



# Confined catalysis under two-dimensional materials

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**Confined microenvironments formed in heterogeneous catalysts have recently been recognized as equally important as catalytically active sites. Understanding the fundamentals of confined catalysis has become an important topic in heterogeneous catalysis. Well-defined 2D space between a catalyst surface and a 2D material overlayer provides an ideal microenvironment to explore the confined catalysis experimentally and theoretically. Using density functional theory calculations, we reveal that adsorption of atoms and molecules on a Pt(111) surface always has been weakened under monolayer graphene, which is attributed to the geometric constraint and confinement field in the 2D space between the graphene overlayer and the Pt(111) surface. A similar result has been found on Pt(110) and Pt(100) surfaces covered with graphene. The microenvironment created by coating a catalyst surface with 2D material overlayer can be used to modulate surface reactivity, which has been illustrated by optimizing oxygen reduction reaction activity on Pt(111) covered by various 2D materials. We demonstrate a concept of confined catalysis under 2D cover based on a weak van der Waals interaction between 2D material overlayers and underlying catalyst surfaces.**

confined catalysis | two-dimensional materials | density functional theory | oxygen reduction reaction | graphene

In heterogeneous catalysis, active sites have long been regarded as one of the most important concepts (1–3), and, recently, the heterogeneous catalysis community has started to recognize that microenvironment around the active site is equally important (4–9). The confined microenvironment on a heterogeneous catalyst can help to stabilize active sites and modulate chemistry at the sites, which has a significant effect on catalytic performance, similar to the role of spheroproteins in an enzyme (10). Hence, understanding fundamentals of confined catalysis has become an important topic in heterogeneous catalysis (11, 12).

Reactions in zero-dimensional (0D) nanocavities of microporous and mesoporous materials such as zeolites and metal–organic frameworks (MOFs) have shown enhanced catalytic performance (6, 9, 13–15). Theoretical investigations reveal that the spatially confined environment increases the molecular orbital energy and changes activity of the confined molecules, which have been recognized as the nest effect and quantum confinement effect (15, 16). In past decades, some experimental studies have demonstrated that carbon nanotubes (CNTs) strongly affect catalytic reactions occurring inside the nanotubes (7, 17, 18), and confined catalysis in 1D nanocavities has been theoretically addressed by studying molecule adsorption on metal clusters encapsulated in CNTs (19). As illustrated in Fig. 1, both 0D nanocavities in zeolites and 1D nanocavities in CNTs are spatially confined in three dimensions and two dimensions, respectively, in which simple and well-defined model systems are not feasible for both theoretical and experimental studies. Moreover, structural and compositional complexity in zeolites, MOFs, and curved nanotubes makes it challenging to understand the confinement effect at microscopic level.

Compared with the 0D and 1D systems, 2D confined microenvironments are much more structurally well defined (Fig. 1). The planar microenvironment walls can be appropriately modeled in theoretical calculations (20, 21) and investigated well by advanced characterization techniques, particularly surface science methods (22–26). The newly emerging 2D materials such as graphene (Gr) and

hexagonal boron nitride (h-BN) have been facilely supported on solid surfaces via surface deposition or transfer methods (27). Many experiments provide solid evidence that 2D spaces under the 2D material overlayers can act as stable nanoreactors for molecule adsorption and chemical reactions, which provide intriguing confined spaces for catalysis (22, 25, 28–31). A few sophisticated theoretical studies have been conducted to understand reactions under graphene covers in a quantitative way (32, 33). Overall, a 2D microenvironment formed under 2D material can provide an ideal and practical model system to explore the fundamentals of confined catalysis.

Herein, we choose graphene/Pt(111) surface as a model system to study confined catalysis via density functional theory (DFT) calculations. A general tendency for weakened adsorption of atoms and molecules in the 2D space between graphene and Pt surfaces has been clearly demonstrated, and catalytic reactions such as oxygen reduction reactions (ORR) occurring in the 2D microenvironment can be effectively tuned. We reveal that both the geometric constraint and the confinement field imposed by the 2D cover result in the observed confinement phenomena. More importantly, the confined catalysis concept can be applied to reactions between two opposite walls interacting with each other through weak van der Waals (vdW) force.

## Theoretical Models and Methods

A  $\sqrt{7} \times \sqrt{7}$  Pt(111) supercell with  $3 \times 3$  graphene overlayer was used for calculations (SI Appendix, Fig. S1). Adsorption energy ( $E_{ad}$ ) is characterized by the binding strength of atoms or molecules with the surface,

$$E_{ad} = [E_{total} - E_{surface} - n\mu] / n,$$

where  $E_{total}$  represents total energies of Gr/Pt(111) or Pt(111) surface with adsorbed atoms or molecules and  $E_{surface}$  represents

## Significance

Small spaces in nanoreactors may have big implications in chemistry, because the chemical nature of molecules and reactions within the nanospaces can be changed significantly due to the nanoconfinement effect. Two-dimensional (2D) nanoreactor formed under 2D materials can provide a well-defined model system to explore the confined catalysis. We demonstrate a general tendency for weakened surface adsorption under the confinement of graphene overlayer, illustrating the feasible modulation of surface reactions by placing a 2D cover on top of the surface. The developed concept “catalysis under cover” can be applied to reactions between two opposite 2D walls interacting with each other through van der Waals force, which helps to design high-performance nanocatalysts interfacing with 2D material overlayers.

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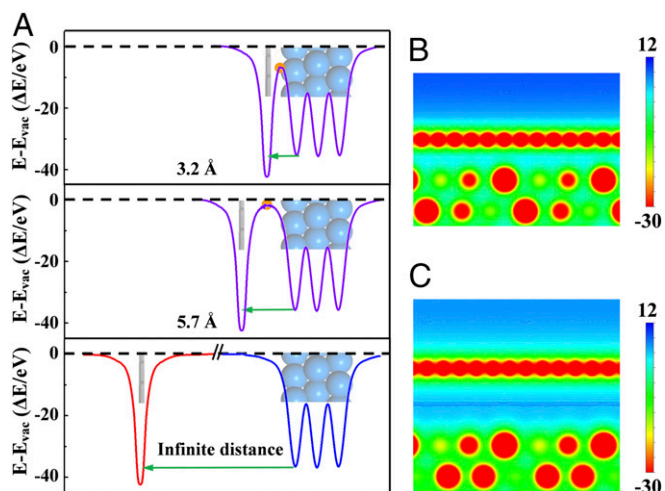
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**Fig. 3.** Confinement field in the 2D confined spaces. (A) The 1D local potential distribution between Gr and Pt(111) surface with  $d_{\text{Gr-Pt}}$  at 3.2 Å (Top), 5.7 Å (Middle), and infinity (Bottom). The potential at vacuum is set to zero. (Insets) The corresponding schematic atomic structures in the real space. (B and C) The maximum points between Gr and Pt(111) surface are shown in orange dots. The 2D potential distribution (side view) at the Gr/Pt(111) interfaces with  $d_{\text{Gr-Pt}}$  at (B) 3.2 and (C) 5.7 Å.

as a descriptor, we find a gradual increase of the potential energy with increasing  $d_{\text{Gr-Pt}}$  (SI Appendix, Fig. S2). It should be noted that  $d$ -band states of Pt atoms at the Gr/Pt(111) interface remain intact in comparison with the bare Pt(111) surface (SI Appendix, Fig. S3) because the localized  $d$ -bands are not susceptible to the weak interaction. The potential distribution in the 2D space is more related to decay of delocalized  $sp$  electronic states into vacuum that are affected by interaction with the Gr layer.

In the case where an atom or molecule is adsorbed into the 2D space, Gr cover is lifted up away from the surface, which enlarges  $d_{\text{Gr-Pt}}$ , increases the potential energy, and consequently makes the system less stable. Placing a graphene cover on the metal surface provides an effective way to modify the surface potential, which can be continuously tuned by  $d_{\text{Gr-Pt}}$ . Such an effect is similar to applying an external electric field onto a solid electrode surface (42). From the perspective of quantum effect, the Gr cover acts as a constraint boundary for molecular orbitals of an adsorbate, which cannot relax farther away from the surface sufficiently compared to the case of adsorption on an open surface (15). Therefore, confining molecule adsorption under Gr implies an increase in energy levels of the molecular orbitals. Overall, the confinement effect in 2D microenvironment can be understood as a kind of confinement field imposed by the Gr cover, which destabilizes the surface adsorption.

**Generalized Confinement Effect in 2D Microenvironment.** The confinement effect aroused in 2D microenvironments is not limited to the graphene cover. To confirm this point, a hypothetical experiment was performed by replacing the graphene layer with a layer of inert gas Ne atoms (SI Appendix, Fig. S4), and the dimension of 2D space was kept unchanged, i.e.,  $d_{\text{Ne-Pt}}$  is the same as  $d_{\text{Gr-Pt}}$ . We see that the change of local potential distribution in the Ne-overlayer-confined space is similar to that in the graphene-confined space.  $E_{\text{con}}(\text{CO})$  in the 2D microenvironment with  $d_{\text{Ne-Pt}}$  at 5.7 Å is calculated as 1.35 eV at 1/7 ML CO coverage, which is also similar to that under the graphene layer (1.41 eV). Considering that Ne atoms are almost chemically inert, the similar influence of the Ne layer on CO adsorption suggests that the confinement effects are closely related to the

vdW interaction between two opposite walls of the confined space. Other noble gas atoms like He and Ar (SI Appendix, Fig. S4) have a similar effect on the confinement energy and surface potential distributions.

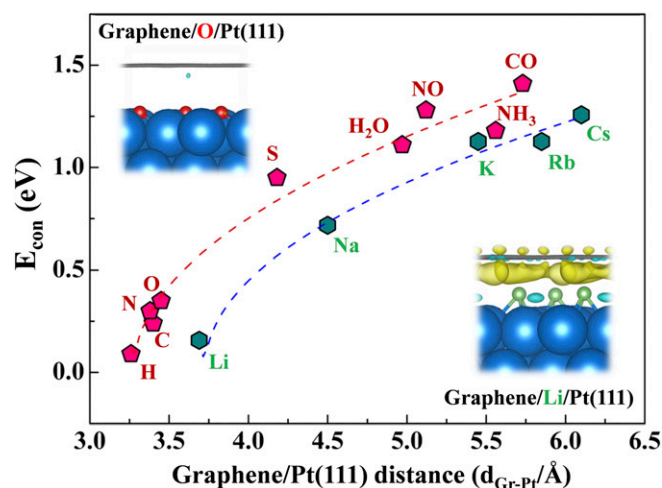
$E_{\text{con}}$  in the 2D space between Gr and Pt(111) has been calculated for various adsorbates, including nonmetal atoms (H, C, N, O, and S), alkali metal atoms (Li, Na, K, Rb, and Cs), and small molecules (CO, NO, H<sub>2</sub>O, and NH<sub>3</sub>). Meanwhile, the equilibrium  $d_{\text{Gr-Pt}}$  with an adsorbate adsorbed between Gr and Pt was obtained as well (SI Appendix, Tables S4 and S5). As shown in Fig. 4, all  $E_{\text{con}}$  values with the adsorbate coverage at 1/7 ML are positive, which means that adsorption of all these adsorbates on the Pt surface is weakened in the confined space. The same tendency was observed at 3/7 ML coverage, but  $E_{\text{con}}$  at 1/7 ML coverage is higher than that at 3/7 ML coverage (SI Appendix, Fig. S5).

For the same coverage,  $E_{\text{con}}$  increases almost monotonically with  $d_{\text{Gr-Pt}}$ .  $E_{\text{con}}$  data of nonmetal atoms and molecules can be fitted by the following equation (red dashed line in Fig. 4):

$$E_{\text{con}} = 1/(8\theta) \cdot (d_{\text{Gr-Pt}} - d_0)^\alpha.$$

In the case of 1/7 ML coverage, the fitted  $\theta$  is 1/7.03,  $d_0$  is 3.27 Å, and  $\alpha$  is 0.49 with the coefficient of determination  $R^2 = 0.97$ . The fitting of  $E_{\text{con}}$  data from 3/7 ML adsorbates on the Gr/Pt(111) surface also produces  $\theta$  around 3/6.89,  $d_0$  around 3.48 Å, and  $\alpha$  at 0.49 with  $R^2 = 0.99$  (SI Appendix, Fig. S5). Therefore, the fitted parameter of  $\theta$  is strongly related to the adsorbate coverage, and  $d_0$  corresponds to the equilibrium distance between Gr cover and Pt(111) surface at the Gr/Pt(111) interface (3.2 Å). This root equation can be used to fit the calculated  $E_{\text{con}}$  data from the h-BN/Pt(111) surface as well (SI Appendix, Fig. S6).

Such a more quantitative analysis of  $E_{\text{con}}$  reveals two interesting points. First,  $E_{\text{con}}$  is dependent on the adsorbate coverage, and is higher at a lower coverage. The coverage-dependent  $E_{\text{con}}$  can be understood as that the confinement effect has been averaged by more adsorbed atoms or molecules at the higher coverage. Second,  $E_{\text{con}}$  is strongly determined by the size of the



**Fig. 4.**  $E_{\text{con}}$  for 1/7 ML nonmetal atoms and molecules (pink dots), as well as alkali metal atoms (green dots) in between Gr and Pt(111) with various  $d_{\text{Gr-Pt}}$  values. The pink dots and green dots are fitted in red and blue dashed lines, respectively. (Insets) Cross-section views of Gr/O/Pt(111) and Gr/Li/Pt(111) interfaces shown with electron density difference at the interface; Gr, gray sticks; Li, green balls; O, red balls; and Pt, blue balls. Light blue and yellow contours in the electron density difference are for electron depletion and electron accumulation, respectively. The isosurface levels are set to be 0.002 e/Bohr<sup>3</sup>.

2D confined space and, more specifically, the change of  $d_{\text{Gr-Pt}}$ , i.e.,  $\Delta d_{\text{Gr-Pt}} = d_{\text{Gr-Pt}} - d_0$ . The stronger response of the confined microenvironment to the adsorption, the stronger the confinement effect induced, which is similar to the dynamic response of spheroproteins in an enzyme to reactions over the cofactor. The 2D confined space under the Gr overlayer provides a flexible microenvironment, in which the space thickness is dynamically adjusted with adsorbates inside. For example, intercalation of CO at Gr/metal interfaces produces a larger space than the H intercalation (25). This structural flexibility in the 2D confined system is in contrast to the 0D and 1D confined systems, which cannot adapt their pore sizes and tube diameters to reactions occurring inside (Fig. 1).

Note that  $E_{\text{con}}$  values of alkali metals are slightly lower relative to other atoms and molecules (blue dashed line in Fig. 4). The difference was understood by analysis of electron density at the interfaces, taking Li and O atoms as examples. As shown by Fig. 4, *Insets*, electron transfer between Li and Gr cover is much stronger than that of O. The strong electronic interaction between adsorbate and Gr makes the adsorbate more stable to stay at the interface, which decreases  $E_{\text{con}}$ . The general tendency, that the 2D confinement effect induces weakened adsorption, relies on a premise that there is a weak interaction between adsorbates and the top cover.

**Modulating Reactions Under 2D Cover.** In light of the Brønsted–Evans–Polanyi (BEP) relation, catalytic activity is related to the dissociative adsorption energy ( $E_{\text{diss}}$ ) of a reactant on a catalyst surface, which presents a volcano curve (1, 43). A good catalyst should have a moderate  $E_{\text{diss}}$ , which is close to the apex of the volcano curve. Assuming that the BEP relation remains intact, in view of the feasible modulation of surface adsorption in 2D confined spaces, we attempt to take advantage of the confinement effect to modulate  $E_{\text{diss}}$  and the reaction activity. Our calculations show that  $E_{\text{diss}}$  values of various molecules at the interface between Gr and Pt(111) are smaller than those on bare Pt(111) surface (*SI Appendix, Fig. S7*), indicating that the dissociation process is more difficult with Gr cover. Therefore, Gr cover can eventually move  $E_{\text{diss}}$  toward the right side in the volcano curve such that the overall activity of reactions on the left side of the volcano curve will be improved whereas those on the right side will be suppressed (*SI Appendix, Fig. S8*).

The confinement-induced modulation of surface reactivity is illustrated in Fig. 5 for Pt-catalyzed ORR under 2D covers. It has been well known that O binding energy is generally used as a descriptor for the ORR reaction activity (44). Although Pt is regarded as a good catalyst for this reaction, there is still much room to improve its performance, because Pt sits on the left side of the volcano curve (Fig. 5). Various routes to weaken the binding of O atoms on the Pt surface have been attempted, to promote the reactions (45, 46). According to the above-mentioned 2D confined catalysis concept, we suggest that the reactivity of Pt(111) toward ORR can be modulated by placing various 2D covers atop. ML graphene, h-BN, graphane (fully hydrogenated Gr) (47), graphone (half hydrogenated Gr) (48), and graphitic ZnO (g-ZnO) (49) were chosen to tune the surface adsorption. Binding energies of surface oxygen species ( $\Delta E_{\text{O}^*}$ ) on bare Pt(111) surface and the Pt(111) surface with different 2D covers were calculated, which decrease in the sequence of Pt(111) > Gr/Pt(111) > h-BN/Pt(111) > graphane/Pt(111) > graphone/Pt(111) > g-ZnO/Pt(111).

Because the calculated binding energies of  $\Delta E_{\text{O}^*}$  on different metals with vdW corrections are close to those without vdW corrections (*SI Appendix, Fig. S9 and Table S6*), the same volcano curve proposed by Nørskov et al. (42) was used here. As predicted in the volcano plot for the different 2D cover/Pt(111) surfaces (Fig. 5), covering the Pt(111) surface with graphene, h-BN, graphane, and graphone MLs all enhance the ORR activity. Among them, the graphane cover exhibits the largest

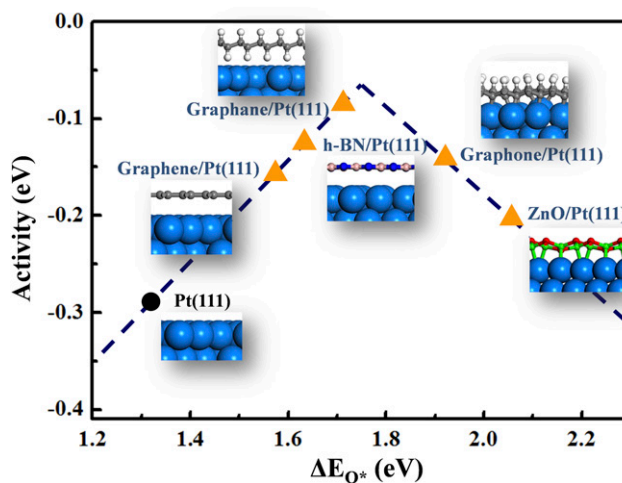


Fig. 5. The volcano curve relation between ORR activity and binding energies of O atoms ( $\Delta E_{\text{O}^*}$ ) on Pt surface. (*Insets*) The interfacial structures. B, purple balls; C, gray balls; H, white balls; N, dark blue balls; O, red balls; Pt, light blue balls; and Zn, green balls.

enhancement, because  $\Delta E_{\text{O}^*}$  has been tuned close to the apex of the volcano curve.

## Discussion

The 2D material layers such as Gr, h-BN, and MoS<sub>2</sub> have been prepared on many substrates (27). Despite ultrathin thickness, the 2D material sheets are quite stable under harsh conditions, e.g., there is no oxidation of graphene at 400 °C (50) and oxidation resistance of h-BN up to 850 °C in O<sub>2</sub> (51). When exposed to gaseous or liquid environments, molecules or solutions can diffuse underneath the 2D covers via an intercalation process, confirming that 2D material/solid interfaces act as stable and practical nanoreactors (see references in ref. 25). Surface science experiments confirm that molecule adsorption in the 2D confined space has been significantly weakened (22, 26, 28, 29, 52), which is consistent with the theoretical prediction in the present work.

Both gas-phase and aqueous phase reactions have been experimentally observed in the 2D spaces. More interestingly, the Gr or h-BN covers can promote reactions underneath the 2D overlayers. For example, CO oxidation on Pt(111) has been enhanced by covering the Pt surface with Gr and h-BN layers (22, 28), and metal corrosion has been accelerated in the presence of Gr overlayers (53, 54). Our calculation results for the feasible modulation of reactions under 2D covers can be solidified by recent reaction data. It should be noted that reactions occurring in the 2D confined spaces may be limited by surface diffusion under the 2D overlayers. To address this issue, we calculated diffusion barriers of CO on Pt(111) with and without Gr overlayer (*SI Appendix, Fig. S10*). It has been shown that molecule diffusion happens with similar barriers on the two surfaces, and diffusion under 2D covers may not be a limiting step.

Finally, the confined catalysis under 2D materials can be applied to supported nanocatalysts. Metal nanoparticles may be encapsulated by 2D materials, forming core–shell nanostructures in which the active core structures are well protected by the outer shells and catalyst stability is improved. Recent reports confirm that CO oxidation, methanation, and ORR reactions happen on the metal nanocatalysts covered with Gr or h-BN shells (55–58). Particularly, enhanced ORR activity has been observed on Pt nanocatalysts with Gr shells (57–59), which is consistent with our theory prediction illustrated in Fig. 5.

## Conclusion

We show that 2D confined microenvironments created between 2D material overlayers and underlying metal surfaces can be used to explore confined catalysis. The vdW interaction between the opposite walls of the 2D microenvironment induces the geometric constraint for adsorbed atoms and molecules. Furthermore, the 2D cover modifies potential distribution at the metal surface, making surface adsorption less energetically stable. The geometric constraint and confinement field aroused in the 2D space result in a general tendency of intercalated species

to adsorb on the metal surface weakly, which can be used to modulate surface reactivity and enhance ORR activity on Pt covered with various 2D materials. This concept can be applied to design novel nanocatalysts interfacing with 2D materials with improved performance.

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