Design of Frustrated Lewis Pair in Defective TiO_2 for Photocatalytic Non-Oxidative Methane Coupling

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Abstract

The efficient C-H polarization is the prerequisite for the low-temperature photocatalytic CH₄ conversion, which however is restricted by the poor stretching ability of short-distanced lattice atoms. Herein, frustrated Lewis pair (FLP) composed of doped ion in TiO₂ as Lewis acid (LA) and neighboring Ti-OH as Lewis base (LB) with a long distance (0.31-0.37 nm) were designed through DFT calculation and fabricated by hydrogenation treatment of metal-doped TiO₂-SiO₂ with macroporous-mesoporous structure. Benefitting from the long LA-LB distance and matched acid-base intensity, hydrogenated Ga-doped composite achieves superior C-H stretching with a high CH₄ conversion rate (139 μmol g⁻¹ h⁻¹) to ethane. The photo-irradiation causes the electron excitation from Ga to Ti-OH according to the time-dependent DFT calculation and *in situ* EPR analysis, which promotes the formation and coupling of ·CH₃. This work provides a key underpinning for regulating the characteristics of FLP for C-H activation and C-C coupling via light irradiation.

Introduction

The increasing abundance of atmospheric methane as a major potent greenhouse gas and the large-scale exploitation of shale gas/combustible ice, have aroused the worldwide research interest for the rational utilization of methane, aiming for cleaner energy development and environmental protection¹⁻³. However, the conversion of methane into high-value chemicals and transportable fuels is a huge challenge because of the high inertness and low electron affinity energy of C-H bond. Harsh reaction conditions are inevitably required in conventional thermal catalysis, resulting in great energy consumption and low product selectivity. Alternatively, photocatalysis driven by solar light has proven to be a promising technology for overcoming the high energy barrier of methane conversion. The key is to enhancing the polarizability of methane at room temperature and the separation rate of photo-induced charge carriers.

Photocatalytic non-oxidative coupling of methane (NOCM) is one of the effective approaches to selectively producing ethane and hydrogen under mild conditions⁴⁻⁷. Our previous work has verified that Pt^{δ+}-Pt pair loaded on TiO₂ can promote the photocatalytic C-H polarization at room temperature^{5,8}. However, the C-H stretching should be still fairly restricted by the comparatively fixed and short lattice distance of adjacent positive-negative pair. A polarized environment with highly tunable and flexible distance is more desirable. Recently, solid frustrated Lewis pair (FLP) composed of long-distanced Lewis acid (LA) and Lewis base (LB) sites on the solid surface have proven efficient for H₂, CO₂ and CO activation⁹⁻¹². The existence of steric hindrance between LA and LB leads to the unremitting attraction between Lewis pairs rather than bonding with each other, which has been extensively studied on metal oxides with unsaturated metal centers and metal terminal hydroxyl groups mediated by oxygen vacancies, typically seen in defective CeO₂ and In₂O_{3-x}(OH)_y¹³⁻¹⁷. While the C-H activation of arenes and heteroarenes by FLP has been achieved, the activation of aliphatic Csp³-H bonds remains a challenge to

be solved^{18–21}. Some theoretic studies have explored the nature of FLP for C-H activation, demonstrating the feasibility of FLP to Csp^3 -H activation, which however has not been put into practice^{22–25}. Recently, photo-irradiation has been used to *in situ* form heterogeneous FLP or tune the acidity-basicity of FLP sites. For examples, Ozin showed that the Lewis acidity and Lewis basicity were strengthened in the photo-excited state, resulting in a lower activation energy of CO_2 ¹⁷. Yan et al reported that the photo-induced Lewis acid can be generated by oxidizing light-unstable terminal hydroxyls at Sn sites²⁶. It is thus necessary to explore the possibility of tuning the FLP property through photo irradiation for practical CH_4 conversion, regarding facilitating C-H activation and C-C coupling.

Herein, based on DFT calculation, anatase- TiO_2 -based frustrated Lewis pair composed of p-type metal dopants (Ga^{3+} , In^{3+} , Zn^{2+} , Ti^{3+}) as LA and Ti-OH as LB with a large spacing were designed, where oxygen vacancy (Vo) is used as steric hindrance between LA and LB. Accordingly, a combinational doping and hydrogenation strategy was adopted to form frustrated metal-Vo-Ti-OH Lewis pairs in anatase TiO_2 . The hydrogenated Ga^{3+} -doped TiO_2 presents the most prominent photocatalytic CH_4 conversion activity. EPR analysis and time-dependent DFT calculation were combined to demonstrate the contribution of light irradiation to tuning the Lewis acidity and basicity of FLP, and with that the nature of light irradiated FLP in promoting CH_4 conversion.

Result

Theoretical calculation

In order to guide the design of TiO_2 -based FLP for CH_4 activation, DFT calculations were first carried out to screen out an ideal model through metal doping strategy. Metal ions (M) of Ga^{3+} , Zn^{2+} , In^{3+} and Ti^{3+} as typical p-type dopants which are prone to forming Lewis acid were adopted to construct FLP in TiO_2 ^{27–32}. It is found the metal ion dopant substituted for the six-coordinated Ti site (Ti_{6c}), together with Ti-OH in the neighboring five-coordinated Ti site (Ti_{5c}), can form M-Vo-Ti-OH with long distances of 0.31–0.39 nm between M and Ti-OH (Fig. 1). By contrast, exchanging the position of metal ion dopant and Ti-OH can not prevent the formation of dative bond (Fig. S1 and Table S1), producing M-O(H)-Ti with a proton simply binding to the bridging oxygen of M-O-Ti. The retarded separation of M-O bond should be attributed to the higher steric hindrance around Ti_{6c} than Ti_{5c} . The formation of M-Vo-Ti-OH is energetically comparable to that of M-O(H)-Ti, but is more favorable than M-Vo-Ti except for the Zn-doped system (Fig. S2 and Table S1). Since the proton is used to compensate the charge difference between p-type metal dopant and Ti^{4+} , the p-type dopant in TiO_2 should be beneficial for the hydrogenation of bridging oxygen according to the calculated formation energy. Zn^{2+} with a lower charge requires two protons to balance the charge, and thus Zn-Vo-Ti is more favorably formed from dehydration compared with Zn-V_O-Ti-OH (Fig. S2). According to the Hirshfeld charge analysis, although the metal substitution decreases the acidity of original Ti_{6c} site and the basicity of bridging oxygen (Fig. S3), both of them can be efficiently improved by hydrogenation treatment, accompanied by the increased distance

between M dopant and Ti-OH (Fig. 1). The metal dopant in M-V_O-Ti-OH is supposed to function as LA, and the Ti-OH plays the role as LB. The electron-localization degree on metal dopants in M-V_O-Ti-OH follows the order of In<Ti<Ga<Zn (Fig. 1a-d), inversely corresponding to the order of LA acidity. Moreover, it is noted the In dopant even has a more positive charge than all of Ti atoms in TiO₂, suggesting it actually behave in the manner of an n-type dopant, which should be attributed to the stronger delocalization tendency of its 4d electrons.

The effect of FLP on the C-H activation was further studied through the comparison with the corresponding non-hydrogenated system. Non-modified TiO₂ does not stretch the C-H bond when the CH₄ molecule resides over Ti_{6c} site (Fig. S4), but the bridging oxygen becomes efficient for hydrogen abstraction from CH₄ when Ti_{6c} is replaced by the metal dopant as observed from M-O-Ti systems. Meanwhile, the hydrogenated TiO₂ (H-TS) is also effective for hydrogen abstraction due to the formation of LB Ti-OH, and the energy for C-H cleavage is further decreased in the hydrogenated and metal-doped system (Fig. 2 and Table S1). Therefore, both the doping and hydrogenation treatment can enhance the hydrogen abstraction ability of original bridging oxygen. The Ti-OH of Zn-V_O-Ti-OH is the most energetically favorable for H abstracting, which should be attributed to the higher charge difference between metal dopant and Ti_{5c}. Accordingly, Ti-V_O-Ti-OH with the least charge difference requires the highest energy for hydrogen abstraction. Moreover, both Ga-V_O-Ti-OH and In-V_O-Ti-OH can efficiently adsorb -CH₃ with obviously observed electron transfer from -CH₃ to LA site. The -CH₃ seems less efficiently adsorbed by LA Ti and Zn sites compared with the lengths of In-C and Ga-C bonds. Especially, -CH₃ locates far away from LA Zn with the largest Zn-C distance, demonstrating LA Zn is the most inefficient for -CH₃ adsorption, which should be ascribed to its low acidity. Based on the above results, the M-V_O-Ti-OH with big charge difference between metal dopant and Ti_{5c} favors the hydrogen abstraction, and the strong LA acidity of metal dopant is essential to achieve efficient -CH₃ adsorption.

Structural characterizations of FLP catalysts

To verify the theoretical calculation results, hierarchical macroporous-mesoporous TiO₂-SiO₂ was adopted as the model to form M-V_O-Ti-OH through doping-hydrogenation treatment, which is expected to promote the formation of uniformly dispersed LA-LB pairs benefitting from the highly accessible pore system and high specific surface area. XPS was used to analyze the surface chemical composition. All samples show two obvious peaks at 458.3 and 464.0 eV attributed to the characteristic peaks of Ti 2p (Fig. S5). Three peaks of O 1s located at 529.7, 531.1 and 532.2 eV are assigned to lattice oxygen, oxygen neighboring to oxygen vacancy and surface -OH, respectively (Fig. S6 and Fig. S7). According to the theoretically calculated M-V_O-Ti-OH model, the ratio of Vo to -OH was used to represent the LA/LB ratio²². Through the fine deconvolution of the O 1s XPS spectra (Table S2, Fig. 3), the hydrogenation treatment improves the percentage of surface -OH and Vo equally for ca. 6% in H-TGS, exceeding those in the other metal-doped samples. The optimized hydrogenation temperature for the formation of FLP is 773 K as the lower (573 K, 673 K) or higher temperature (873 K) fails to equivalently enhance the

concentrations of Vo and surface -OH (Fig. S8). Specifically, the -OH concentration is more obviously improved at a lower temperature of 673 K, which is accordant with the DFT calculation that the hydrogenation of bridging oxygen is more favorable compared with the formation of oxygen vacancy. More Vo is formed when the hydrogenation temperature increases to 773 K, suggesting the formation of uncoordinated LA and LB. The temperature of 873 K should be over high, which may force neighboring -OH groups to leave as H₂O or cause the severe distortion the crystal lattice, resulting in a decreased FLP concentration.

The contribution of the porous structure to the formation of FLP was demonstrated using commercial P25 as the control sample. FLP can not be efficiently formed in commercial P25 through the same Ga doping and hydrogenation treatment, which verifies that the porous H-TGS with highly accessible TiO₂ crystallite embedded in the framework is essential for forming FLP composed of uncoordinated LA and LB (Fig. 3). The BET specific surface areas of all porous composites are above 110 m²/g. Using H-TGS as the demonstration, it has hierarchical macroporous-mesoporous structure with an average macroporous diameter of 170 nm and an average mesoporous size of ca. 5 nm, according to the N₂ adsorption-desorption isotherm and HRTEM analyses (Fig. S9, S10). The lower surface -OH concentration of H-TZS is accordant with the DFT calculation that the hydrogenation of Zn-doped TiO₂ favors the formation of Zn-Vo-Ti through dehydration. Moreover, the lower fitted -OH and V_O concentrations of In-doped H-TIS may be attributed to the shorter LA-LB distance according to the DFT calculation, which diminishes the difference between Vo and surface -OH, making the analysis based on binding energy less discerning. Based on these results, H-TGS with more FLP is considered to be the most potential catalyst for methane conversion.

Photocatalytic NOCM performance

In order to verify the structure-property relationship, the nonoxidative coupling of methane was carried out over different FLP (Eq. 1). As shown in Fig. 4a, the highest CH₄ conversion rate (139 μmol g⁻¹ h⁻¹) was achieved on H-TGS with a selectivity to alkane over 90%. The alkane/H₂ ratio is nearly equal to 1 (Table S3), demonstrating methane is converted in the NOCM way. Compared with that of H-TS, the activity is doubled through Ga doping, but is not obviously enhanced from the doping of the other metal ions. The doping of Zn even deteriorates the NOCM activity of H-TS. Moreover, both TGS and TS show negligible activity compared to other samples (Fig. S11a), suggesting the necessity of hydrogenation treatment. H-TGS displays NOCM activity as a function of FLP concentration, with a maximum activity reached on H-TGS (773 K), indicating the matched concentration of oxygen vacancy and hydroxyl group is essential to achieving a sound NOCM activity. The increased light irradiation intensity significantly improves its performance (Fig. 4b), demonstrating the photocatalytic nature of the reaction over H-TGS. Fig. 4c, d show the enhanced Lewis acidity of H-TGS (Table S4).

In order to confirm the cooperation between Lewis pairs for CH₄ conversion, pyridine and pyrrole were used to cover the acidic and basic sites of H-TGS, respectively. The activities are decreased by ca. 70% and 80% from the quenching of Lewis acidic and basic sites by pyridine and pyrrole (Fig. 4a). Moreover, H-TGS can preserve sound photocatalytic stability for 6 cycles (Fig. S11b), demonstrating LA and LB cooperate effectively in C-H cleavage and the subsequent intermediate desorption. In accordance with the calculation results, the activities of H-TS, H-TZS and H-TIS were much lower than that of H-TGS, verifying the more efficient C-H polarization by Ga-V_O-Ti-OH (Fig. S5)³³. The contribution of the band-gap narrowing through doping-hydrogenation treatment is excluded since there is no obvious difference can be observed from different composites (Fig. S11).

Determination of the local structure of active FLP sites

In order to verify the real local fine structure of H-TGS, synchrotron radiation-based X-ray absorption fine structure spectroscopy (XAFS) was further used to obtain information regarding the valence states and local structural environment of Ti and Ga sites in active H-TGS. X-ray absorption near-edge structure (XANES) spectra of Ti K-edge (Fig. 5a) reveals visible similarities in structural and electronic properties between all the samples and that of the TiO₂ reference. The pre-edge peaks are assigned to the electric quadrupole and electric dipole transitions, reflecting the symmetry of hybridized orbitals in Ti_{3d}³⁴⁻³⁵. The higher intensity of the pre-edge peak at 4972 eV of H-TGS indicates the most distorted octahedral geometry of Ti sites. In addition, associated with XPS (Fig. S5), the absorption edge of H-TGS obviously shifts towards lower energy, implying the improved electron density of titanium species from H₂ reduction.

The Ga K-edge XANES spectra of TGS and H-TGS (Fig. 5b) also show the similar absorption edge to that of the Ga₂O₃ reference, while the Ga K-edge extended X-ray absorption fine structure (EXAFS) spectra indicate the distinct coordination environments of Ga atoms between Ga-doped samples and Ga₂O₃ reference (Fig. S12). The *k*³-weighted Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra were used to analyze the differences in local structures. Ti K-edge FT-EXAFS spectra of all samples show two obvious peaks attributed to Ti-O and Ti-Ti bond (Fig. 5c). A Ti-Ti interaction peak in the shell of second-nearest neighbors surrounding Ti atoms (2-3 Å) in H-TS, TGS and H-TGS slightly shifts to longer distance compared to TiO₂ reference, in good agreement with XRD for the expanded lattice (Fig. S13). The Ga K-edge FT-EXAFS spectra show a Ga-Ga interaction peak near 2.9 Å, which represents the shell of second-nearest neighbors surrounding Ga atoms in the Ga₂O₃ reference (Fig. 5d). In contrast, no Ga-Metal peak distinctly appears at 2-3 Å and only the first shell peaks at around 1.4 Å assigned to Ga-O peak exists, revealing the isolated state of Ga atom in TGS and H-TGS, which is accordant with the DFT calculation. The wavelet transform-EXAFS (WT-EXAFS) spectra of H-TGS and TGS show a distinct signal compared with that of Ga₂O₃ reference (Fig. 5e, Fig. S14), further verifying the atomic dispersion of Ga.

In order to quantify these differences more accurately in local structure, the spectra were also fitted to extract key structural parameter values (Table S5 and S6). The curvefit of H-TGS well fits the main peak of EXAFS shown in k^3 -weighted k -space and R -space through first-nearest scattering path attributed to the metal-O structure (Fig. 5f, g, other spectra are displayed in Fig. S15). The prepared TGS has lower coordination numbers ($CN_{Ti-O} = 4.7$) compared to TS ($CN_{Ti-O} = 4.9$). The coordination environment changes due to the incorporation of heterogeneous atoms. Moreover, the coordination numbers of H-TGS ($CN_{Ti-O} = 4.2$) become much lower, as well as that of H-TS ($CN_{Ti-O} = 4.5$), suggesting highly structural distortion and rich surface defects caused by H_2 treatment, which is consistent with the observed presence of oxygen vacancy and surface hydroxide in XPS. However, the unsaturation of Ti in H-TS ($CN_{Ti-O} = 4.5$) is smaller than that in H-TGS ($CN_{Ti-O} = 4.2$) which again highlight the function of Ga. In addition, the Ga coordination number of H-TGS ($CN_{Ga-O} = 4.7$) also shows a downward trend relative to the TGS ($CN_{Ga-O} = 5.0$), further implying a distinct structural difference resulted by the hydrogenation. Based on the above analyses, we confirm that the frustrated Lewis pairs have been successfully constituted by the isolated and coordinately unsaturated Ga species along with surface V_O and $-OH$.

Light-regulated electron transfer of FLP

As demonstrated above, the XAFS analysis confirms the structure of single-site FLP is accordant with the DFT calculation. Furthermore, *in situ* electron paramagnetic resonance (EPR) spectra with and without reactant CH_4 were recorded to explore the photo-induced electron transition of Ga-Vo-Ti-OH and its effect on the characteristics of LA and LB. In Ar atmosphere, the EPR signals of Vo and free electrons are observed in H-TGS (Fig. 6a). The light irradiation does not cause obvious signal variation. The signal of Vo disappears in methane atmosphere, accompanied with the increasing signal of free electrons, which should be attributed to the methane adsorption. Under the continuous irradiation, the signal of free electrons gradually decreases with the recovery of the Vo signal, suggesting the completion of NOCM reaction and product desorption. Compared with that in H-TGS, the signal of Vo is more distinct in H-TIS and does not vary with the surrounding atmosphere of argon or methane (Fig. 6b). The light irradiation can further improve the Vo intensity under both conditions. Compared with that in H-TIS, the lower signal of Vo in H-TGS suggests the electrons in the neighborhood should be more delocalized, which is accordant with the more obvious appearance of signal of free electrons. In methane atmosphere, the C-H cleavage of CH_4 molecule produces $-CH_3$ and $-H$ adsorbed on LA Ga and LB Ti-OH according to the DFT calculation, leading to the redistribution of the local charge around FLP sites. The excess negative charge from $-CH_3$ and $-H$ adsorption is calculated as -0.14 (Fig. S16). The disappearance of Vo signal of H-TGS from CH_4 adsorption should be caused by the further reduction of Vo by excess electrons or the enhanced electron delocalization by the repelling force of adsorbed $(CH_3)^\delta-$. Considering the simultaneously improved signal of free electrons from methane adsorption, the excess electron produced from methane adsorption in the neighborhood of FLP should tend to delocalize from Vo as repelled by the adsorbed $(CH_3)^\delta-$, resulting in the signal disappearance of Vo. In contrast, the higher EPR signal of Vo in H-TIS demonstrates the neighboring In atom helps stabilize the single-electron occupied Vo, and the improved

Vo signal from light irradiation further confirms this assumption that photo-induced electrons tend to be captured by Vo in In-Vo-Ti-OH. Moreover, considering the more positively charged LA In in In-Vo-Ti-OH system, the repelling force of the excess electrons from methane adsorption to the single electron of Vo should be weaker than that in Ga-Vo-Ti-OH, which is accordant with the unvaried EPR of H-TIS from methane adsorption. The light-induced signal variation of CH₄-adsorbed H-TGS demonstrates the light irradiation is essential for the C₂H₆ production through C-C coupling.

To explicitly explore the contribution of light irradiation to the C-H activation and C-C coupling, time-dependent DFT calculation was carried out over H-TGS and H-TIS. The excited state with stronger oscillator strengths (> 0.02) is selected within the range of excitation (Fig. S17). In the excited state of Ga-V_O-Ti-OH, electrons originally localized near Ga are transferred to the terminal hydroxyl group (green group). As shown in the electron-hole pair analysis (Fig. 6c), the charges are efficiently separated, simultaneously increasing the intensity of LA and LB, which should favor the oxidation of CH₃^{δ-} and the reduction of adsorbed H^{δ+}. While in the ground state of In-V_O-Ti-OH, electrons are originally localized on Ti. Upon excitation, no electron transition from Ti_{6c} to In is observed, suggesting the light irradiation should have no effect on tuning the FLP characteristics. Thus, ·CH₃ can not be efficiently transformed from adsorbed CH₃^{δ-} to further undergo C-C coupling, which is accordant with the inefficiency of HIS in promoting the methane conversion (Fig. 6d).

Based on the above analysis, the mechanism of photocatalytic methane conversion on TiO₂-based FLP can be reasonably explained as follows (Fig. 7). TiO₂-based FLP M-Vo-Ti-OH composed of p-type metal dopant as LA and Ti_{5c}-OH as LB with enlarged LA-LB distance designed through DFT calculation is theoretically considered efficient for promoting the stretching of the C-H bond, with (CH₃)^{δ-} and H^{δ+} adsorbed on LA and LB based on DFT calculation. However, only Ga-Vo-Ti-OH proves particularly active in real NOCM reaction. The gap between theoretic calculation and the real NOCM reaction efficiency was explained by combining *in situ* EPR and time-dependent DFT to achieve sufficient understanding of the dynamic change of FLP site during photocatalytic methane conversion. For Zn-Vo-Ti-OH, although it requires the lowest energy for C-H breakage, the more energetically favorable dehydration forms deactivated Zn-Vo-Ti, resulting in unsustainable FLP for C-H activation. The Ti-Vo-Ti-OH is least energetically favorable for hydrogen abstracting and -CH₃ adsorption due to the little charge difference between LA Ti and LB Ti-OH. However, the LA and LB intensity should be simultaneously strengthened from the light irradiation, thus enhancing the NOCM efficiency compared with the non-hydrogenated TiO₂. Ga-Vo-Ti-OH and In-Vo-Ti-OH with the bigger charge difference of LA-LB and the stronger LA acidity theoretically prove more favorable for the simultaneous hydrogen abstracting and -CH₃ adsorption. Using the Ti-Vo-Ti-OH with the least charge difference as the reference, the further improved activity over Ga-Vo-Ti-OH should be attributed to the more efficient photo-induced electron transition from LA Ga to LB TiO₂. Under continuous light irradiation, both of the LA and LB in Ga-Vo-Ti-OH can be refreshed, forming ·CH₃ and ·H radicals from separated LA and LB and thus resulting in sustainable production of C₂H₆ through C-C coupling. In contrast, since In has a more positive charge than the neighboring Ti_{5c}, no excess

electron can be excited from In in the In-Vo-Ti-OH. Therefore, it is suggested that even if abundant In-Vo-Ti-OH can be fabricated on TiO_2 , the mismatching between C-H activation and light-induced charge transition can not lead to sound turnover rate over this type of FLP site.

Conclusion

In summary, as guided by the DFT calculation, we designed and prepared solid FLP based on hierarchical porous $\text{TiO}_2\text{-SiO}_2$ by combining metal-doping and hydrogenation strategies for photocatalytic non-oxidative coupling of methane. Benefitting from the appropriate atomic structure of Ga dopant, high concentration of FLP was formed from Ga-doped composites, providing Ga-Vo-Ti-OH with a long LA-LB distance and strong acid and base intensities for C-H bond stretching. The effect of light irradiation on improving the intensities of LA Ga and LB Ti-OH was confirmed based on the calculated electron transition from LA to LB, which is the key to forming methyl and hydrogen radicals for the further coupling production of C_2H_6 . This work provides in-depth insight into the key to the design and construction of photocatalytically active FLP for $\text{Csp}^3\text{-H}$ polarization. This work is expected to significantly promote the application of FLP system in mild and selective alkane conversion.

Methods

Synthesis of PS

Polystyrene (PS) microspheres were synthesized by emulsion polymerization according to the literature³⁶. 0.45 g of lauryl sodium sulfate (SDS) and 0.6 g of potassium persulfate (KPS) were dissolved in 120 mL of EtOH and 270 mL of H_2O in a 500 mL three-neck flask and ultrasonic mixed for 30min. Then the solution was deoxygenated and exchanged with N_2 . The flask was heated to 344 K under constant stirring in an oil bath, and 35 mL of styrene was injected. The reaction was cooled down to room temperature after 19 h. The polystyrene array was finally obtained by drying the polystyrene emulsion in a 343 K oven for 24h.

Preparation of TGS, TS, TZS and TIS

The Ga^{3+} doped $\text{TiO}_2\text{-SiO}_2$ (TGS) was synthesized by the evaporation induced self-assembly (EISA) method. Typically, the as prepared PS microspheres was soaked in the mixture of 2 g of P123, 0.16 g of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 30 mL of EtOH, 0.89 mL of TEOS, 0.53 mL of TiCl_4 , and 3.3 mL of TTIP, which was stirred for 4 h. Then the moist $\text{Ga}^{3+}\text{-Ti-Si}$ precursor was evaporated at 341 K and 55% relative humidity for 3 d and then dried at 340 K for 3 d. The obtained blocks were calcined at 773 K for 5 h with a heating rate of 2 K/min. After that, the samples were collected and washed with water two times for further use. For the preparation of TS, the process was the same, except no addition of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$. For the preparation of TZS and TIS, we replaced $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ with 0.186 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.188 g of $\text{In}(\text{NO}_3)_3$ respectively and kept other steps unchanged.

Preparation of Ga-P25

The impregnation method will be used to prepare Ga-P25. Theoretically, since all Ga sources will be deposited on the surface of P25 in this method, in order to maintain the consistency of Ga loading, we add gallium nitrate according to the actual Ga content in TGS. The actual mass fraction of Ga in TGS was 1.5 wt% measured by ICP. 0.2 g of P25 and 0.011 g of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ with 20 mL of H_2O were mixed together for 1 h under continuous stirring. Then, the mixture was dried slowly in a 343 K electric thermostatic drying oven. After that, the samples were collected and annealed in a muffle furnace at 773 K (2 K/min) for 4 h. Finally, the as prepared samples were washed with water two times and dried for further use

Hydrogenation Treatment

The as prepared sample was placed in quartz ware and was hydrogenated in H_2 atmosphere (20 mL/min) at different temperature (573 K, 673 K, 773 K and 873 K). The samples were heated for 4 h with a heating rate of 2 K/min in a tube furnace and then naturally cooled to room temperature. The samples were named as H-TGS-573K, H-TGS-673K, H-TGS and H-TGS-873K. For comparison, H-TS, H-TZS, H-TIS and H-Ga-P25 were prepared under the temperature of 773 K to investigate the effects of Ga^{3+} doping and periodic pore structure

Characterization of photocatalysts

The morphology was characterized by transmission electron microscopy (TEM, JEM1400). The scanning electron microscopy (SEM) analysis was performed using a TESCAN Nova III scanning electron microscope. The structures of samples were analyzed by HRTEM (JEM-2100). The diffraction peak of samples was characterized by XRD (Rigaku D/MAX 2550, Cu K radiation, $\lambda = 1.5406 \text{ \AA}$), whose operation voltage and current was set at 40 kV and 40 mA. The visible light absorption of the sample was tested by an ultraviolet-visible spectrophotometer (Shimadzu, Japan, UV-2450). The sample was a solid powder and then BaSO_4 was used as a reference. The test range was from 200 to 800 nm. The BET surface area of samples were characterized by ASAP2020. The surface chemical states in different samples were characterized by high-resolution XPS (Perkin-Elmer PHI 5000C ESCA system: Al K α radiation, operated at 250 W), and the shift of the spectra caused by the relative surface charging was calibrated according to the standard binding energy of C (sp²) at 284.6 eV. The actual Ga loading in samples were characterized by ICP-AES analysis (Agilent 725 ICP-OES). The carrier separation efficiency of samples was measured by Photoluminescence spectra (RF-5301PC), the excitation wavelength was 365 nm. Mott-Schottky tests were carried out on a ZAHNER PP211 electrochemical station with a three electrode cell. The working electrode is made of FTO glass and the sample, the counter electrode was Pt and the reference electrode was a saturated calomel electrode. The Na_2SO_4 aqueous solution (0.5 M) was added as electrolyte. Electron Paramagnetic Resonance (EPR) was performed on a JEOL-FA200 instrument (frequency 100.00 MHz, magnetic field 0.35 T, magnetic field sweep 5.00 T, magnetic field resolution 0.03 T, test at room temperature, g factor is used for comparison due to the weak change of magnetic field). The data analysis of the XAFS spectra were conducted using the Demeter

software package (ATHENA and ARTEMIS, respectively)³⁷. All fits were performed in the R space with k-weight of 3. We applied the Continuous Cauchy Wavelet Analysis (CCWT) to the EXAFS spectra which allows determining the identity of the atoms in noisy signals^{38,39}.

Photocatalytic test

2 mg of catalyst was evenly dispersed by 3 mL of water and spread on the glass slide to form a ultrathin film. Before the test, the catalyst was pretreated under vacuum for 4 h at 393 K to remove the adsorbed water and other molecules. Then it was placed at the bottom of a sealed quartz reactor (45 cm³), which was then evacuated for 10 min to remove air. Afterward, 1 mL of pure methane (99.99%) was injected into the reactor and waited for 1 h to achieve an adsorption-desorption balance. The reactor was irradiated by a 300 W Xe lamp for 4 h at room temperature. The hydrocarbon products were analyzed by gas chromatography (Shimadazu GC-2014) with a flame-ionization detector (FID). The relative deviation of detection was less than 5% for GC. The quenching experiment of FLP was carried out with pyrrole and pyridine. The catalyst was placed at the bottom of a sealed quartz reactor and evacuated for 10 min to remove air. Afterward, 0.5 mL of pyrrole (or pyridine) was injected and kept in dark for 1 h to achieve an adsorption-desorption balance. Then the reactor was evacuated, and the subsequent steps were consistent with the photocatalytic test.

In situ EPR analysis

100 mg of sample was placed at the bottom of a vacuum sealed capillary quartz tube and then the ambient gas (Ar or CH₄) was introduced. The EPR signals were collected in dark and every 15 minutes under irradiation.

Computational Detail

In this work, calculations for the total energy and geometric optimization were performed using the CASTEP program within the framework of DFT⁴⁰⁻⁴¹. The ultrasoft pseudopotential was used for electron-ion interactions, and the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was employed to describe the exchange-correlation functional⁴². In the optimization process, the bulk atoms are fixed and the surface (subsurface) layers are optimized.

For the time-dependent DFT calculation, H-TGS clusters and H-TIS clusters were extracted from the (101) crystal structure. In the optimization process, the main part is fixed, and the Ga and In parts are optimized. In the whole optimization process, the B3LYP functional⁴³⁻⁴⁴ and Def2SVP basis sets⁴⁵ under the framework of density functional theory (DFT)⁴⁶ are combined with SDD pseudopotential⁴⁷ and DFT-D3 dispersion correction⁴⁸ in Gaussian 16 A03⁴⁹. The electronic excitation calculation adopts the time-dependent DFT method, combining the CAM-B3LYP functional⁵⁰ and the same level basis functions to consider the long-range electronic correlation, and output all configuration coefficients. The electron-hole pair analysis is implemented by the Multiwfn-3.8 program⁵¹⁻⁵² and are drawn using VMD-1.9.3⁵³.

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Declarations

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Author contributions

Jiayu Ma carried out the sample preparation and characterization, and wrote the manuscript. Qingqing Zhang carried out the sample preparation and assisted with writing the manuscript. Jiayu Ma and Lingzhi Wang carried out the DFT calculations. Ziyu Chen assisted with fitting the XAS data. Kai Kang, Lihan Pan, Shiqun Wu, Chen Chen and Zhiqin Wu assisted with the sample preparation and characterization. Jinlong Zhang and Lingzhi Wang contributed materials and analysis tools. Lingzhi Wang conceived the project, directed the study and assisted with writing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper

Figures

Figure 1

Schematic models of $M-V_O-Ti-OH$. Electron localization function isosurface of $M-V_O-Ti-OH$. **a**, Ti, **b**, Ga, **c**, Zn, **d**, In. The Hirshfeld charge is shown in black font. The color of Ti, O and H atoms are grey, red and white, respectively.

Figure 2

Schematic models of methane adsorption on FLP. Electron density difference isosurface of C-H stretching on FLP. **a**, Ti FLP, **b**, Ga FLP, **c**, Zn FLP, **d**, In FLP. The distance of C-H and metal-CH₃ is shown in blue font and the Hirshfeld charge is shown in black font. The color of Ti, O and H atoms are grey, red and white, respectively.

Figure 3

Analysis of surface composition. Concentration of surface -OH and Vo of different composites.

Figure 4

The photocatalytic performance for NOCM reaction. **a**, Rate of CH₄ conversion and products for the photocatalysts. **b**, Effect of optical power density (mW/cm^2) on photocatalytic performance. **c**, NH₃-TPD and **d**, Pyridine-IR spectra of TS, TGS, H-TS and H-TGS.

Figure 5

Local structure of FLP sites. XANES spectra of **a**, Ti K-edge and **b**, Ga K-edge. The k^3 -weighted Fourier-transformed EXAFS spectra of **c**, Ti K-edge and **d**, Ga K-edge. **e**, WT-EXAFS signals of H-TGS. **f**, Ga K-edge EXAFS (points) and the curvefit (line) for H-TGS, shown in k^3 -weighted k -space. **g**, Ga K-edge EXAFS (points) and the curvefit (line) for H-TGS, shown in R -space (FT magnitude and imaginary component). The data are k^3 -weighted and not phase-corrected. Reference: anatase TiO₂, Ti, Ga and Ga₂O₃.

Figure 6

Study on the electron transfer of FLP tuned by photo excitation. **a**, EPR spectra in Ar atmosphere or in CH_4 atmosphere over H-TGS. **b**, EPR spectra in Ar atmosphere or in CH_4 atmosphere over H-TIS. Analysis of electron-hole pairs in the excited state of **c**, Ga- V_O -Ti-OH (H-TGS) and **d**, In- V_O -Ti-OH (H-TIS). The green and blue groups in **c**, **d** represent the distribution of electrons and holes, respectively. The doped metal atom is in the dotted circle and the color of Ti, O and H atoms are pink, red and white, respectively.

Figure 7

Schematic diagram of Photocatalytic NOCM mechanism.

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