RESEARCH ARTICLE



Modeling adsorption reactions of ammonium perchlorate on rutile and anatase surfaces

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Abstract

In this work, the effects of two TiO₂ polymorphs on the decomposition of ammonium perchlorate (NH₄ClO₄) were studied experimentally and theoretically. The interactions between AP and various surfaces of TiO2 were modeled using density functional theory (DFT) calculations. Specifically, the adsorption of AP on three rutile surfaces (1 1 0), (1 0 0), and (0 0 1), as well as two anatase surfaces (1 0 1), and (001) were modeled using cluster models, along with the decomposition of adsorbed AP into small molecules. The optimized complexes of the AP molecule on TiO₂ surfaces were very stable, indicating strong covalent and hydrogen bonding interactions, leading to highly energetic adsorption reactions. The calculated energy of adsorption (ΔE_{ads}) ranged from -120.23 to -301.98 kJ/mol, with highly exergonic calculated Gibbs free energy (ΔG_{ads}) of reaction, and highly exothermic enthalpy of reaction (ΔH_{ads}). The decomposition of adsorbed AP was also found to have very negative ΔE_{dec} values between -199.08 and -380.73 kJ/mol. The values of ΔG_{dec} and ΔH_{dec} reveal exergonic and exothermic reactions. The adsorption of AP on TiO₂ surfaces anticipates the heat release of decomposition, in agreement with experimental results. The most common anatase surface, (101), was predicted to be more reactive for AP decomposition than the most stable rutile surface, (1 1 0), which was confirmed by experiments. DFT calculations show the mechanism for activation of the two TiO_2 polymorphs is entropy driven.

KEYWORDS

ammonium perchlorate, anatase, DFT calculations, energetic materials, rutile

INTRODUCTION 1

Titanium dioxide (TiO₂) is one of the most widely investigated surfaces in photocatalysis and semi-conductor sciences,¹⁻³ with applications ranging from water dissociation,⁴ bioimplants,⁵ pigments,⁶ sunscreen,⁷ and gas sensing.⁸ The most common stable TiO₂ polymorph is rutile, and its predominant surface is along the plane (1 1 0).^{4,9,10} Another polymorph of interest is anatase, and its most common surface is (101).¹⁰ Although most of the studies on adsorption at the TiO₂ surface involve the dissociation of molecules

such as water, carbon monoxide, methanol, and ethanol through photocatalysis,¹¹ TiO₂ has been found to improve thermally driven processes by reducing the reaction temperature.

Qi et al.¹² used Pt and Pt-Cu supported on TiO₂ to promote lowtemperature combustion of toluene. By using TiO₂ doped with 0.5 wt % Pt, 80% of all toluene intake decomposed at 100°C, while the addition of 0.4 wt% Pt and 0.1 wt% Cu reduced the temperature even further, to only 77°C. Reduced temperature was partly attributed to the photoexcitation properties of TiO₂ since the photo-thermal catalysis mechanism offers more pathways for excitation compared

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with thermal-catalysis alone. The highly adaptable oxidation states of Ti atoms in titanium oxides were explored by Hao et al.¹³ Their goal was to use titanium oxides to stabilize the highly reactive Pt⁰ thereby reducing oxidation during combustion and enabling Pt⁰ to remain active for catalysis. As a result, the synthesized Pt@TiO_x/TiO₂ catalyst was successful at reducing ignition of C_3H_8 and C_3H_6 to temperatures below 300°C.

In similar studies, the addition of TiO₂ nanoparticles to a waterin-diesel emulsion fuel improved combustion efficiency by up to 5.65% while decreasing the emission of carbon monoxide and unburned hydrocarbon.¹⁴ A thermodynamic enhancement was also observed when TiO₂ nanoparticles were added to coal-water fuel, increasing its thermal conductivity by 9%-17% while decreasing the heat capacity by 12%-23%, leading to a reduction of 20%-22% in the ignition delay, and of 15% in the fuel droplet burning time.¹⁵

Another application of TiO₂ is in the field of energetic materials to accelerate the decomposition of ammonium perchlorate (NH_4CIO_4 , AP).¹⁶⁻¹⁸ an oxidizing salt used in propulsion applications.¹⁹⁻²¹ Ammonium perchlorate (AP) has a complex, multi-stage decomposition process, which starts with endothermic gasification, producing NH₃ and HClO₄. Further decomposition into smaller molecular products such as N₂, Cl₂, H₂O, and O₂ produces heat and provides oxygen to react with fuels.²² The initial endothermic gasification is the bottleneck for increasing AP reaction rates due to its highly endothermic balance. Reducing the energy required for the initial AP decomposition stage and increasing AP gas generation rate will consequently increase the burn rate of the propellant formulation.¹⁷ Controlling the kinetics associated with AP decomposition motivates studies on the exothermic interactions of AP with burn rate modifiers designed to increase the AP decomposition rate.²³ Burn rate modifiers investigated include aluminum iodate hexahydrate iodic acid,²⁴ and several metal oxides including titanium oxide,16-18,23 cupric oxide,25 ferric oxide,²⁶ nickel oxide,²⁷ and cobalt oxide.²⁶

Nanoparticles naturally have a high specific surface area that aids surface interface reactions. Because TiO₂ particle surfaces promote thermal decomposition in both low^{12,13} and high^{14,15} temperature processes, TiO₂ nanoparticles are an ideal burn rate modifier to promote decomposition for AP.¹⁶⁻¹⁸ The size effect of TiO₂ particles on the decomposition of AP was first analyzed by Fujimura and Miyake.¹⁶ They showed smaller TiO₂ particles with higher specific surface area leads to lower decomposition temperatures. Elbasuney and Yehia¹⁷ encapsulated AP particles with 1% wt. TiO₂. They revealed a reduction of endothermic energy required for AP decomposition from 102.5 to 20.8 J/g with the addition of encapsulated particles. Reduced energy required for decomposition was accompanied by increased total heat release of 18%, that is, from 835.5 J/g in two steps to a single 990.1 J/g step. Other researchers also explored composite particles for AP decomposition. For example, TiO_2 was combined with graphitic carbon nitride ($TiO_2/g-C_3N_4$) to form a high specific area mesoporous structure, then added to AP at a 2 wt% concentration.¹⁸ The result was a 26°C AP reduction of decomposition temperature, and 44% reduction of the activation energy.

The molecular level interactions between TiO₂ and AP are not well understood. The studies described above emphasize catalysis as a mechanism for TiO₂ activation of AP decomposition. Details of the catalytic effect merit further investigation. The objective of this study is to use density functional theory (DFT) calculations to investigate the effects of TiO₂ in the decomposition of AP. The interaction of AP was analyzed with different TiO2 surfaces represented by cluster models using DFT calculations. The models represent the most common surfaces of rutile ((1 1 0), (0 0 1), and (1 0 0)), and anatase ((1 0 1) and (0 0 1)). Two distinct reactions were investigated: (1) adsorption of AP at the TiO₂ surfaces, followed by (2) AP decomposition. The analysis of the optimized complexes explains the stability of AP-TiO₂ interactions, with detailed covalent and van der Waals bonds. For each complex, the adsorption energy (ΔE_{ads}) was calculated, and the thermal effects were evaluated through computed Gibbs free energy (ΔG_{ads}) and enthalpy (ΔH_{ads}) of reaction. All data provide insight about the thermal balance of reactions at each surface. Finally, the comparison between the different TiO₂ surfaces enable identification of the reaction mechanisms that promote AP decomposition. To supplement the modeling study, mixtures of AP containing 5 wt% rutile or 5 wt% anatase nanoparticles were investigated through thermogravimetric analysis in comparison with pure AP. The experimental results provide support for the modeling and simulations.

2 **METHODS**

2.1 **Computational details**

First principles calculations were performed at the density functional theory (DFT) level using Perdew-Burke-Ernzerhof (PBE) functional,²⁸ as implemented in the Turbomole package.²⁹ The initial calculations were performed using a split valence basis set with polarization functions (not for hydrogen) (SV(P)).³⁰ A larger triple-zeta valence polarization (TZVP) basis set was then used for the final calculations. The larger basis set reduces superposition error of investigated complexes as shown by Schäfer et al.³¹ for compound molecules. Dispersion interactions were considered by employing a modified version of the general empirical dispersion correction D3 proposed by Grimme.³² To maintain the basic structural features of the TiO₂ surface, the Cartesian coordinates of the titanium atoms were held fixed during all calculations. The stationary points were analyzed through numerical frequency computations, revealing no imaginary frequencies for the investigated systems.

Calculations performed in this work used surface cluster models of rutile and anatase. The cluster models were derived from known experimental bulk structures by slicing them along specified crystallographic planes, thereby exposing low faced surfaces. In this way, the periodic slab models with the pristine surfaces (0 0 1) and (1 0 1) of anatase and (1 1 0), (0 0 1), and (1 0 0) of rutile were created. Slicing was done in a manner to create topmost surface termination as proposed in previous literature.³³ Subsequently, clusters were extracted from these periodic slab models, shaped roughly like a plate with a

diameter of 16–18 Å. All dangling Ti–O bonds on the edges and surface oxygen atoms were saturated by hydrogen atoms to provide the overall neutral charge of the final cluster. Hydrogen linked to oxygen was considered as H⁺; if linked to titanium, it was considered as H⁻. As a result, the clusters of the rutile (0 0 1), (1 0 0), and (1 1 0) surfaces comprised 135, 192, and 345 atoms, and of the anatase (0 0 1) and (1 0 1) surfaces contained 240 and 185 atoms. Cluster models are shown in Figure S1a–e in Supporting Information (SI).

The interactions between AP and TiO_2 surfaces were modeled in two steps: (a) adsorption of AP molecule (NH₄ClO₄) at the TiO₂ surface (Equation 1), and (b) decomposition of adsorbed AP, producing Cl₂, N₂, H₂O, and O₂ (Equation 2).

$$\mathsf{NH}_4\mathsf{CIO}_4 + \mathsf{TiO}_2 \to \mathsf{AP} - \mathsf{TiO}_2, \tag{1}$$

$$AP - TiO_2 \rightarrow TiO_2 + 0.5CI_2 + 0.5N_2 + 2H_2O + O_2. \tag{2}$$

The energetics of these reactions (i.e., Equations 1 and 2) were evaluated using balances of energy (ΔE), enthalpy (ΔH) and Gibbs free energy (ΔG). The ΔH and ΔG interactions were calculated for the gas phase using the standard harmonic oscillator/rigid rotator/ideal gas approximation. The number of moles (*N*), ideal gas constant (*R*) and absolute temperature (*T*) were included in the calculations of ΔE , ΔH , and ΔG , (Equation 2) to account for the energy of gaseous reactants. Subscripts "ads" and "dec" correspond to adsorption (Equation 1), and decomposition (Equation 2). The thermochemistry calculations were performed at temperatures of 200–500°C, for example, the range AP was experimentally observed to decompose.

2.2 | Experimental methods

The AP powder, rutile, and anatase TiO_2 nanoparticles were provided by the Naval Air Warfare Center, Weapons Division, China Lake. A Hitachi S-4700 Field Emission Scanning Electron Microscope (SEM) was used to analyze AP powders. Figure 1 shows a rounded morphology with size ranging from roughly 100–200 µm. A Hitachi H-9500 Transmission Electron Microscope (TEM) was used to analyze TiO_2 nanoparticles and confirm their morphology (see Figure 2). Phase was further confirmed using X-Ray Diffraction (XRD) performed using a Rigaku Miniflex II powder diffractometer and results are shown in CHEMISTRY WILEY 3

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Figure S2 of the SI. The composition of each sample was confirmed using Bragg–Brentano geometry (Figure S2).

Brunauer–Emmett–Teller (BET) surface area measurements were conducted using a Quantachrome Autosorb iQ-MP micropore analyzer through physisorption of nitrogen onto both rutile and anatase TiO_2 nanoparticles. The specific surface areas of anatase and rutile samples were 88 and 25 m²/g, respectively.

The AP and 5 wt% of rutile or anatase powder by mass were mixed in a Retsch Cryomill for 20 min at 25 Hz to achieve homogenous mixing. The SEM with Energy Dispersive Spectroscopy (EDS) using a Zeiss crossbeam 540 equipped with Oxford EDS system was used to analyze the mixtures. Figure 3 shows a representative mixture image with anatase particles (orange) coating the AP particles (yellow).

Thermogravimetric Analyses (TGA) were conducted using a NETZSCH STA 449 F3 Jupiter. Samples were 2 mg of pure AP or AP + 5 wt% anatase or rutile mixtures. Experiments were performed in open crucibles in an inert argon environment with 100 mL/min gas flow. Samples were heated at 10°C/min from room temperature up to \sim 500°C while mass change was measured. The TGA mass calibration was performed using calcium oxalate and within 0.5% of reference values. All experiments were performed in triplicate.

3 | RESULTS

3.1 | AP and AP@TiO₂

The main three rutile surfaces exhibit different patterns and coordination of alternating Ti and O surface atoms. The coordination of surface Ti atoms varies from 4 to 6, while surface oxygen atoms range from 2 to 3 in coordination. Specifically, the (0 0 1) surface features 4-coordinated Ti atoms and doubly coordinated O atoms, the (1 0 0) surface presents 5-coordinated Ti atoms and doubly coordinated O atoms, and the (1 1 0) surface displays 5- and 6-coordinated Ti atoms, and 2- and 4-coordinated O atoms. In contrast, both anatase surfaces (i.e., (0 0 1) and (1 0 1)) exclusively showcase one type of 5-coordinated Ti atoms, and one type of doubly coordinated O atoms. However, these two surfaces differ in the arrangements of Ti and O surface atoms. The relaxed structures of all clusters representing 3 rutile and 2 anatase surfaces are displayed in the SI (Figure S1a-e).



FIGURE 1 SEM images of AP powder at (A) 500 µm and (B) 50 µm scales, as indicated in the images.

Note that H atoms visible in the figures are those coming from the saturation of dangling bonds at the edges of the clusters to achieve the charge neutral clusters.

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The NH₄ClO₄ molecule consists of an ionic pair of NH₄⁺ and ClO₄⁻ ions. After a proton transfer from NH₄⁺ to ClO₄⁻, a molecular pair NH₃ + HClO₄ is formed. This proton transfer is the first step of AP dissociation, which involves a phase change from solid to gaseous phase. The geometries of the isolated (NH₄ClO₄) and (NH₃ + HClO₄) species optimized in the gas phase are shown in Figure 4. The

NH₄ClO₄ molecule is held together by electrostatic interaction between NH₄⁺ and ClO₄⁻ ions and by two hydrogen bonds of lengths 1.619 and 1.622 Å, with a N···Cl distance of 3.142 Å. The NH₃···HClO₄ molecular pair has a single strong hydrogen bond (1.480 Å) between NH₃ and HClO₄, which stabilizes the molecular compound, resulting in a N···Cl distance of 3.368 Å. The interaction energy between HClO₄ and NH₃ in the NH₃ + HClO₄ molecular pair is 79.7 kJ/mol. This molecular pair is also 4.81 kJ/mol more stable than the isolated NH₄ClO₄ molecule. Note that this result was





FIGURE 2 TEM images of (A, B) rutile TiO_2 and (C, D) anatase TiO_2 showing nano-sized particles in both samples.

FIGURE 3 Two SEM images with EDS colorizing of (A) chlorine (yellow) and (B) titanium in anatase AP + 5% TiO₂ mixtures (orange).

achieved using large basis set of the def2-TZVP^{34,35} quality, different from the TZVP basis set used for large cluster models.

The adsorption of an AP molecule (NH₄ClO₄) is optimized at the different TiO₂ surfaces, presenting different sets of covalent and non-covalent interactions. The details of the optimized structure of AP at the rutile (0 0 1) surface (AP@(0 0 1)R) are displayed in Figure 5A. The whole structure is shown in Figure S3a of the SI. The initial configuration featured monodentate binding of CIO_4^- to the surface Ti atom. During the optimization, a bidentate mononuclear binding of CIO_4^- was formed, with two strong bonds between CIO_4^- and a titanium atom at the surface with lengths 2.166 and 2.186 Å. In the pristine surface, the titanium atom is undercoordinated (4-fold coordination) and the oxygen atoms of the AP anion complete the original titanium 6-fold coordination existing in the TiO_2 crystal. The NH_4^+ cation, on the other hand, formed a noncovalent interaction with the surface being connected with three different surface oxygen atoms through strong-to-medium hydrogen bonds of 1.679, 1.831, and 1.989 Å, respectively. The N…Cl distance is 4.179 Å (Table 1). Owing to the strong interactions, the formed complex is very stable with ΔE_{ads} of -301.89 kJ/mol (Table 1). The surface topology of Ti atoms also allows a possibility of another configuration, in which ClO_4^- anion can bind to the surface as a bidentate binuclear complex (binding to two neighboring Ti atoms). The geometry optimization of this complex resulted in a slightly more stable structure (Figure 5B) compared to the bidentate mononuclear complex (Figure 5A) with an ΔE_{ads} of -323.86 kJ/mol (Table 1). The complete structure is shown in the SI (Figure S3b). In this bidentate binuclear complex, CIO_4^- is bound to the surface with Ti–O bonds of 2.069 and 2.159 Å, and to the neighboring



FIGURE 4 PBE-D3/def2-TZVP optimized configurations of (A) NH₄ClO₄ ionic pair, and (B) NH₃ + HClO₄ molecular pair, both in gas phase. Atoms color code: Cl–green, N–gray, O–red, and H–light pink.

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 NH_4^+ cation through a weak hydrogen bond of 2.058 Å. NH_4^+ is linked to the surface through two strong hydrogen bonds of 1.502 and 1.596 Å, respectively.

Adsorption of AP on the rutile (1 0 0) surface (AP@(1 0 0)R), Figure 6 (complete structure in Figure S3c of SI) is less stable than on the (0 0 1) surface with adsorption energy of -120.23 kJ/mol (Table 1). The (1 0 0) surface has a different arrangement of surface Ti and O atoms compared to the (0 0 1) surface. Surface Ti atoms are 5-coordinated, arranged in rows, which allows for mono- or bidentate (binuclear) binding of ClO₄⁻.The initial monodentate configuration transformed in the more stable bidentate binuclear complex during the optimization, as shown in Figure 6. Two covalent bonds between the ClO₄⁻ and the surface were formed with lengths of 2.168 and 2.224 Å, similar to the rutile (0 0 1) complex (Figure 5). The NH₄⁺ ion formed two hydrogen bonds, one with an oxygen of ClO₄⁻ anion that

TABLE 1 Calculated ΔE_{ads} and ΔE_{dec} (kJ/mol) of AP at different TiO₂ surfaces, and N···Cl distance (Å).

Surface	$\Delta \pmb{E}_{ads}$	$\Delta \boldsymbol{E}_{ extsf{dec}}$	N⊷Cl
(a) Rutile (0 0 1)	-301.89	-199.08	4.179
(b) Rutile (0 0 1)	-323.86	-221.06	3.950
Rutile (1 0 0)	-120.23	-380.73	3.816
Rutile (1 1 0)	-219.84	-281.13	3.665
Anatase (0 0 1)	-148.95	-352.02	3.455
Anatase (1 0 1)	-202.81	-298.16	3.600



FIGURE 6 Optimized configuration of AP adsorption at rutile (1 0 0) surface (AP@(1 0 0)R) showing selected bond lengths. Atoms color code: Ti-blue, Cl-green, N-gray, O-red, and H-light pink.



FIGURE 5 Optimized configurations of AP adsorption at rutile (0 0 1) surface (AP@(0 0 1)R) showing selected bond lengths. (A) Bidentate mononuclear, and (B) bidentate binuclear binding. Atoms color code: Cl–green, N–gray, O–red, and H–light pink.



FIGURE 7 Optimized configuration of AP adsorption at rutile (1 1 0) surface (AP@(1 1 0)R) showing selected bond lengths. Atoms color code: Ti-blue, Cl-green, N-gray, O-red, and H-light pink.



FIGURE 8 Optimized configuration of AP adsorption at anatase (0 0 1) surface (AP@(0 0 1)A) showing selected bond lengths. Atoms color code: Ti-blue, Cl-green, N-gray, O-red, and H-light pink.

also is bonded to the surface by a hydrogen bond of 1.773 Å, and another hydrogen bond with the surface of 1.654 Å. The N \cdots Cl distance at surface (1 0 0) is shorter than in the surface (0 0 1), of 3.816 Å (Table 1).

The AP adsorption on the rutile (1 1 0) surface (AP@(1 1 0)R) is shown in Figure 7 (complete structure is shown in Figure S3d of SI). This surface has active sites for AP adsorption represented by 5-fold coordinated Ti atoms and bridging O atoms. Additionally, two initial configurations were optimized for this surface, similar to the (100) surface (mono- and bidentate binuclear complexes). The geometry optimization of the monodentate complex resulted in the formation of the bidentate binuclear configuration, as shown in Figure 7. In this complex, two covalent bonds are observed, in addition to three hydrogen bond interactions. The AP ions are connected through a 1.849 Å hydrogen bond. The NH₄⁺ ion is connected to two different oxygen atoms at the surface, with distances of 1.674 and 1.882 Å. The $ClO_4^$ ion is connected to surface Ti atoms with bonds of lengths 2.248 and 2.290 Å. The N···Cl distance is 3.665 Å and the adsorption energy is -219.84 kJ/mol (Table 1). The adsorption process on the rutile (1 1 0) surface produces a more stable complex than the (1 0 0) surface, but less stable than the (0 0 1) surface.



FIGURE 9 Optimized configuration of AP adsorption at anatase (1 0 1) surface (AP@(1 0 1)A) showing selected bond lengths. Atoms color code: Ti-blue, Cl-green, N-gray, O-red, and H-light pink.

In addition to rutile, two anatase surfaces were studied. These two surfaces also exhibited mono- and/or bidentate binding of CIO_4^- anion. In both cases, bidentate binding changed to the monodentate configuration during the geometry optimization, which are discussed in the following text. The complete structures of AP adsorbed on the (0 0 1) and (1 0 1) anatase surfaces are shown in Figure S3e,f of the SI.

AP adsorption at the anatase (0 0 1) (AP@(0 0 1)A) displayed two hydrogen bonds (Figure 8) linking both AP ions (1.562 Å) and NH_4^+ to the surface (1.789 Å) with N···Cl distance of 3.455 Å. The adsorption energy of this complex is -148.95 kJ/mol (Table 1).

Adsorption of AP at the pristine anatase (1 0 1) surface (AP@ (1 0 1)A) is characterized by the separation of the two ions with N···Cl distance of 3.600 Å (Table 1, Figure 9). The ClO₄⁻ anion is bound to the 5-coordinated surface Ti atom forming a Ti-O bond of length 2.176 Å and to NH₄⁺ through a 2.061 Å hydrogen bond. The NH₄⁺ cation formed hydrogen bonds with the surface oxygen atoms that are weaker in comparison to the (0 0 1) surface. The adsorption results in an ΔE_{ads} of -202.81 kJ/mol (Table 1) and a complex more stable than the (0 0 1) surface.

The N···Cl distances in all complexes (i.e., Figures 5-9, Table 1) are larger than 3.220 and 3.449 Å in the isolated molecule NH_4ClO_4 or molecular pair $NH_3 + HClO_4$ in Figure 4. The larger N···Cl distances indicate that AP is adsorbed at the rutile and anatase surfaces as separated NH_4^+ and ClO_4^- ions are mainly due to surface arrangement of Ti and O atoms. Indeed, these two ions are still in contact by hydrogen bonding.

3.2 | Thermodynamics of adsorption and decomposition of AP

Thermodynamic data for adsorption reactions (i.e., Equation 1) are shown in Figure 10 and calculated for a temperature range from 200 to 500°C, covering the experimentally observed temperature range of the AP decomposition reaction.³⁶ Note that the

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FIGURE 10 Calculated (A) ΔG_{ads} and (B) ΔH_{ads} for AP adsorption at different TiO₂ surfaces.

thermodynamic data for the rutile (0 0 1) surface are discussed for the bidentate mononuclear configuration (Figure 5A), as the results for the bidentate binuclear configuration were very similar. The calculated values of ΔG_{ads} (Figure 10A) indicate stable adsorptions throughout the temperature range for all but one surface (i.e., Rutile (1 0 0)) at temperatures above 250°C. The most exergonic adsorption occurs at rutile (0 0 1), with ΔG_{ads} ranging from -192 to -139 kJ/mol. The ΔG_{ads} of rutile (1 1 0) ranges from -114 and -62 kJ/mol. In contrast, thermodynamic instability sets is for the rutile (0 0 1) surface at approximately 250°C when ΔG_{ads} changes from negative to positive values.

The two anatase surfaces have similar ΔG_{ads} throughout the entire temperature range. Anatase (1 0 1) has ΔG_{ads} of -106 kJ/mol at 200°C while anatase (0 0 1) is -89 kJ/mol at this temperature. Both surfaces experience an increase in ΔG_{ads} at higher temperatures, with anatase (1 0 1) showing a more rapid increase. Both surfaces have ΔG_{ads} around -60 kJ/mol at 500°C. The adsorption complex of the most common surface of rutile, (1 1 0), exhibits a similar trend of ΔG_{ads} , as AP adsorption complexes at both anatase surface (Figure 10A).

The adsorption of AP at all TiO₂ surfaces was highly exothermic, evidenced by notably negative values of calculated ΔH_{ads} (Figure 10B). There exists a significant difference in ΔH_{ads} for three rutile surfaces reflecting an observed difference in ΔE_{ads} (Table 1). Particularly, the adsorption at rutile (0 0 1) surface releases considerable heat, with ΔH_{ads} equal to -280 kJ/mol at 200°C followed by the rutile (1 1 0) surface with ΔH_{ads} equal to -200 kJ/mol at 200°C . The smallest ΔH_{ads} value, although still considerable, is observed for the AP complex at the rutile (1 0 0) surface (-98 to -90 kJ/mol). On the other hand, the complexes of anatase (0 0 1) and (1 0 1) surfaces have ΔH_{ads} of -132 and -184 kJ/mol at 200°C respectively, and -120 and -176 kJ/mol at 500°C, respectively. The changes in ΔH_{ads} with respect to increasing temperature are minimal, reaching approximately 10 kJ/mol at 500°C for all five surface complexes. Therefore, both TiO₂ polymorphs are expected to release significant heat when exposed to AP through adsorption reactions, with rutile (0 0 1) potentially providing the highest exothermicity and the most likely burn rate modifier candidate for inducing accelerated AP decomposition. It is important to note a considerable difference between changes in Gibbs free energy (ΔG) and enthalpy (ΔH), indicating that the entropy contribution ($T\Delta S$) is considerable, thus characterizing the analyzed reactions as entropy-driven reactions.

The decomposition of adsorbed AP (Equation 2) is energetically favorable for all surfaces, with negative values of ΔE_{dec} (Table 1). The released energy of the reaction follows the trend observed for the adsorption. The largest amount is found for the weakest adsorption complex (AP@(100)R, -380.73 kJ/mol), followed by the AP complex at the anatase (0 0 1) surface (-366.89 kJ/mol). The strongest ΔE_{dec} is from AP@(100)R, -380.73 kJ/mol, followed by the AP@(0 0 1)A, with -366.89 kJ/mol. The most common rutile surface (1 1 0) has ΔE_{dec} of -323.44 kJ/mol, while the most common anatase surface is (1 0 1) with ΔE_{dec} of -298.16 kJ/mol. Finally, the decomposition reaction for the strongest adsorption complexes AP@(0 0 1)R released the smallest energy of -199.08/-221.06 kJ/mol, which is still guite large amount. Higher decomposition energy is inherently associated with lower adsorption energy, and visa-versa. An ideal burn rate modifier would likely have a higher adsorption energy because the adsorption reaction is the first step in the sequence of elementary decomposition reactions responsible for accelerating the rate of the overall reaction.

The thermodynamic calculations revealed exergonic and exothermic decomposition reactions (Equation 2) at all TiO₂ surfaces (Figure 11A). The trends of ΔG_{dec} , and ΔH_{dec} showed a decrease with the increasing temperature, indicating that increasing temperature accelerated the AP decomposition process The decomposition of the most stable AP@(0 0 1)R complex has ΔG_{dec} of -535 kJ/mol at 200°C, decreasing to -725 kJ/mol at 500°C. Both anatase complexes have similar decomposition with ΔG_{dec} , equal -639 and -622 kJ/mol at 200°C for AP@(0 0 1)A and AP@(1 0 1) respectively, decreasing to around -800 kJ/mol at 500°C. The trend of ΔG_{dec} for AP@(1 1 0)R complex is similar to AP complexes at anatase surfaces (Figure 11A). The AP decomposition of the weakest adsorption complex, AP@ (1 0 0)R is the most exergonic, with ΔG_{dec} of -719 kJ/mol at 200°C and -911 kJ/mol at 500°C.

Calculated ΔH_{dec} (Equation 2) is displayed in Figure 11B and shows similar behavior with respect to increasing temperature as



FIGURE 11 Calculated (A) ΔG_{dec} and (B) ΔH_{dec} for AP adsorption at different TiO₂ surfaces.



FIGURE 12 Average DTG-measured mass loss rates of AP, AP $+ 5\% 25 \text{ m}^2/\text{g}$ rutile TiO₂ and AP $+ 5\% 88 \text{ m}^2/\text{g}$ anatase TiO₂.

enthalpy of adsorption. Only a small change is observed with increasing temperature for all complexes. The least exothermic reaction is the decomposition of AP@(0 0 1)R with ΔH_{dec} ranging from -232 and -242 kJ/mol. AP@(1 1 0)R promotes a ΔH_{dec} of -312 kJ/mol at 200°C, shifting down 11 kJ/mol when reaching 500°C. The decomposition of AP@(1 0 1)A has ΔH_{dec} of -328 and -338 kJ/mol at 200 and 500°C respectively. At 200°C, the AP decomposition on the anatase (0 0 1) surface exhibits ΔH_{dec} of -380 kJ/mol and shifts to -394 kJ/mol at 500°C, while decomposition of AP@(1 0 0)R, the most exothermic with ΔH_{dec} of -414 and -424 kJ/mol at the same temperature. It is also observed in decomposition reactions a significant difference between reaction Gibbs free energy (ΔG_{dec}) and reaction enthalpy (ΔH_{dec}), signifying that these reactions are entropy-driven reactions.

3.3 | Experimental

The derivative of the TGA data (i.e., DTG) for the decomposition of AP, AP + 5 wt% 25 m^2/g rutile, and AP + 5 wt% 88 m^2/g anatase are

shown in Figure 12. The decomposition of AP and AP + TiO₂ begins at ~275°C, intensifying rapidly until about 290°C when the mass loss approaches 4%/min. The initial stage of mass loss results in porosity formed at the AP particle surface. Pores trap gaseous species that release heat upon reaction to provide energy to the decomposition process.²⁴

When the porous surface reaches a maximum surface area, the first peak mass loss rate (PMR) is achieved corresponding to the first DTG peak in the region of \sim 290°C. Mass decomposition then slows before increasing at about 325°C corresponding with a shift to gasification mass loss without gas trapping.

For pure AP (black line in Figure 12), decomposition increases at an accelerated rate after 325°C until reaching the second peak mass loss rate (PMR) of 17%/min at 402°C. Shortly after reaching this PMR, the mass loss rate decreases, getting close to zero around 425°C. The introduction of 5 wt% rutile nanoparticles reduces the intensity of the first decomposition peak (~290°C) but increases the second PMR to 17.84%/min and lowers the PMR temperature to 396°C (from 402°C for pure AP). With the addition of 5 wt% anatase, the second PMR increases to 18.74%/min at a further reduced temperature of 394°C. While DFT calculations predict rutile (0 0 1) may incite more exothermic adsorption reactions and thereby increase the PMR, experimental results in Figure 12 indicate both polymorphs increase the PMR over pure AP in a similar way. It is noted that the higher specific surface area associated with anatase may play a more effective role increasing the exothermic adsorption reactions as evident in simulations (Table 1).

4 | DISCUSSION

The adsorption of AP molecules on cluster models of rutile (0 0 1), (1 0 0) and (1 1 0), and anatase (0 0 1) and (1 0 1) surfaces revealed strong sets of covalent and non-covalent interactions. Surface charges help stabilize the NH₄⁺ and ClO₄⁻ ions, leading to highly stable chemisorbed complexes. The most stable AP adsorption complex was found for rutile (0 0 1) surface, with ΔE_{ads} of -301.89 kJ/mol, followed by (1 1 0) with -219.84 kJ/mol, and finally the (1 0 0) surface

with -120.23 kJ/mol, which can be considered the least reactive surface. The most stable adsorption complex was found for the anatase (101) surface with ΔE_{ads} of -202.81 kJ/mol, therefore the most reactive, compared with ΔE_{ads} of -148.95 for (0 0 1) less stable, but still strong adsorption complex. The Gibbs free energy (ΔG_{ads}) and enthalpy (ΔH_{ads}) of formation calculated at temperatures from 200 to 500°C show rutile (001) is the most exergonic ΔG_{ads} of -192 through -139 kJ/mol. The rutile (100) surface is -8 kJ/mol at 200°C, but is upshifted at higher temperature, becoming positive around 250°C and reaching 47 kJ/mol at 500°C. The most common rutile surface, (1 1 0), has ΔG_{ads} of -114 kJ/mol at 200°C, and becomes less exergonic at higher temperatures, ending in -62 kJ/mol at 500°C. The most common anatase surface, (1 0 1), has ΔG_{ads} of -106 kJ/mol at 200°C, and -58 kJ/mol at 500°C, while the (0 0 1) surface has ΔG_{ads} ranging from -89 and -65 kJ/mol at the same temperature range. The calculated ΔH_{ads} revealed exothermic adsorptions for all cases, including rutile (1 0 0), which is endergonic. The ΔH_{ads} for AP@(0 0 1)R ranges from -280 and -272 kJ/mol in the temperature range, and between -98 and -90 kJ/mol for AP@(1 0 0)R. The ΔH_{ads} at rutile (1 1 0) ranges from -200 and -191 kJ/mol. The anatase surfaces (0 0 1) and (1 0 1) have ΔH_{ads} of -132 and -184 kJ/ mol at 200°C, and -120 and -176 kJ/mol at 500°C. Adsorption modeling demonstrates active sites at TiO₂ surfaces stabilize AP molecules and promote spontaneous reactions that release heat. The heat released from the absorption reactions contribute toward further decomposition. The adsorption reactions are the first step in AP decomposition and the highly exothermic adsorption reactions seen here are responsible for accelerating AP decomposition rate (Figure 12).

The decomposition of adsorbed AP (i.e., Equation 2) is also energetically favorable, with negative decomposition energy (ΔE_{dec}) for all surfaces (Table 1). The AP@(100)R decomposes with ΔE_{dec} of -380.73 kJ/mol, followed by AP@(0 0 1)A of -352.02 kJ/mol. The most common rutile surface (1 1 0) exhibits ΔE_{dec} of -281.13 kJ/mol, while the most common anatase surface (101) has ΔE_{dec} of -298.16 kJ/mol. Finally, the decomposition from AP@(0 0 1)R has ΔE_{dec} of -199.08 kJ/mol. The ΔG_{dec} was calculated to range from -535 and -719 kJ/mol at 200°C, becoming even more exergonic at 500°C, ranging from -725 and -911 kJ/mol. The calculated ΔH_{dec} indicates very exothermic reactions, with values varying around -237 kJ/mol for AP@(0 0 1)R, -332 kJ/mol for AP@(1 0 1)A, -317 kJ/mol for AP@(1 1 0)R, -387 kJ/mol for AP@(0 0 1)A, and -418 kJ/mol for AP@(1 0 0)R. The results indicate that the spontaneous and exothermic interactions between decomposing AP and the TiO₂ surfaces promote heat release that further accelerate gas generation and burn rates.

Experimental data support the modeling and simulation calculations. The TGA data were analyzed for changes in mass loss. Results indicated that the addition of 5 wt% TiO₂ nanoparticles to AP reduces the temperature of the peak mass loss rate (PMR) and increases the PMR of AP decomposition. While the experiments were performed for the two phases of TiO₂ examined numerically, the two samples have a measurable difference in specific surface area. The two variables (surface area and phase) make a direct comparison between modeling and experiments challenging. However, the experiments under equilibrium conditions show that rutile and anatase have a similar effect on increasing the PMR for AP decomposition. Specifically, 5 wt% of rutile or anatase reduces the temperature of the PMR by about 10°C and increases the PMR by about 1%.

Beyond experiments performed here, DTG data from Reid et al.³⁶ compared the decomposition of AP with AP + 1 wt% rutile (with a specific surface area of $3.5 \text{ m}^2/\text{g}$) and AP + 1 wt% anatase (with a specific surface area of $35 \text{ m}^2/\text{g}$). Similar trends to Figure 12 were observed, that is, the PMR was increased with the addition of TiO₂, that is, from 17.15%/min for AP, to 21.86% for AP + rutile, and to 20.49%/min for AP + anatase. The PMR temperature of AP was 439.76°C, while for AP + rutile was 442.17°C and for AP + anatase was 414.46°C.

The modeling results (Table 1) indicate that the surface terminations of the varied rutile and anatase surfaces promote exothermic adsorption and further decomposition of AP. The exothermic energy derived from Equations (1) and (2) incite accelerated AP decomposition evidenced in Figure 12 and the results from Reid et al.³⁶ (reproduced in Figure S4 of SI). However, in practice, tuning the burn rate modifier for the optimized surface (i.e., (0 0 1) vs. (1 0 1)) may be less practical than generally increasing the burn rate modifier specific surface area. By increasing surface contact between AP and the titania, greater exothermicity can be produced to offset the energy required to initiate AP decomposition. This study shows the mechanism for TiO₂ catalysis in AP decomposition is entropydriven.

5 | CONCLUSIONS

The interaction between ammonium perchlorate (NH₄ClO₄, AP) and different titania (TiO₂) surfaces was investigated using density functional theory (DFT) calculations supplemented by thermogravimetric analysis (TGA) experiments. Two distinct reactions were investigated: (1) adsorption of AP at the TiO₂ surfaces, followed by (2) AP decomposition. Three rutile surfaces and two anatase surfaces were modeled with AP. In all cases the adsorption and decomposition reactions are exothermic and likely to occur. The rutile surfaces showed more thermodynamic variability while the two anatase surfaces produced similar results. Experiments complement the numerical models and demonstrate accelerated mass loss rates associated with the titania additives. Experimentally, differences between rutile and anatase may be a stronger function of specific surface area rather than the polymorphs themselves. All these results reveal the mechanism for activation of the burn rate modifier on AP decomposition occurs at electronic energy level promoting thermodynamics that increase reaction rates and are entropy-driven.

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DATA AVAILABILITY STATEMENT

-WILEY-

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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