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Long LA–LB distance and strong acid and base intensities promote the stretching of the C–H bond. The effect of light irradiation on improving the intensities of LA Ga and LB Ti–OH was confirmed based on the electron transition from LA to LB, which is the key to forming methyl and hydrogen radicals for the further coupling production of C$_2$H$_6$.

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Highlights
Frustrated Lewis pair (FLP) in defective TiO$_2$ was designed by DFT calculation
139 $\mu$mol g$^{-1}$ h$^{-1}$ CH$_4$ conversion rate in NOCM is achieved under irradiation
FLP with long distance and suitable Lewis intensity is conducive to C–H stretching
Photo-irradiation promotes the formation and coupling of CH$_3$
Design of frustrated Lewis pair in defective TiO$_2$ for photocatalytic non-oxidative methane coupling

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SUMMARY
The efficient C–H polarization is the prerequisite for the low-temperature photocatalytic CH$_4$ conversion, which is restricted by the poor C–H stretching ability of short-distance adjacent lattice atoms. Here, a frustrated Lewis pair (FLP) composed of doped metal in TiO$_2$ as Lewis acid (LA) and neighboring Ti–OH as Lewis base (LB) with a long distance (0.31–0.37 nm) was designed through DFT calculation and fabricated by hydrogenation treatment of metal-doped TiO$_2$–SiO$_2$ with macroporous-mesoporous structure. Benefiting from the long LA-LB distance and matched acid-base intensity, hydrogenated Ga-doped composite achieves superior C–H stretching with a high photocatalytic CH$_4$ conversion rate ($139 \, \mu$mol g$^{-1}$ h$^{-1}$). The photo-irradiation causes 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 ·CH$_3$. 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 (CH$_4$) as a major potent greenhouse gas and the large-scale exploitation of shale gas/combustible ice have aroused worldwide research interest for the rational utilization of CH$_4$, aiming for cleaner energy development and environmental protection. However, the conversion of CH$_4$ into high-value chemicals and transportable fuels is a huge challenge because of the high inertness and low electron affinity energy of the 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 CH$_4$ conversion. The key is to enhance the polarizability of CH$_4$ at room temperature and the separation rate of photo-induced charge carriers.

Photocatalytic non-oxidative coupling of CH$_4$ (NOCM) under mild conditions is one of the effective approaches to selectively produce ethane and hydrogen on TiO$_2$, ZnO, or other materials. Our previous work has verified that a Pt$^{\text{II}}$–Pt pair loaded on TiO$_2$ can promote photocatalytic C–H polarization at room temperature. However, C–H stretching still should be fairly restricted by the comparatively fixed and short lattice distance of adjacent positive-negative pairs. A polarized environment with a highly tunable and flexible distance is more desirable. Recently, a solid frustrated Lewis pair (FLP) composed of long-distance Lewis acid (LA) and Lewis base (LB) sites on the solid surface have proven efficient for...
H₂, CO₂, and CO activation. 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 such as defective CeO₂ and In₂O₃₋ₓ(OH)ₓ. 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. Some theoretic studies have explored the nature of FLP for C–H activation, demonstrating the feasibility of FLP to Csp³–H activation, which has not been put into practice. Recently, photo-irradiation has been used to in situ form heterogeneous FLP or tune the acidity-basicity of FLP sites. For examples, Ghuman and colleagues showed that the Lewis acidity and Lewis basicity were strengthened in the photo-excited state, resulting in a lower activation energy of CO₂. Wang et al. reported that the photo-induced Lewis acid can be generated by oxidizing light-unstable terminal hydroxyls at Sn sites. It is thus necessary to explore the possibility of tuning the FLP property through photo-irradiation for practical CH₄ conversion, regarding facilitating C–H activation and C–C coupling.

Here, based on DFT calculation, an anatase-TiO₂-based FLP composed of p-type metal dopants (Ga³⁺, In³⁺, Zn²⁺, Ti³⁺) as LA and Ti–OH as LB with large spacing were designed, in which oxygen vacancy (V₀) is used as steric hindrance between LA and LB. Accordingly, a combined doping and hydrogenation strategy was adopted to form frustrated metal–V₀–Ti–OH Lewis pairs in anatase-TiO₂. The hydrogenated Ga³⁺-doped TiO₂ presents the most prominent photocatalytic CH₄ conversion activity. Electron paramagnetic resonance (EPR) analysis and time-dependent density functional theory (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 CH₄ conversion.

RESULTS AND DISCUSSION

Theoretical calculation

To guide the design of TiO₂-based FLP for CH₄ activation, DFT calculations were undertaken to screen out an ideal model through a metal doping strategy. Metal ions (Ms) of Ga³⁺, Zn²⁺, In³⁺, and Ti³⁺ as typical p-type dopants which are prone to forming LA were adopted to construct FLP in TiO₂. It is found that the M dopant substituted for the six-coordinated Ti site (Ti₆c), together with Ti–OH in the neighboring Ti₅c site, can form M–V₀–Ti–OH with long distances of 0.31–0.39 nm between M and Ti–OH (Figures 1 and S1). Since the proton is used to compensate for the charge difference between the p-type metal dopant and Ti⁴⁺, the p-type dopant in TiO₂ should be beneficial for the hydrogenation of bridging oxygen according to the calculated formation energy (Figure S2; Table S1). Zn²⁺ with a lower charge (0.41 in Zn-doped TiO₂; Figure S3) requires two protons to balance the charge, and thus Zn–V₀–Ti is more favorably formed from dehydration as compared with Zn–VO–Ti–OH (Figure S2). According to the Hirshfeld charge analysis, although the metal substitution decreases the acidity of the original Ti₆c site (0.59) or the basicity of bridging oxygen (−0.32) (e.g., the charges of Ga site and bridging oxygen decrease to 0.51 and −0.19, respectively; Figure S3). Both of them can be efficiently improved by hydrogenation treatment (the charge of the Ga site and Ti–OH are increased to 0.54 and −0.32, respectively) (Figure 1), accompanied by the increased distance between the M dopant and Ti–OH. The metal dopant in M–V₀–Ti–OH is supposed to function as LA, and the Ti–OH plays the role of LB. The electronic-localization degree on metal dopants in M–V₀–Ti–OH follows the order of Ga³⁺ > In³⁺ > Zn²⁺ > Ti³⁺.

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In < Ti < Ga < Zn (Figures 1A–1D), inversely corresponding to the order of LA acidity. Moreover, it is noted that the In dopant has an even more positive charge than all of the Ti atoms in TiO$_2$, suggesting it actually behaves 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 TiO$_2$ does not stretch the C–H bond when the CH$_4$ molecule resides over the Ti$_{6c}$ site, but the bridging oxygen becomes efficient for hydrogen abstraction from CH$_4$ when Ti$_{6c}$ is replaced by the metal dopant as observed from M–O–Ti systems (Figure S4). Meanwhile, the hydrogenated TiO$_2$ (H-TS) is also effective for hydrogen abstraction due to the formation of LB Ti–OH (Figure 2), and the energy for CH$_4$ adsorption is further decreased in the hydrogenated metal-doped system (E-adsorb CH$_4$: Ti > Ga > In > Zn; Table S1). Therefore, both the doping and hydrogenation treatment can enhance the hydrogen abstraction ability of the original bridging oxygen. The Ti–OH of Zn–V$_O$–Ti–OH is the most energetically favorable for H abstraction, which should be attributed to the higher charge difference between the metal dopant and Ti$_{5c}$. However, Zn–V$_O$–Ti–OH is the most kinetically unfavorable for the C–H stretching, mainly because Zn does not adsorb CH$_3$ (the largest Zn–C distance). Meanwhile, the theoretical calculation shows that Zn doping is not conducive to the formation of FLP, but to the formation of Zn–V$_O$–Ti, which is supposed to further prevent the Zn-doped system from promoting the practical NOCM reaction. The barrier of the C–H bond activation follows the order of Ga < Ti < In < Zn (Figure S5), where the difference between the final state energy and that in Table S1 is attributed to the inconsistency of the calculation parameters. Based on the above results, the M–V$_O$–Ti–OH with the big charge difference between the metal dopant...
and Ti 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–VO–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 (Ga-, Zn-, In-, and Ti-doped samples after hydrogenation are expressed as H-TGS, H-TZS, H-TIS, and H-TS, respectively). X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemical composition. All of the samples show two obvious peaks at 458.3 and 464.0 eV attributed to the characteristic peaks of Ti 2p (Figure S6). 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 (Figures S7 and S8). According to the theoretically calculated M–Vo–Ti–OH model, the ratio of Vo to –OH was used to represent the LA/LB ratio. Through the fine deconvolution of the O 1s XPS spectra (Figure 3; Table S2), the hydrogenation treatment improves the percentage of surface –OH and Vo equally for approximately 6% in H-TGS, exceeding those in the other metal-doped samples. Although the atomic contents of O of different metal-doped systems vary in the range of 57%–67% (Table S2), the variation should be partly caused by the detection error, since the variation tendency seems independent of the valence of doped metal. Here, the variation of the ratio between Vo and surface...
hydroxyl from XPS analysis is used to roughly demonstrate that FLP can be more readily formed from the Ga-doped system according to the comparable increasing tendency of VO and –OH. 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 (Figure S9). Specifically, the –OH concentration is more obviously improved at a lower temperature of 673 K, which is in accordance 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 of 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. A tiny amount of Ga (1.5 wt %) was doped in P25, and no diffraction peak of Ga2O3 was observed in the X-ray diffraction (XRD) of H-Ga-P25 (Figure S10). Therefore, no Ga2O3 nanoparticles or clusters were considered to cover the surface. FLP cannot 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 to forming FLP composed of uncoordinated LA and LB (Figure 3). The Brunauer-Emmett-Teller (BET)-specific surface areas of all porous composites are above 110 m²/g. Using H-TGS for demonstration, it has a hierarchical macroporous-mesoporous structure with an average macroporous diameter of 170 nm and an average mesoporous size of approximately 5 nm, according to the N2 adsorption-desorption isotherm and high-resolution transmission electron microscopy (HRTEM) analyses (Figures S11 and S12). The lower surface –OH concentration of H-TZS is in accordance 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 VO 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 CH4 conversion, which is in accordance with the DFT calculation results.
Photocatalytic NOCM performance

\[ 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2 \]  

(Equation 1)

To verify the structure-property relationship, the non-oxidative coupling of CH\(_4\) was carried out over different FLPs (Equation 1). The surface temperature of the catalyst was measured by infrared thermometer under the light intensity of approximately 2,200 mW/cm\(^2\). The results showed that the surface temperature stayed below 120°C and no product was detected in the dark at 120°C. As shown in Figure 4A, the products mainly contain ethane and hydrogen. Propane can be detected in some samples, and there are no other hydrocarbons in the test. The highest CH\(_4\) conversion rate (139 μmol g\(^{-1}\) h\(^{-1}\)) was achieved on H-TGS with a selectivity to ethane of over 80%. The alkane/H\(_2\) ratio is nearly equal to 1 (Tables S3 and S4), demonstrating that CH\(_4\) 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 Ms. The doping of Zn even deteriorates the NOCM activity of H-TS. Moreover, both TGS and TS show negligible activity compared to other samples (Figure S13A), suggesting the necessity of hydrogenation treatment. H-TGS displays NOCM activity as a function of FLP concentration, with maximum activity reached on H-TGS (773 K), indicating that 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 (Figure 4B), demonstrating the photocatalytic nature of the reaction over H-TGS. Figures 4C and 4D show the enhanced Lewis acidity of H-TGS (Table S5).

To confirm the cooperation between Lewis pairs for CH₄ conversion, pyridine and pyrrole were used to cover the acidic and basic sites, respectively, of H-TGS. The activities are decreased by approximately 70% and 80% from the quenching of Lewis acidic and basic sites by pyridine and pyrrole (Figure 4A). Moreover, H-TGS can preserve sound photocatalytic stability for 6 cycles (Figure S13B), demonstrating that 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.37 The contribution of the band-gap narrowing through doping-hydrogenation treatment is excluded since no obvious difference can be observed from different composites (Figures S13C and S13D).

Determination of the local structure of active FLP sites

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 (Figure 5A) reveal visible similarities in structural and electronic properties between all of 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 Ti₃.38,39 The higher intensity of the pre-edge peak at 4,972 eV of H-TGS indicates the most distorted octahedral geometry of the Ti sites. In addition, associated with XPS (Figure S6), the absorption edge of H-TGS obviously shifts to lower energy, implying the improved electron density of Ti species from H₂ reduction.

The Ga K-edge XANES spectra of TGS and H-TGS (Figure 5B) also show the an absorption edge similar 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 (Figure S14). The k³-weighted Fourier-transformed (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 the Ti–O and Ti–Ti bonds (Figure 5C). A Ti–Ti interaction peak in the shell of the second-nearest neighbors surrounding the Ti atoms (2–3 Å) in H-TS, TGS, and H-TGS slightly shifts to longer distances compared to the TiO₂ reference, which is in good agreement with XRD for the expanded lattice (Figure S15). The Ga K-edge
FT-EXAFS spectra show a Ga–Ga interaction peak near 2.9 Å, which represents the shell of the second-nearest neighbors surrounding Ga atoms in the Ga$_2$O$_3$ reference (Figure 5D). In contrast, no Ga–metal peak distinctly appears at 2–3 Å and only the first shell peaks at approximately 1.4 Å assigned to Ga–O peak exist, revealing the isolated state of the Ga atom in TGS and H-TGS, which is in accordance with the DFT calculation. The wavelet transform-EXAFS (WT-EXAFS) spectra of H-TGS and TGS show a distinct signal compared with that of Ga$_2$O$_3$ reference (Figures 5E and S16), further verifying the atomic dispersion of Ga.

To quantify these differences more accurately in local structure, the spectra were also fitted to extract key structural parameter values (Tables S6 and S7). The curve fit of H-TGS fits the main peak of EXAFS shown in k$^2$-weighted k-space and R-space through the first-nearest scattering path attributed to the metal–O structure (Figures 5F and 5G, other spectra are displayed in Figure S17). The prepared TGS has lower coordination numbers (CN$_{Ti–O}$ = 4.7) compared to TIS (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 do those of H-TIS (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 V=O and surface hydroxide in XPS. However, the unsaturation of Ti in H-TIS (CN$_{Ti–O}$ = 4.5) is smaller than that in H-TGS (CN$_{Ti–O}$ = 4.2), which again highlights 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 that a distinct structural difference resulted from the hydrogenation. Based on the above analyses, we confirm that the FLPs 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 that the structure of single-site FLP is in accordance with the DFT calculation. Furthermore, *in situ* EPR spectra with and without reactant CH$_4$ were recorded to explore the photo-induced electron transition of Ga–V=O–Ti–OH and its effect on the characteristics of LA and LB. In Ar atmosphere, the EPR signals of V=O and free electrons are observed in H-TGS (Figure 6A). The light irradiation does not cause obvious signal variation. The signal of V=O disappears in CH$_4$ atmosphere, accompanied by the increasing signal of free electrons, which should be attributed to the CH$_4$ adsorption. Under the continuous irradiation, the signal of free electrons gradually decreases with the recovery of the V=O signal, suggesting the completion of the NOCM reaction and product desorption. Compared with that in H-TGS, the signal of V=O is more distinct in H-TIS and does not vary with the surrounding atmosphere of Ar or CH$_4$ (Figure 6B). The light irradiation can further improve the V=O intensity under both conditions. Compared with that in H-TIS, the lower signal of V=O in H-TGS suggests that the electrons in the neighborhood should be more delocalized, which is in agreement with the more obvious appearance of the signal of free electrons. In CH$_4$ 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 $-0.14$ (Figure S18). The disappearance of the $V_O$ signal of H-TGS from CH$_4$ adsorption should be caused by the further reduction of $V_O$ by excess electrons or the enhanced electron delocalization by the repelling force of adsorbed (CH$_3$)$_2$. Considering the simultaneously improved signal of free electrons from CH$_4$ adsorption, the excess electron produced from CH$_4$ adsorption in the neighborhood of FLP should tend to delocalize from $V_O$ as repelled by the adsorbed (CH$_3$)$_2$, resulting in the signal disappearance of $V_O$. In contrast, the higher EPR signal of $V_O$ in H-TIS demonstrates that the neighboring In atom helps stabilize the single-electron occupied $V_O$, and the improved $V_O$ signal from light irradiation further confirms this assumption that photo-induced electrons tend to be captured by $V_O$ in In–V$_O$–Ti–OH. Moreover, considering the more positively charged LA In in the In–V$_O$–Ti–OH system, the repelling force of the excess electrons from CH$_4$ adsorption to the single electron of $V_O$ should be weaker than that in Ga–V$_O$–Ti–OH, which coincides with the unvaried EPR of H-TIS from CH$_4$ adsorption. The light-induced signal variation of CH$_4$-adsorbed H-TGS demonstrates that light irradiation is essential for C$_2$H$_6$ 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 (Figure S19). 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 (Figure 6C), the charges are efficiently separated, simultaneously increasing the intensity of LA and LB, which should favor the oxidation of CH$_3$ and the reduction of adsorbed H$^{5+}$. 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 that light irradiation should have no effect on tuning the FLP characteristics. Thus, CH$_3$ cannot be efficiently transformed from adsorbed CH$_3$ to further undergo C–C coupling, which is in accordance with the inefficiency of H-TIS in promoting the CH$_4$ conversion (Figure 6D).

Based on the above analysis, the mechanism of photocatalytic CH$_4$ conversion on TiO$_2$-based FLP can be reasonably explained as follows (Figure 7): TiO$_2$-based
FLP M–V O–Ti–OH composed of p-type metal dopant as LA and Ti₅c–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)⁺ and H⁺ adsorbed on LA and LB based on DFT calculation. However, only Ga–V O–Ti–OH proves particularly active in real NOCM reactions. The gap between theoretic calculation and the real NOCM reaction efficiency was explained by combining in situ EPR and time-dependent DFT to achieve a sufficient understanding of the dynamic change of the FLP site during photocatalytic CH₄ conversion. For Zn–V O–Ti–OH, although it requires the lowest energy for C–H breakage, the more energetically favorable dehydration forms deactivated Zn–V O–Ti, resulting in unsustainable FLP for C–H activation. The Ti–V O–Ti–OH is least energetically favorable for H abstraction 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 light irradiation, thus enhancing the NOCM efficiency compared with the non-hydrogenated TiO₂. Ga–V O–Ti–OH and In–V O–Ti–OH with the greater charge difference of LA-LB and the stronger LA acidity theoretically prove more favorable for the simultaneous hydrogen abstraction and –CH₃ adsorption. Using the Ti–V O–Ti–OH with the least charge difference as the reference, the further improved activity over Ga–V O–Ti–OH should be attributed to the more efficient photo-induced electron transition from LA Ga to LB Ti–OH. Under continuous light irradiation, both of the LA and LB in Ga–V O–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 Ti₅c, no excess electron can be excited from In in the In–V O–Ti–OH. Therefore, it is suggested that even if abundant In–V O–Ti–OH can be fabricated on TiO₂, the mismatching between C–H activation and light-induced charge transition cannot lead to a sound turnover rate over this type of FLP site.

Conclusions
As guided by the DFT calculation, we designed and prepared solid FLPs based on hierarchical porous TiO₂–SiO₂ by combining metal doping and hydrogenation strategies for photocatalytic non-oxidative coupling of CH₄. Benefitting from the appropriate atomic structure of the Ga dopant, a high concentration of FLP was formed from Ga-doped composites, providing Ga–V O–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 C₂H₆. This work provides in-depth insight into the key to the design and construction of photocatalytically active FLP for Csp³–H polarization. This work is expected to significantly promote the application of the FLP system in mild and selective alkane conversion.

EXPERIMENTAL PROCEDURES
Resource availability
Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Lingzhi Wang (wlz@ecust.edu.cn).

Materials availability
This study did not generate new materials.

Data and code availability
This study did not generate any datasets.
Synthesis of PS
Polystyrene (PS) microspheres were synthesized by emulsion polymerization according to the literature. A total of 0.45 g sodium lauryl sulfate (SLS) and 0.6 g potassium persulfate (KPS) were dissolved in 120 mL EtOH and 270 mL H2O in a 500-mL 3-neck flask and ultrasonic mixed for 30 min. Then, the solution was deoxygenated and exchanged with N2. The flask was heated to 344 K under constant stirring in an oil bath, and 35 mL styrene was injected. The reaction was cooled down to room temperature after 19 h. The PS array was finally obtained by drying the PS emulsion in a 343-K oven for 24 h.

Preparation of TGS, TS, TZS, and TIS
The Ga³⁺-doped TiO₂-SiO₂ (TGS) was synthesized by the evaporation-induced self-assembly (EISA) method. Typically, the as-prepared PS microspheres were soaked in a mixture of 2 g P123, 0.16 g Ga(NO₃)₃·xH₂O, 30 mL EtOH, 0.89 mL tetraethyl orthosilicate (TEOS), 0.53 mL TiCl₄, and 3.3 mL titanium tetraisopropoxide (TTIP), which was stirred for 4 h. Then, the moist Ga³⁺-Ti-Si precursor was evaporated at 341 K and 55% relative humidity for 3 days and dried at 340 K for 3 days. 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 Ga(NO₃)₃·xH₂O was added. For the preparation of TZS and TIS, we replaced Ga(NO₃)₃·xH₂O with 0.186 g Zn(NO₃)₂·6H₂O and 0.188 g In(NO₃)₃, respectively, and kept other steps unchanged.

Preparation of Ga-P25
The impregnation method was used to prepare Ga-P25. Theoretically, since all of the Ga sources would be deposited on the surface of P25 in this method, to maintain the consistency of Ga loading, we added gallium nitrate (Ga(NO₃)₃) according to the actual Ga content in TGS. The actual mass fraction of Ga in TGS was 1.5 wt % measured by inductively coupled plasma (ICP). A total of 0.2 g P25 and 0.011 g Ga(NO₃)₃·xH₂O with 20 mL H₂O were mixed together for 1 h under continuous stirring. Then, the mixture was dried slowly in a 343-K electric thermostat 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 quartzware and was hydrogenated in a H₂ atmosphere (20 mL/min) at different temperatures (573, 673, 773, 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 called 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 a temperature of 773 K to investigate the effects of Ga³⁺ doping and periodic pore structure.

Photocatalytic test
Approximately 2 mg sample is filmed on the glass slide. During photocatalysis, the irradiation spot diameter of Xe light was fixed to keep the light intensity constant; therefore, a larger quantity of photocatalyst means a less efficient interaction between the incident light and stacked solid due to a higher stacking density. As a result, the photocatalytic activity as a function of catalyst weight can be improved by decreasing the quantity of photocatalyst in film form, when expressed in per-catalyst weight within a certain weight range. A higher photocatalyst dosage forms a
thicker film with a stronger diffuse reflection, decreasing the interaction chance between the incident light and interior active sites of the film. However, the light transmission becomes predominant when an overly thin film is used. In our work, the film coated with 2 mg of the photocatalyst provided the most enhanced activity.

Approximately 2 mg catalyst was evenly dispersed by 3 mL water and spread on the glass slide to form an 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 the air. Afterward, 1 mL pure CH₄ (99.99%) was injected into the reactor and was kept 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 (GC; Shimadzu GC-2014) with a flame-ionization detector (FID). The relative deviation of detection was less than 5% for GC.

The quenching experiment of the 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 the air. Afterward, 0.5 mL pyrrole (or pyridine) was injected and kept in the dark for 1 h to achieve an adsorption-desorption balance. Then, the reactor was evacuated. The subsequent steps were consistent with the photocatalytic test.

**In situ EPR analysis**

A total of 100 mg sample was placed at the bottom of a vacuum-sealed capillary quartz tube and ambient gas (Ar or CH₄) was introduced. The EPR signals were collected in the dark and every 15 min 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 DFT. The ultra-soft pseudopotential (USPP) was used for electron-ion interactions, and the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was used to describe the exchange-correlation functional. We adopted the evaporation-induced self-assembly method to form microporous TiO₂-SiO₂ using PS microarray as the hard template, in which SiO₂ is used as the buffer for preventing the porous structure from collapse during high-temperature crystallization of TiO₂. TiO₂ nanoclusters embedded in the porous framework are supposed to be separated from each other by SiO₂. The non-doped TiO₂-SiO₂ has negligible activity in the NOCM reaction, demonstrating that the presence of SiO₂ does not contribute to the C–H activation. Meanwhile, the bottom length of the unit cell of the anatase TiO₂(101) surface that we used in the DFT calculation is approximately 1 nm, which is smaller than the size of the TiO₂ cluster observed from the HRTEM image, demonstrating that the structure model we constructed for DFT calculation is sufficient to explore the effect of metal doping (Figure S20). Therefore, the addition of Si in the calculation is not considered. 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 functional and Def2SVP basis sets under the framework of the DFT are combined with the Stuttgart/Dresden (SDD) pseudopotential and DFT-D3 dispersion correction in Gaussian 16 A03. The electronic excitation calculation adopts
We performed the first-principles calculations in the frame of DFT with the program package CASTEP,\textsuperscript{42,55} using the plane-wave (PW)-USPP method and the PBE form of the GGA exchange-correlation energy functional.\textsuperscript{56} The structure optimizations of initial CH$_4$ adsorption on Ga-, In-, and Zn-doped and pure TiO$_2$ (101) surfaces and corresponding decomposed structures have been carried out by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm by fixing the bottom 4 layers and allowing other atomic positions to vary. They stop until the total energies are converged to $10^{-5}$ eV/atom; the forces on each unconstrained atom were smaller than 0.3 eV/Å, the stresses were lower than 0.05 GPa, and the displacements were less than 0.001 Å. The plane-wave cutoff, $E_{\text{cut}}$, was chosen to be 340 eV. The k-point mesh of $2 \times 4 \times 2$ was used for Brillouin zone (BZ) sampling. To obtain the decomposition energy barrier of CH$_4$ adsorption on Ga-, In-, and Zn-doped and pure TiO$_2$ (101) surfaces, the transition state (TS) searches were performed by using the complete linear synchronous transit/quadratic synchronous transit (LST/QST) method.\textsuperscript{57}

Characterization of photocatalysts
The morphology was characterized by 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, $\lambda = 1.5406$ Å), whose operation voltage and current was set at 40 kV and 40 mA, respectively. The visible light absorption of the sample was tested by an ultraviolet-visible spectrophotometer (UV-2450, Shimadzu). The BET surface areas of samples were characterized by ASAP2020 (Micromeritics). The surface chemical states in different samples were characterized by high-resolution XPS (Perkin-Elmer PHI 5000C ESCA system: Al K$_\alpha$ 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 (sp$^2$) at 284.6 eV. The actual Ga loading in samples was characterized by ICP-atomic emission spectroscopy (AES) analysis (Agilent 725 ICP-OES). The carrier separation efficiency of samples was measured by photoluminescence spectra (RF-5301PC), and the excitation wavelength was 365 nm. EPR was performed on a JEOL-FA200 instrument ($f_{100.00}$ md0.35 × 1 am5.00 × 100 tc0.03, tested at room temperature; g factor is used for comparison due to the weak change of the magnetic field). The data analysis of the XAFS spectra was conducted using the Demeter software package (ATHENA and ARTEMIS).\textsuperscript{58} All of the 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 the determination of the identity of the atoms in noisy signals.\textsuperscript{59,60}

SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.checat.2022.05.016.

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AUTHOR CONTRIBUTIONS

J.M. carried out the sample preparation and characterization and wrote the manuscript. Q.Z. carried out the sample preparation and assisted with writing the manuscript. J.M. and L.W. Z.C. assisted with fitting the X-ray absorption spectroscopy (XAS) data. K.K., L.P., S.W., C.C., and Z.W. assisted with the sample preparation and characterization. J.Z. and L.W. contributed materials and analysis tools. L.W. conceived the project, directed the study, and assisted in writing the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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