

Electronic Supporting Information:

Shape Selective Plate-Form Ga₂O₃ with Strong Metal Support Interaction to Overlying Pd for Hydrogenation of CO₂ to CH₃OH

Xiwen Zhou, Jin Qu, Feng Xu, Jingping Hu, John S Foord, Ziyang Zeng, Xinlin Hong and Shik Chi Edman Tsang

1. Synthesis, Equipment and Techniques

1.1 Synthesis methods:

Rod Ga₂O₃ nanocrystals were synthesized according to Zhao *et al* [1]. In a typical synthesis, 0.006 mol Ga(NO₃)₃ was dissolved in DI water at a molar ratio of 1:100, which was then heated to 80°C. A 1.5 mol L⁻¹ NaOH solution was added dropwise into the gallium containing solution to form precipitate. The pH after the mixing was around 6.3-6.5. The mixture was then sealed in a container and shaken at a rate of 100rpm at 80°C for 2 hours. The resulting precipitate was collected by centrifuge and washed with water repeatedly to remove soluble species such as sodium nitrate. The precipitate was then mixed with a small quantity of water and stirred at room temperature for 2h before it was hydrothermally treated at 100°C for 2 days, washed with water extensively and dried in air at 80°C. The dried solid was calcined in air to form Ga₂O₃ nanocrystals at 900°C for 2h at a heating rate of 2.5°C/min. The plate Ga₂O₃ was synthesized by a solid state synthesis technique according to Yan *et al* [2]. First, KGaO₂ was prepared by heating a stoichiometric mixture of K₂CO₃ and Ga₂O₃ at 950°C in air for 12h. 20.0 mL of CH₃COOH (0.2mol/L) was added to 20.0 mL of KGaO₂ solution (0.2 mol/L made up from the powder) and stirred for 3 h to form plate GaOOH. The sediment was separated by centrifugation, washed repeatedly and dried at 60°C overnight. The final plate Ga₂O₃ nanocrystals were obtained by heating the as-prepared GaOOH at 800°C for 3 h with a heating rate of 5°C/min in air. For Pd doping a wetness impregnation method with appropriate volume of solution was used. Corresponding Pd(NO₃)₂ solution was added to Ga₂O₃ crystallite to make the 5 wt%. loading. The samples were dried, calcined (50ml/min air at 3°C/min until 300°C for 2h) and in-situ reduced in H₂ to obtain Pd/Ga₂O₃.

1.2 Computational Details

All calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP)[3-6]. The projector-augmented wave (PAW) potentials[7,8] were used for the core electron interaction. The Perdew–Burke–Ernzerhof (PBE) functional[9,10] based on the generalised gradient approximation(GGA) was employed to evaluate the non-local exchange-correlation energy.

In the bulk and (002), (110) surface unit cell optimisations and DOS calculations, a plane wave basis set with a cutoff energy of 400 eV and a k-point grid determined by the Monkhorst-Pack method were used. The k-point sampling used a 2×8×4 grid for the bulk and 4×8×1, 4×4×1 for the (002), (110) slabs, respectively. For structure optimisation, all the ionic positions were allowed to relax until the forces were less than 0.01 eV/Å.

The unit cell for the bulk Ga₂O₃ optimisation contained 4 Ga₂O₃ units. The optimised cell parameters are a=12.255 Å, b=3.052 Å, c=5.828 Å, in good agreement with the experimental values (a=12.230 Å, b=3.040 Å, c=5.800 Å). The Ga₂O₃ (002) and (110) surfaces were modeled by periodic models. Each contained 8 Ga₂O₃ molecular units. The 1×1 surface unit cell (6.315×3.052 Å²) of (002) and (5.828×6.315 Å²) of (110) slab were utilised in this study. A vacuum layer of 15 Å along the z direction perpendicular to the surface was employed to prevent spurious interactions between the repeated slabs.

Two different terminated energetic Ga₂O₃(002) surface unit cells were built. We used a non-stoichiometric model to keep the top and bottom layer symmetric in the slab. The O-terminated slab contained 26 O atoms and 16 Ga atoms, while the Ga-terminated slab contained 22 O atoms and 16 Ga atoms. The slab unit cell parameters of the polar (002) were the same as those in non-polar model.

To estimate the oxygen vacancy formation energy, we used a 2×2 supercell for (002) and a 1×2 supercell for (110) to make the surface vacancy density the same. A cutoff energy of 350 eV and a force convergence threshold of 0.05 eV/Å were used. The k-point sampling used a 2×4×1 grid for the (002) and 4×2×1 for the (110) slabs.

1.3 Powder X-Ray Diffraction (XRD)

XRD were performed on a Philips PW1050/81 diffractometer, operating in Bragg-Brentano focusing geometry and using CuKα radiation (λ = 1.5418 Å) from a generator operating at 40kV and 30 mA.

1.4 X-ray Photoelectron Spectroscopy

XPS was performed using Kratos Ltd XSAM800. Samples for XPS were pre-reduced in diluted H₂ (H₂/N₂=1:2) at 200°C for 1h with gas flow rate of 50ml/min and transferred to the equipment in glove bag without exposure to air.

1.5 Transmission Electron Microscopy (TEM)

TEM images were obtained using a JEOL 2010 microscope with a high resolution pole piece. The samples were prepared by placing a drop of nanoparticle ethanol suspension onto a carbon-coated copper grid, and allowing the solvent to evaporate.

1.6 Cyclic Voltammetry (CV) and CO stripping

The CV and CO stripping spectra were carried out using Ivium CompactStat instrument.

1.7 Temperature Programmed Reduction (TPR)

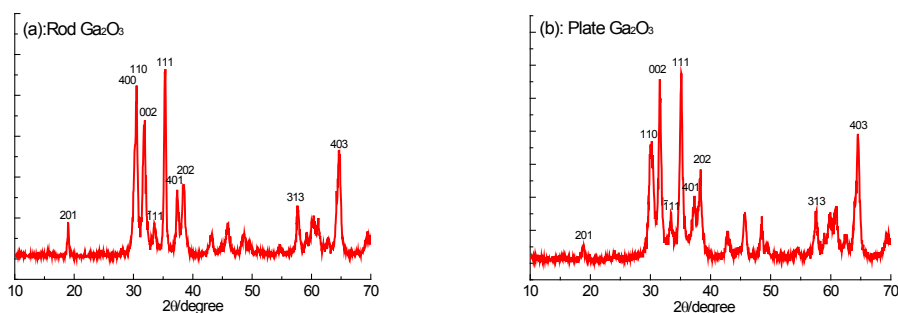
TPR was obtained using a CE Instruments TPDRO1100, with the ramping rate of 10 K/min from room temperature to 1073K under a flowing stream of 5% H₂/Ar.

1.8 Electron Paramagnetic Resonance

X-band CW EPR spectra were recorded on a Bruker EMX spectrometer using an Elecsys probehead with 17-40 mg sample placed in 4 mm tube separately.

2 Testing and Characterization

Catalyst tests in the hydrogenation of CO₂ were carried out at total pressure of 5 MPa using a tubular fixed bed reactor (12.7 mm OD) with a catalyst weight of 0.2 g. The catalytic performances were below those thermodynamic predicted values in order to ensure the conditions were in kinetic controlled regime. A CO₂-H₂ reaction mixture with a molar ratio of about 1/3 was fed at the rate of 20 stp mLmin⁻¹ through the catalyst bed. The reaction temperature was fixed at 523K. Before each test, the catalysts were pre-reduced in situ at 523 K for 1h under the H₂ flow (20 stp mLmin⁻¹). The products (methanol and CO) were the carbon containing products with no methane and dimethylether detected) were analysed by a calibrated GC equipped with a TCD detector after passing the reactants over the catalyst for 2h.

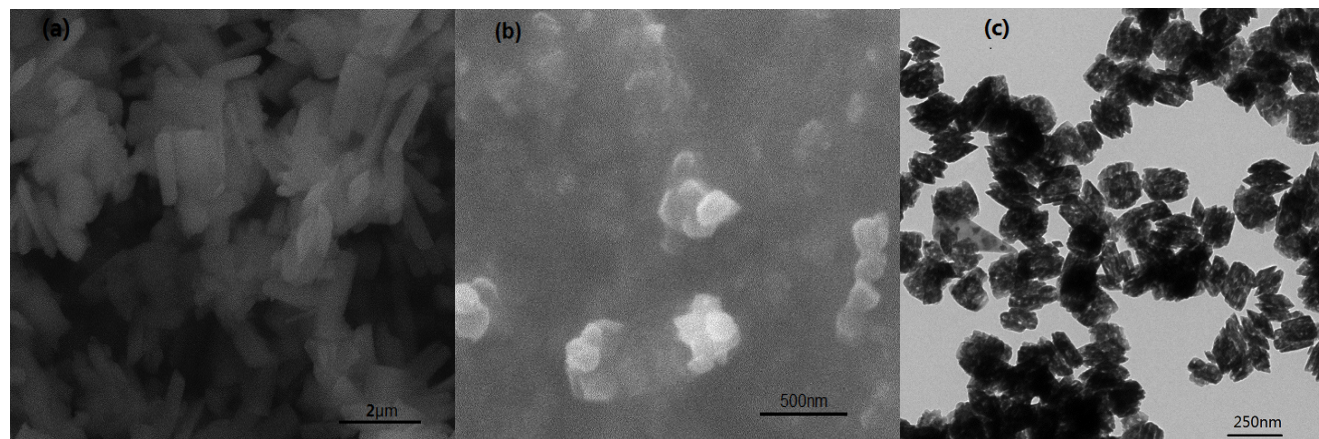


S Fig.1: XRD patterns of β -Ga₂O₃ (a) rod form; (b) plate form

XRD

Both rod and plate Ga₂O₃ with and without Pd showed monoclinic β -Ga₂O₃ (see spectra in main text) but with no significant Pd peak even after reduction and catalytic reaction tests, indicating the Pd dispersion was extensive in both cases.

SEM images in S Fig. 2 confirmed that the synthesized β -Ga₂O₃ crystals are in rod shape and plate shape, respectively. The rod Ga₂O₃ is around 400-550nm in diameter and 2.5μm in length (S Fig. 2a, see corresponding TEM in 1c in main text). S Fig. 2b (SEM) and c (TEM) reveal that the plate Ga₂O₃ is a regular rhombic shape single crystal with a diameter of around 150-200 nm.

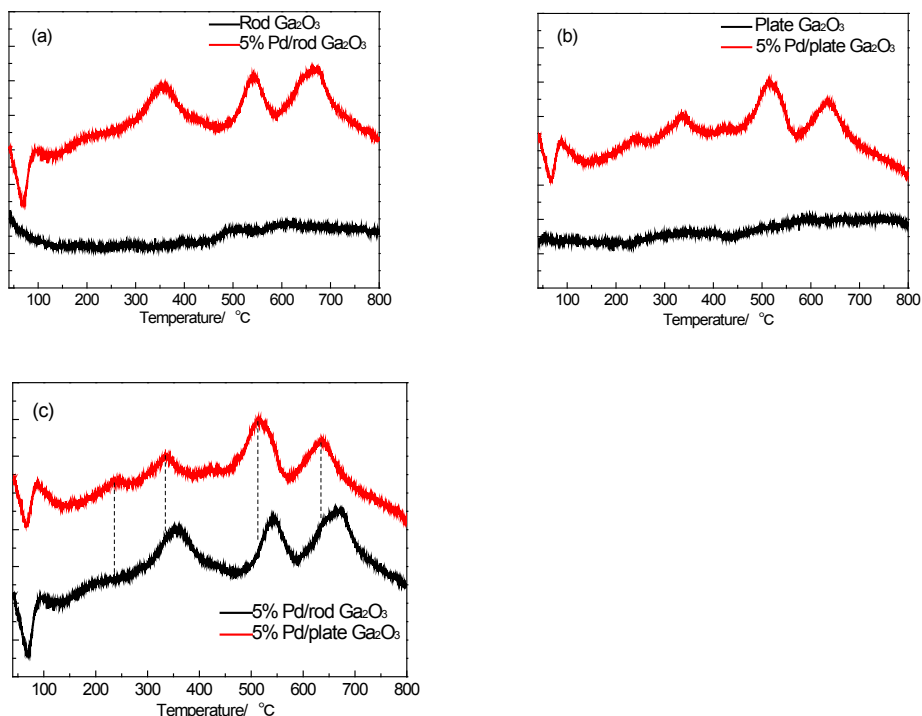


S Fig. 2: SEM images of β -Ga₂O₃ in rod form (a) and in plate form (b) and corresponding TEM image in plate form (c)

TPR

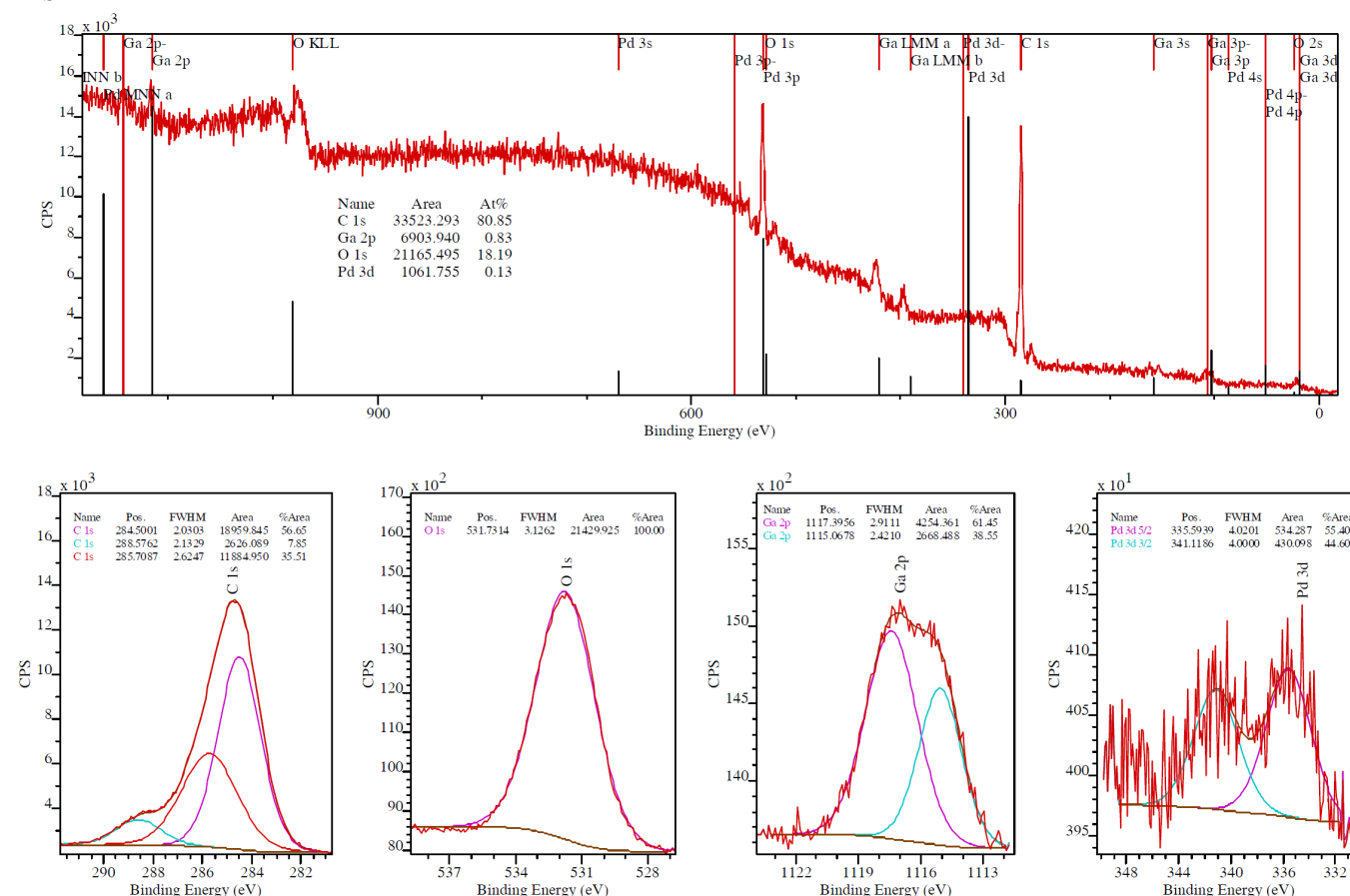
The interaction between Pd and the two forms of Ga₂O₃ were studied by temperature programmed reduction (TPR). It was shown that pure Ga₂O₃ will not undergo reduction in hydrogen until 900°C[11]. S Fig. 3a displays TPR profiles of Pd/rod Ga₂O₃ and pure rod Ga₂O₃. The pure Ga₂O₃ rods indeed did not undergo reduction under the flowing hydrogen, whereas the sample with Pd showed three apparent reduction

peaks at 365, 555, and 670°C, respectively. For plate Ga_2O_3 (S Fig. 3b) there was no reduction taken place but the incorporation of Pd rendered the reduction of plate Ga_2O_3 more readily to take place than the rod form. Four reducing peaks centered 240, 340, 520, and 640°C, respectively are clearly seen in S. Fig. 3b. Comparison of the two Pd/ Ga_2O_3 TPR profiles (S Fig. 3c) clearly reveals that a stronger interaction between plate Ga_2O_3 and Pd with all the reduction peaks shifting towards lower temperature than rod form. It is noted that PdO is readily reduced to Pd⁰ at sub-ambient temperature and the observation of a negative peak (hydrogen desorption from Pd hydride) at 70°C in both spectra clearly suggest that the presence of Pd⁰. The reduction peaks of Ga_2O_3 in the presence of Pd⁰ are thought to associate with the reduction of surface oxygens to generate oxygen vacancies at low temperatures, followed by deep reduction of lattice oxygen ions at high temperature due to the slow lattice ions diffusion. No further assignment of the types of oxygen was attempted.



S Fig. 3 TPR profiles (a) rod Ga_2O_3 with and without Pd (b) plate Ga_2O_3 with and without Pd (c) Pd on rod and plate Ga_2O_3 .

XPS



S Fig. 4 XPS survey scan of Pd/plate Ga₂O₃ and the regions for binding energies of C 1s, O 1s, Ga 2p, Pd 3d.

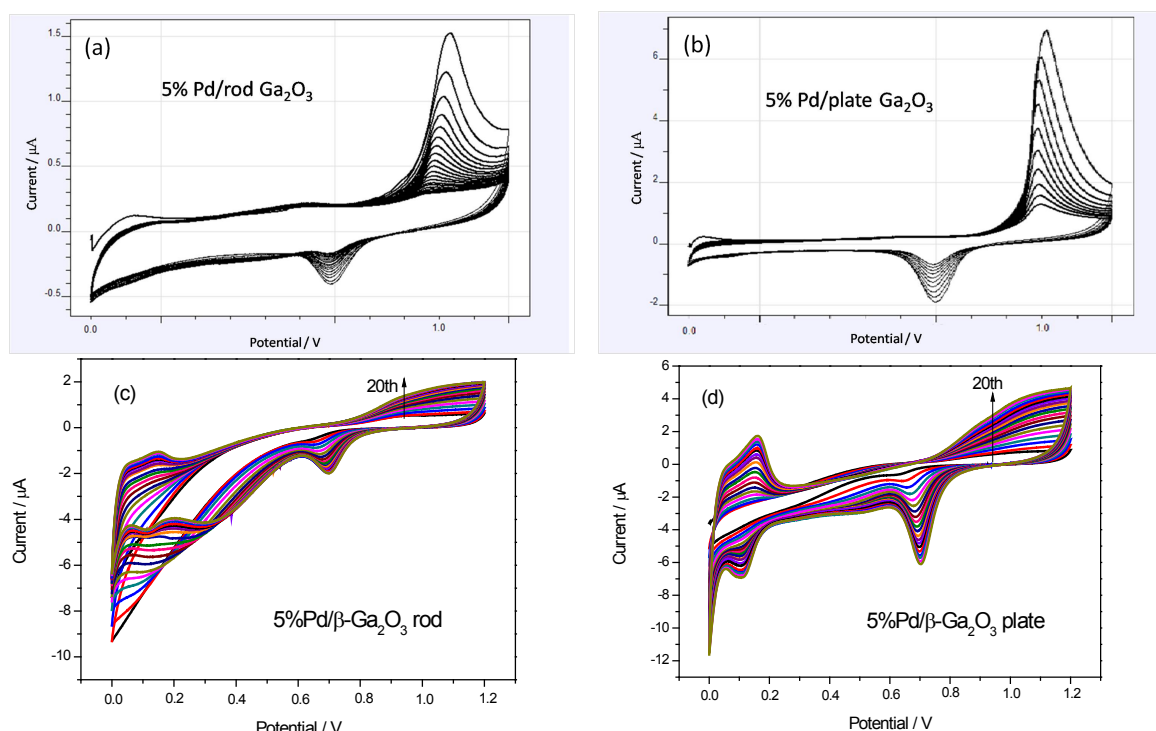
XPS analysis of Pd/plate Ga₂O₃ was only performed to characterize the electronic properties of Ga₂O₃ surface in the presence of Pd after its pre-reduction in diluted H₂ (H₂/N₂=1:2) at 200°C without exposure to air. It is noted that there are two Ga 2p signals (BE 1117.4 and 1115.1 eV) at the area ratio of 43:27, which may be attributed to Ga³⁺ and reduced Ga⁺/Ga⁰, respectively. There was also a slight shift in Pd signals (Pd_{3d5/2} of 335.9 and Pd_{3d3/2} of 341.1 eV) indicative of PdGa alloy formation but the signals were too poor to be ascertained [12].

Electrochemical Characterization

The cyclic voltammetry was carried out in a conventional three-electrode cell containing 0.5M H₂SO₄ at ambient temperature. 3 mg catalysts, 500 µl Millipore water (18.2 MΩ at 25°C) and 50 µl Perfluorosulfonic acid-PTFE copolymer (5% w/w solution, Alfa Aesar) were ultrasonically mixed for 10 min to form an ink. Then 24 µl ink was pipetted onto a glassy carbon electrode (GC electrode). The GC electrode was pre-polished to a mirror-like finish using an aluminum oxide (<50nm) slurry on a polishing cloth (purchased from BASI), the electrode geometric area exposed to the electrolyte was 0.071 cm². The electrode was dried under vacuum at ambient temperature for 30min, the Pd loading was 0.092 mg•cm⁻². The electrolyte was purged with ultra high purity Argon for 30min before testing. For CO stripping, the electrode was immersed in the Ar pre-saturated electrolyte and bubbled with ultra high purity CO for 30min. After the CO bubbling, the electrode was rinsed with plenty of Millipore water and moved into the testing cell. The CV and CO stripping tests were carried out using Ivium CompactStat instrument. Platinum wire and saturated calomel electrode (SCE) were used as counter electrode. GC electrode, platinum wire and SCE were all purchased from BASI. The scan rate was set at 0.05 V•s⁻¹. The CO stripping was used to calculate the electrochemical active surface (EAS) by means of the following equation:

$$EAS_{Co} = \frac{Q_{Co}}{[Pd] \times 4.84}$$

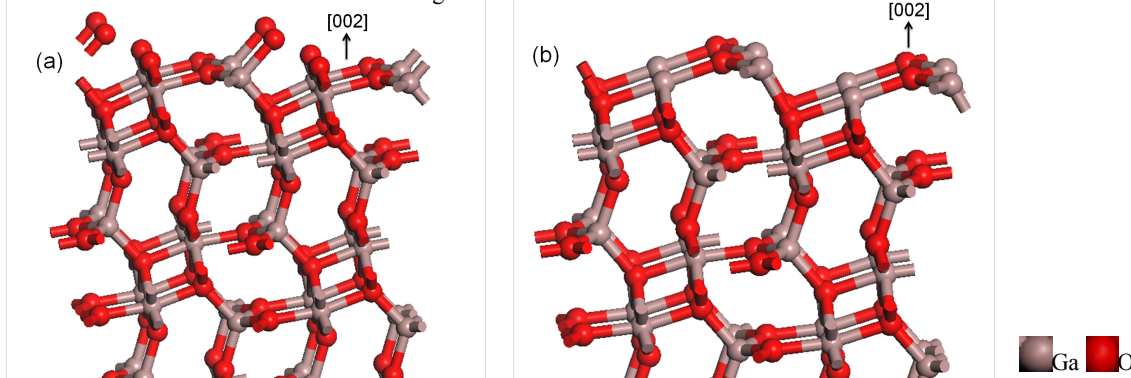
Where Q_{co} is the charge for CO desorption (C) and 4.84 (C•m⁻²) represents the charge density required to oxidize a CO monolayer on Pd surface, [Pd] represents the Pd loading (g)[13].



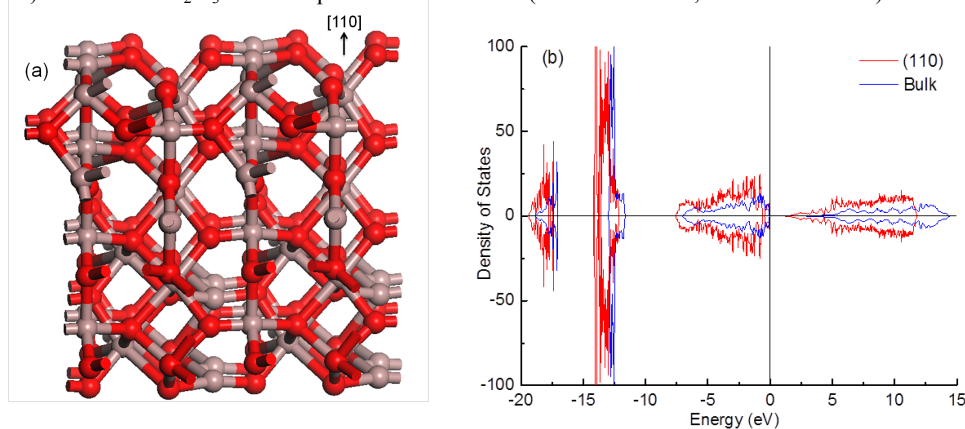
S Fig 5 Consecutive CO stripping spectra of Pd on (a) rod and (b) plate Ga_2O_3 ; Cyclic Voltammetry (CV) of Pd on (c) rod and (d) plate Ga_2O_3 scanned from 0.0 V to 1.2 V (vs. SHE) at $50\text{mV}\cdot\text{s}^{-1}$, all the 20 cycles shown.

DFT Calculations and Modeling

It is found that the majority of exposed surfaces of the plate Ga_2O_3 are covered with (002) surfaces. Two possible terminations, namely O and Ga terminated surfaces and shown in the S Fig. 6.



S Fig. 6. (002) surfaces of Ga_2O_3 with two possible terminations (O termination: a; Ga termination: b)



S Fig. 7a: Atomistic model to show (110) non polar surface of Ga_2O_3 ; b: DOS of (110) non polar surface in comparison with bulk Ga_2O_3 . The (110) surface of Ga_2O_3 is taken for comparison where cations and anions resident on the same surface with no polarity (dipole) created with the layers (S Fig. 7a). It is noted from S Fig. 7b that the (110) non polar surface shows a very similar DOS structure compared to bulk Ga_2O_3 .

Mechanism and Active Site Considerations

The mechanism of methanol synthesis from catalytic hydrogenation of CO and nature of active site are still very unclear despite the intense research over the past 40 years let alone the CO₂ hydrogenation. From kinetic and spectroscopic studies, surface stepwise hydrogenations involving formate, methylenebisoxo, methoxy to methanol have been proposed for both Cu/ZnO and Pd/Ga₂O₃ based catalysts [14-17]. Electron rich surfaces have found to favor the catalytic hydrogenation [18,19]. The assignments of active sites ranging from simple metal sites, sites on small metal islands under high isomorphic strain on support, optimum balance between metallic and partial oxidised species, metal sites decorated with heteroatoms from the extensive oxide support reduction (CuZn and PdGa) and synergetic sites created between metal and support have been suggested[14-19].

In this paper, it is stressed that we did not attempt to address the mechanism nor identify active sites for this reaction but we have focused on the materials interaction between metal and type of support oxide surface.

Reference

- [1] Y.Y. Zhao, R.L. Frost, W.N. Martens, *J. Phys. Chem. C*, 2007, **111**, 16290-16299.
- [2] S. Yan, L. Wan, Z. Li, Z. Zou, *Chem. Commun.*, 2010, **46**, 6388-6390.
- [3] G. Kresse, J. Hafner, *Phys. Rev. B*, 1993, **47**, 558.
- [4] G. Kresse, J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
- [5] G. Kresse, J. Furthmüller, *Comput. Mat. Sci.*, 1996, **6**, 15.
- [6] G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- [7] P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.
- [8] G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
- [9] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- [10] J. P. Perdew, K. Burke, M. Ernzerhof, Erratum, *Phys. Rev. Lett.*, 1997, **78**, 1396. .
- [11] E. Gebauer-Henke, J. Grams, E. Szubiakiewicz, J. Farbotko, R. Touroude, J. Rynkowski, *J. Catal*, 2007, **250**, 195.
- [12] C. D. Wagner, *Faraday Discuss. Chem. Soc.*, 1975, **60**, 291.
- [13] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, *J. Power Sources*, 2002, **5**, 13.
- [14] X. M. Liu, G. Q. Lu, Z. F. Yan, J. Beltramini, *Ind. Eng. Chem. Res*, 2003, **42**, 6518.
- [15] M. Saito, *Catalysis Surveys from Japan* 1998, **2**, 175.
- [16] T. Ressler, B. L. Kniep, I. Katsatkin, R. Schlögl, *Angew Chem*. 2005, **44**, 4704.
- [17] Behrens, et al. *Science* 2012, **336**, 893.
- [18] F.L. Liao, Z. Zeng, C. Eley, Q. Lu, X. Hong, S.C.E. Tsang, *Angew Chem*. 2012, **51**, 5832.
- [19] F.L. Liao, Y.Q. Huang, J.W. Ge, W.R. Zheng, K. Tedsree, P. Collier, X. L. Hong and S. C. Tsang, *Angew. Chem*. 2011, **123**, 2210.