet-chemistry method. The widely accepted reaction mechanism over Au-Ti catalysts is that the synergy between Au nanoparticles (NPs) for the synthesis of H_2O_2 and the Ti atom in the framework of TS-1 for the epoxidation between propylene and Ti-OOH[19, 22, 24, 25]. Therefore, the different performance could be originated from the regulation of sodium-decorated microenvironment around Au-Ti bifunctional sites.

3.2 Sodium-decorated TS-1 support

The different microenvironments around Au-Ti bifunctional sites of the catalysts were then analyzed. In the direct propene epoxidation with H_2 and O_2, the H_2O_2 from Au nanoparticles by surface transfer reacts with the isolated Ti active sites on support to form Ti-OOH intermediates, which catalyze the epoxidation of propene. The transfer of H_2O_2 is related to the microenvironment around Ti sites in the TS-1 support. Due to

the location of Ti sites both on internal bulk or external surfaces[26], the silanols distribution around Ti sites inside or outside of TS-1 microporous channels[27] should be very important for the H_2O_2 transfer. The Fourier transform infrared (FT-IR) spectrum in the region of hydroxyl stretching was used to evaluate the silanol environment around Ti sites[28]. It is found that with the addition of sodium in the alkalis-strengthened wet-chemistry method, the intensity of different silanols species in the three regions from 3400-3800 cm^{-1} both gradually decreased shown in Figure 2a.

In the FT-IR spectra, the regions I, II, and III were attributed to the isolated external silanols, internal silanols, and hydrogen-bonded silanol nets[29]. The silanols species could be gradually shifted from Si-OH species to Si-ONa species after the ion exchange by sodium. The decreasing areas of isolated external silanols, internal silanols, and hydrogen-bonded silanol nets were attributed to the formation of Si-ONa species by the alkalis-strengthened wet-chemistry method[30]. Due to the smaller radius of 0.204 nm[31] than the pore size of TS-1 (0.54×0.56 nm)[32], the sodium can not only decrease the number of external silanols but also diffuse into the microporous channels to reduce the internal silanols, especially for the hydrogen-bonded silanol nets. The quantitative results of silanols were further characterized by the ^{29}Si MAS NMR (Figure S15 and 2b). The gradually decreased ratio of Q_3/Q_4 demonstrated the lower content of silanols, which is in consistent with the FT-IR results.

The relative decomposition rate of H_2O_2 was further performed to evaluate the stability of H_2O_2 over different catalysts after the shift from Si-OH species to sodium decorated Si-OH species. With the increase of sodium content on the support, the

decomposition rate of H_2O_2 was gradually decreased. The low relative decomposition rate of H_2O_2 on the sodium-decorated TS-1 support is beneficial for the surface transfer of H_2O_2. It is found that the NH_4-Au/TS-1 has the highest relative decomposition rate of H_2O_2 (50 %/h) compared with the other three catalysts in Figure 2c. The sodium-decorated TS-1 decrease the relative decomposition rate of H_2O_2, and the 0.48Na-Au/TS-1 has the highest H_2O_2 stability with the lowest relative decomposition rate of H_2O_2 of 43.9%/h due to more Si-ONa species on the TS-1 support. Therefore, the sodium decorated Si-OH species could restrain the decomposition of H_2O_2 compared with Si-OH species due to the weak hydrogen bond with H_2O_2, and further better surface transfer of H_2O_2 from Au nanoparticles to isolated Ti atoms. Furthermore, the formed H_2O_2 on the Au active sites were further transferred to the epoxidation center of tetrahedrally coordinated Ti active sites via the transfer pathway containing the sodium decorated Si-OH or Si-OH species to form reaction intermediate Ti-OOH species.

The operando UV-vis-NIR system was used to determine the relative content of the reaction intermediate Ti-OOH species on the TS-1 support. In Figure 2d, the intensity of the peak at 370 nm was recorded to reflect the change of Ti-OOH reaction intermediate on the catalyst[33]. It is found that the content of Ti-OOH species was gradually increased from 40 to 120 ^oC with feeding gas including H_2, O_2, C_3H_6, and N_2. The intensity of Ti-OOH species remained unchanged after 120 ^oC which could be attributed to the balance between the generation on the Au nanoparticles and consumption over Ti active sites. Moreover, the 0.04Na-Au/TS-1 catalyst shows higher

intensity than that of NH_4-Au/TS-1 catalyst from 40 to 200°C, demonstrating that more Ti-OOH species over TS-1 support caused by the sodium-decorated transfer path. In the Figure S1, compared with the hydrogen efficiency of NH_4-Au/TS-1 (~5%), 0.04Na-Au/TS-1 shows higher hydrogen efficiency (~15%) than that of NH_4-Au/TS-1. It means that the addition of sodium could effectively increase the hydrogen efficiency further indicating that the Si-ONa species could be better for the surface transfer of H_2O_2 to form the Ti-OOH species and further propene epoxidation. The better hydrogen utilization of the sodium-decorated catalysts prepared by the alkalis-strengthened wet-chemistry method is consistent with the results shown in the Figures 2c and 2d. These results demonstrate that the sodium-decorated TS-1 could effectively improve the surface transfer of H_2O_2 and further formation of reaction intermediates Ti-OOH species by the sodium decorated species to strengthen the cooperation between the Ti sites and Au sites.

The UV-vis and FT-IR (Figures S2 and S3) were used to characterize the coordinated environment of Ti species in the TS-1 support. It is found that this TS-1 support shows isolated framework Ti^{4+} species (~220 nm) which are considered as the active center for propene epoxidation[34, 35] without extra-framework TiO_2 species of (~330 nm)[36, 37]. The FT-IR spectrum shows two peaks at 550 and 1230 cm^{-1} which are attributed to the typical feature of the MFI framework[2], and the important peak at 960 cm^{-1} which is ascribed to the incorporation of Ti atoms into the MFI framework[38, 39]. These results demonstrate the superior configuration of Ti species which contains tetrahedrally coordinated Ti species without TiO_2. Therefore, the formed H_2O_2 could be effectively

utilized by the isolated framework Ti species to form Ti-OOH and further synthesis of propylene oxide.

The propylene oxide synthesized on the isolated Ti sites was further desorbed and diffused outside of the TS-1 microporous channels. The narrow microporous channels lead to the carbonaceous deposits and thus blocking the channel. This finally accelerates the deactivation of catalysts, especially in the initial period[2, 15]. The Si-OH species were considered as the main reason for the carbide deposition. Less Si-OH species caused by the more Si-ONa species in the sodium-decorated TS-1 represent higher hydrophobicity could restrain the ring opening and further pore blocking.

The pore volume of the catalyst after the reaction was analyzed to reveal the degree of pore blocking. In order to better analyze the pore blocking after reaction, the parameter (V_{nb}) were introduced into the calculation. The V_{nb} represents the difference of pore volume between the catalyst before and after the reaction, and higher value of V_{nb} represents more carbonaceous deposits in the channel. It can be seen from Figure 3a that the values of $V_{nb}/V_{support}$ gradually decreased from 21.0 to 8.6 with the addition of sodium, demonstrating that the Si-ONa species could effectively restrain the blocking of carbonaceous deposits in the microporous channel by enhanced hydrophobicity. Moreover, the more sodium may occupy the channel and lead to the distribution of Au nanoparticles outside the channels, which could decrease the blocking degree by carbonaceous deposits and enhance the stability. Therefore, the 0.48Na-Au/TS-1 catalyst shows the least carbonaceous deposits in the channels than other catalysts.

The TGA profiles revealed the weight loss of different catalysts shown in Figure 3b. The weight loss between 200-800 ^{o}C and below 200 ^{o}C were ascribed to carbonaceous deposits and water, respectively. It can be seen that the content of carbonaceous deposits gradually decreases with the increase of sodium content. The DSC analysis of different catalysts (Figure 3c) after propene epoxidation was further used to give the exothermic curve of carbonaceous deposits[40]. It is found that the addition of sodium promotes the shift of the peak at ca. 450^{o}C to lower temperature, indicating that the suppression of heavier carbonaceous deposits. Moreover, the peak at ca. 620^{o}C appears in the NH_4-Au/TS-1 shifted to a lower temperature (600^{o}C) in the 0.04Na-Au/TS-1. A similar peak at ca. 600^{o}C does not appear in the 0.23Na-Au/TS-1 and 0.48Na-Au/TS-1 catalysts. The DSC analysis demonstrates that the sodium-decorated TS-1 could effectively restrain the formation of heavy carbonaceous deposits in the Au-Ti catalyst. The FT-IR was used to give the carbonaceous deposits in different catalysts after propene epoxidation at 200^{o}C. It can be seen from Figure 3d that the carbonaceous deposits (i.e., branched alkanes, polyalkenes, and aromatic species)[41] appear in NH_4-Au/TS-1, 0.04Na-Au/TS-1 and 0.23Na-Au/TS-1 catalysts. With the more addition of sodium in the 0.48Na-Au/TS-1catalysts, the aromatic species disappeared due to the suppression of heavier carbonaceous deposits. Due to the lowest PO formation rate (~8 $g_{PO}h^{-1}kg_{Cat}^{-1}$), the aromatic species are not obvious in the NH_4-Au/TS-1 catalyst.

Therefore, the 0.23Na-Au/TS-1 and 0.48Na-Au/TS-1 show better reaction stability compared with the 0.04Na-Au/TS-1 catalyst during the propene epoxidation of ca. 10 h. On the one hand, this is because the sodium-decorated TS-1 with more Si-ONa

species could suppress the ring opening and further oligomerization, restraining the formation of heavy carbonaceous deposits. In addition, the more sodium may occupy the channel and lead to the distribution of Au nanoparticles outside the channels, inhibiting pore blocking phenomenon.

3.3 Sodium-decorated Au nanoparticles

In the synergic mechanism between Au and Ti bifunctional active sites for the propene epoxidation, the first step is the O_2 adsorption in the synthesis of H_2O_2 on the surface of Au nanoparticles. Therefore, the enhanced O_2 adsorption could boost the formation of H_2O_2. The unique property of Au nanoparticles was deeply affected by their geometric structure and electronic structure[22, 42-44].

The geometric structure of Au nanoparticles was revealed by HRTEM images shown in Figure 4. Figures 4a-4d clearly showed the small-sized Au nanoparticles supported on the TS-1 support. Compared with the NH_4-Au/TS-1 catalyst, the addition of sodium significantly reduced the size of Au nanoparticles from 9.8 nm to ca. 2 nm. The larger Au size of the NH_4-Au/TS-1 catalyst than the Na-Au/TS-1 catalyst could be attributed to the addition of NH_4^+. With the further increase of Na content, the Au nanoparticle size gradually decreased from 2.4 nm to 1.9 nm. These results demonstrate that the sodium around the Au nanoparticles could effectively restrain the Ostwald ripening, thus forming more Au nanoparticles with a smaller size.

In addition, it is found that the Au nanoparticles shows a lattice spacing of 0.234 nm in Figure S14. The fast Fourier transform (FFT) of the selected area in the Au nanoparticle shows the top facet (111) which is following the lattice spacing[45].

Combined with the catalytic performance, the 0.23Na-Au/TS-1 exhibits the higher PO formation rate (310 > 292 > 16 $g_{PO}h^{-1}g_{Au}^{-1}$) compared with the NH_4-Au/TS-1 and 0.04Na-Au/TS-1 catalysts, which is accordance with the Au nanoparticles size (9.8 nm > 2.4 nm > 2.2 nm). However, the 0.48Na-Au/TS-1 has the smallest diameter (1.9 nm) but lower PO formation rate (208 $g_{PO}h^{-1}g_{Au}^{-1}$), which could be attributed that the excess amount of sodium could cover the active sites of Au nanoparticles.

The electronic structure of sodium-decorated Au nanoparticles was further investigated. With the addition of sodium, the binding energy of metallic Au $4f_{2/5}$ gradually decreased from 88.0 to 87.4 eV and Au $4f_{2/7}$ gradually decreased from 84.4 to 83.8 eV shown in Figure 5a. Figure 5b demonstrated that the valence state of the Na element was +1 (~1072 eV)[46, 47]. The decreased binding energy of Au nanoparticles means that the Au nanoparticles which are surrounded by the sodium withdraw more electrons from sodium with more addition of Na elements[48].

In order to further reveal the effect of the alkalis-strengthened wet-chemistry method on the electronic structure of Au nanoparticles, the DFT calculation was performed based on the Vienna ab initio simulation. Due to the decomposition of chloroaurate at high temperature to form the corresponding chloride[49], the NaCl was used as the precursor to adsorb on the surface (111) of Au nanoparticles to investigate the effect of Cl and Na atoms. The end-on and side-on adsorption of the NaCl molecule on the Au nanoparticles were shown in Figures 5c and 5d, respectively. The blue means gaining electrons and red means losing electrons. It is found that the Cl atom withdraws electrons from the Na atom in both adsorption models. However, all surface Au atoms

gain electrons in the end-on adsorption model, and all surface Au atoms withdraw electrons in the side-on adsorption model except the Au atom under the Cl atom. It demonstrated that the Na effectively improve the detrimental effect of Cl.

The Bader charge analysis was performed to further reveal the distribution of electrons in the adsorption model. Figure 5e-5f and Figure S4-S5 show that the NaCl molecule in the side-on model could transfer more electrons to Au nanoparticles than the end-on model (0.25 e > 0.13 e). Moreover, the more negative adsorption energy of side-on model (-0.93 eV vs -0.35 eV) indicated that the side-on model is more stable than the end-on model, which is consistent with the distribution of electrons. The differential charge density plots shown in Figures 5g-5h and Figures S6-S7 demonstrate that the bond between the Na atom and Cl atom was weakened and the bond between the Na atom and Au atom was strengthened.

The improved O_2 adsorption could further enhance the rate-relevant step (i.e., the H_2O_2 synthesis from H_2 and O_2 on Au nanoparticles)[14, 22, 43] for the propene epoxidation with H_2 and O_2 and the DFT calculation is further performed on the more stable side-on model of the NaCl molecule on the Au nanoparticles for the O_2 adsorption. Moreover, the O_2 adsorption on the pure Au nanoparticles was used as the reference. On the surface of Au (111), the four sites including the top site, bridge site, fcc site, and hcp site were considered to adsorb the oxygen[14, 22]. The bond distance of O_2, adsorption energy, and detailed adsorption configurations were shown in Figures 6a-6d and Figures S8-S13. It is found the bond distance of O_2 on the fcc site (1.321 Å) in the pure Au nanoparticle is longer than that on the top, bridge, and hcp site. The adsorption energies (E_{ad}) are nearly

the same (ca. -0.40 eV). Meanwhile, the bond distance of O_2 on the fcc site (1.413 Å) in the Au nanoparticle with the side-on adsorption of the NaCl molecule is also longer than other sites. These results demonstrate that the fcc site in the Au nanoparticle is better to activate the absorbed O_2 molecules. Compared with the fcc site in the pure Au nanoparticles, the fcc site in the Au nanoparticles with the side-on adsorption of the NaCl molecule shows elongated bond distance (1.413 Å > 1.321 Å), more negative adsorption energy (-0.97 eV vs -0.41 eV), and more obtained electrons (0.75 e > 0.47 e). These results demonstrate the stronger electronic interaction between the O_2 and the Au nanoparticles with the side-on adsorption of NaCl than that between the O_2 and pure Au nanoparticles, thus causing a more obvious redistribution of charge density.

In order to get more insights into the electronic structure, the density of state (DOS) and partial density of state (PDOS) of the pure oxygen and adsorbed oxygen were further calculated (Figures 6e-6g). Compared with the DOSs of pure oxygen and oxygen adsorbed on the Au nanoparticles, the DOS of oxygen adsorbed the Au nanoparticles with the side-on adsorption of NaCl shows broader peaks in region II. In addition, the s-orbital PDOSs of different O_2 molecules all show a narrow and high-intensity peak, but the p-orbital PDOSs of O_2 adsorbed on the Au nanoparticles show broader peaks, thus causing the difference of the DOS. These results demonstrate that the strong electronic interaction between the Au nanoparticles and sodium could promote the adsorption of O_2.

The sodium-decorated Au nanoparticles could boost the adsorption of O_2 and further enhance the formation of H_2O_2 and Ti-OOH intermediates. On the one hand, the

geometric structure of Au nanoparticles was optimized by decreasing the diameter. On the other hand, the electronic interaction between Au nanoparticles and the 2*p* orbital of O_2 was improved by higher electron density of Au nanoparticles.

3.4 Enhanced surface molecular transfer by sodium-decorated Au-Ti bifunctional sites

The schematic diagram of direct propene epoxidation with H_2 and O_2 shown in Figure 7 includes the O_2 adsorption and formation of H_2O_2 (step 1). The surface H_2O_2 transfers to isolated framework Ti^{4+} sites, forming reaction intermediate of Ti-OOH. The Ti-OOH further oxidizes propene (step 2) and the PO desorbs from the microporous channel (step 3).

The O_2 adsorption for the synthesis of H_2O_2 (step 1) is improved by the sodium-decorated Au nanoparticles. The geometric structure could be optimized via decreasing the diameter in the sodium-decorated Au nanoparticles to increase the capacity of O_2 adsorption. The electronic interaction between electron-riched Au nanoparticles and the 2*p* orbital of O_2 was strengthened to synthesize H_2O_2. In subsequent step 2, this sodium-decorated TS-1 could further improve the stability of H_2O_2 during the surface mass transfer, and further increase reaction intermediates Ti-OOH by constructing Si-ONa surface with weaker hydrogen bond. For the last step 3, the Si-ONa species could suppress the ring-opening of PO and formation for aromatic carbonaceous deposits to improve the epoxidation stability. Therefore, the sodium-decorated Au-Ti bifunctional sites significantly improve the direct propene epoxidation with H_2 and O_2 by enhancing the O_2 adsorption, surface transfer of oxidative species (H_2O_2), and desorption of epoxidation products as shown in Figure 7.

4. Conclusion

In summary, the alkalis-strengthened wet-chemistry method was developed, and the surface molecular transfer was regulated by the sodium-decorated Au-Ti bifunctional sites to enhance the direct propene epoxidation with H_2 and O_2. The sodium-decorated TS-1 support could effectively restrain the decomposition and further improve the surface transfer of H_2O_2 on the Si-ONa species, thus forming more reaction intermediates Ti-OOH. Meanwhile, the Si-ONa species could further restrain the carbonaceous deposits in the channel of TS-1, especially for the formation of aromatic species. This leads to enhanced catalytic stability for direct propene epoxidation with low blocking degree of channels. In addition, the O_2 adsorption was enhanced by the sodium-decorated Au nanoparticles to boost the formation of H_2O_2. This is attributed to the improved geometric structure with decreasing the diameter and electronic structure with stronger interaction between the O 2*p* orbitals and electron-riched Au nanoparticles. The sodium-decorated Au-Ti catalyst of 0.23Na-Au/TS-1 significantly increases the PO formation rate to 310 $g_{PO}h^{-1}g_{Au}^{-1}$ which is ca. 20 times higher than that of NH_4-Au/TS-1 without the sodium-decorated microenvironment. The improved surface molecular transfer based on the sodium-decorated Au-Ti sites sheds new light on the design of bifunctional catalyst microenvironment for propene epoxidation.

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