## ChemComm

## COMMUNICATION

## **RSC**Publishing

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 1747

Received 24th November 2012, Accepted 11th January 2013

DOI: 10.1039/c3cc38455a

www.rsc.org/chemcomm

Shape selective plate-form Ga<sub>2</sub>O<sub>3</sub> with strong metal–support interaction to overlying Pd for hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH<sup>†</sup>

Xiwen Zhou,<sup>a</sup> Jin Qu,<sup>a</sup> Feng Xu,<sup>a</sup> Jingping Hu,<sup>a</sup> John S. Foord,<sup>a</sup> Ziyan Zeng,<sup>b</sup> Xinlin Hong<sup>b</sup> and Shik Chi Edman Tsang<sup>\*a</sup>

A stronger metal-support interaction between Pd and plate-form  $Ga_2O_3$  nanocrystals covered with the predominant 002 surface than other  $Ga_2O_3$  surfaces is found, which gives higher methanol yield in catalytic  $CO_2$  hydrogenation.

Global warming caused by increasing atmospheric carbon dioxide  $(CO_2)$  concentration and the depletion of fossil fuels are becoming the focus of worldwide attention.<sup>1,2</sup> On site catalytic conversion of  $CO_2$  to liquid fuels or chemicals, given a steady supply of the  $CO_2$  substrate and excess energy, is a promising route that may offer a solution to these important environmental and energy issues.<sup>3,4</sup> In particular, installation of chemical reactors for the hydrogenation of  $CO_2$  to methanol could be an attractive supplement to coal fired power stations, iron refineries and incinerators, which not only offers the abatement of  $CO_2$  on site but also provides transportable fuel from this reaction. The convenient production of hydrogen on a large scale from renewable sources (solar energy, hydropower, biomass, or excess chemical heat *etc.*) close to the point of use for this application may support such a green integrated process.<sup>5,6</sup>

Majority of current research on catalytic  $CO_2$  hydrogenation has been using modified industrial Cu/ZnO based catalysts from synthesis gas hydrogenation technology, which are operated at relatively slow gas flow and elevated temperature and pressure due to slow kinetics.<sup>7–9</sup> For the conversion of  $CO_2$  to fuels it would be economic and technically more viable if the  $CO_2$  fixation can be carried out more readily under milder conditions. There are some combinations of metal and metal oxide catalysts, which have been claimed to display higher turnover frequency towards methanol than Cu/ZnO catalysts.<sup>10</sup> For example, the higher activity of Pd/  $Ga_2O_3$  but with slightly lower selectivity than Cu/ZnO has been noted.<sup>11,12</sup> We have been interested in understanding the strong metal–support interaction (SMSI) of these catalysts, which plays an important role in this area.<sup>13,14</sup> Here, we report a remarkable activity dependence on the shape of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> where oxygen and gallium ions terminated (002) surfaces of plate nanocrystal exert a stronger electronic interaction with Pd than other surfaces, giving a higher yield for methanol production from CO<sub>2</sub> hydrogenation. This result has echoes of the previously reported shape effect of ZnO in Cu/ZnO for the same reaction where the electron rich (002) face, as alternative oxygen and zinc ions layers in plate form a ZnO crystal, also shows a stronger material synergy with Cu than other ZnO facets.<sup>14</sup> DFT calculations and characterization clearly suggest that these high energetic oxide surfaces interact more strongly with overlying metal particles for beneficial SMSI for this important reaction.

Two forms of crystalline Ga<sub>2</sub>O<sub>3</sub> nano-crystals (rod and plate) were first synthesized, followed by deposition of Pd for each sample (see ESI<sup>†</sup>). X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction (ED) data shown in Fig. 1 confirm both rod and plate-shaped particles from the observed morphologies, comprising a highly crystalline monoclinic β-Ga<sub>2</sub>O<sub>3</sub> structure with a = 12.225 Å, b = 3.039 Å, c = 5.801 Å (JCPDS 43-1012). Only extremely broad Pd XRD peaks were detected in both samples when Pd was incorporated, indicative of very high metal dispersion, and it was therefore not possible to derive the particle size within acceptable accuracy. Analysis near the edges of the rod Ga<sub>2</sub>O<sub>3</sub> nanocrystals by TEM and ED suggested that the majority of their surfaces were terminated with either (111) or (110) faces, with the rod growth extending along the [110] growth direction; such stable low index terminations are expected in high temperature synthesis and the rod shape reflects the monoclinic crystal structure. In contrast, for plate form Ga<sub>2</sub>O<sub>3</sub>, the same analysis showed that the more open, higher energy (002) face was generally observed for the dominant plate faces, suggesting a high preference for this surface termination. A higher (002) XRD peak intensity (Fig. 1b) also reflects the dominance of this plane. Note that the single crystal nature of the Ga2O3 nanoplate with the (002) surface prepared by the same method was also identified.<sup>15</sup>

Catalytic results of impregnated 5 wt% Pd on rod and plate  $Ga_2O_3$  for methanol production from  $CO_2$  hydrogenation are shown in Table 1 (testing conditions, see ESI<sup>†</sup>). CO was the only side product detected in this reaction. As seen from Table 1, Pd on plate  $Ga_2O_3$  clearly exhibits higher activity than on the corresponding rod

<sup>&</sup>lt;sup>a</sup> Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford, OX1 3QR, UK. E-mail: Edman.Tsang@chem.ox.ac.uk

<sup>&</sup>lt;sup>b</sup> College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, P. R. China

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/ c3cc38455a



Fig. 1 (a) XRD of rod  $Ga_2O_{3}$ ; (b) XRD of plate  $Ga_2O_{3}$ ; TEM, lattice fringes, electron diffraction at edges of (c) rod  $Ga_2O_3$ ; (d) plate  $Ga_2O_3$ .

form, despite the fact that the same metal loading was used and the BET surface areas for the two forms were low but comparable to each other ( $\sim 15-20 \text{ m}^2 \text{ g}^{-1}$ ). One possibility is that a higher dispersion of Pd was obtained on the plate oxide due to enhanced interaction of the Pd precursor with this support. It is noted that the plate oxide also gives higher selectivity towards methanol than the rod form. As a result, the methanol yield of 5% Pd on plate Ga<sub>2</sub>O<sub>3</sub> is nearly double that seen using the rod support, indicative of the remarkable activity dependence on the morphology of the support oxide used. Our earlier report on a similar trend from catalysts prepared by the physical mixing of plate or rod ZnO nanocrystals with preformed Cu nanoparticles is included for comparison.<sup>14</sup>

It is noted from Table 1 that Pd/Ga<sub>2</sub>O<sub>3</sub> catalysts indeed give higher activity than Cu/ZnO catalysts but with poorer selectivity in this work.<sup>11,12</sup> Interestingly, Ga<sub>2</sub>O<sub>3</sub> (monoclinic) and ZnO (wurtzite) are structurally different oxides, but when using higher energy (002) surfaces both can interact favourably with metals to give higher activity to methanol. Note that the cation and anion arrangements over the exposed (002) surfaces of these two oxides are unbalanced that they give an overall non-zero polarity in top layers.<sup>16,17</sup> Depending on the degree of covalency, the coloumbic repulsion between ions of the same charge tends to give rise to a higher surface energy than those of other exposed surfaces. Energetic oxide surfaces have not been well studied as metal catalyst supports, but the high methanol yields noted in this work clearly suggest that they could be of considerable catalytic interest. We believe that such energetic polar oxide surfaces interact strongly with deposited metals and precursors, thereby imparting superior catalytic performance as demonstrated in the formation of methanol on the plate forms of Ga2O3 and ZnO. Thus, the recent tailored synthesis of metal and oxide nanoparticles for

Table 1 Summary of catalytic performance of 5% Pd on rod and plate  $\beta\text{-}Ga_2O_3$  crystals in comparison to Cu on rod and plate ZnO

Catalyst	$CO_2$ conv. (%)	Methanol select. (%)	Methanol yield (%)
5% Pd/rod Ga <sub>2</sub> O <sub>3</sub>	11.0	41.3	4.5
5% Pd/plate Ga <sub>2</sub> O <sub>3</sub>	17.3	51.6	8.9
Cu/rod ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>14</sup>	15.8	41.0	6.5
Cu/plate ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>14</sup>	15.5	64.5	10.0



**Fig. 2** (a) Cyclic Voltammetry (CV) of Pd/plate and Pd/rod Ga<sub>2</sub>O<sub>3</sub>, scanned from 0.0 V to 1.2 V (vs. SHE) at 50 mV s<sup>-1</sup>, the stable 20th cycle was recorded; (b) CO stripping of Pd on rod and plate Ga<sub>2</sub>O<sub>3</sub> (ESI†).

careful morphology controls may give an exciting way to optimize catalytic performances by this mean.

In order to assess the possible electronic interaction between metal and semiconducting oxide, Pd nanoparticles attached to the plate and rod forms of the Ga2O3 nanocrystals, dispersed on glassy carbon electrodes, were characterized by cyclic voltammetry and CO stripping voltammetry (details in ESI<sup>+</sup>) and the data are shown in Fig. 2. It is noted from Fig. 2a that both Pd/plate Ga2O3 and Pd/rod Ga2O3 are clearly electrochemically active but the former shows a considerably higher CV signal, derived from H adsorption/desorption below 0.2 V, and Pd oxidation/reduction around 0.7 V. Also, the absence of a charactersitic hump at 0.3 V in Pd/plate Ga<sub>2</sub>O<sub>3</sub> may suggest a primary (001) Pd deposition (epitaxyl deposition) instead of mixed Pd phases deposition in Pd/rod Ga2O3. There are no electrochemical signals for the two pure Ga2O3 supports, indicating that the activity is only associated with the presence of Pd and interfaces with the oxides. Electrochemical oxidative CO stripping was also conducted following the pre-adsorption of CO on the supported Pd (Fig 2b). The calculated electrical active surface (EASco) from the charge passed reveals a surprisingly large difference between the two Pd supported samples, being 0.42 and 0.07  $m^2 \ {g_{Pd}}^{-1}$  for 5% Pd/plate  ${\rm Ga_2O_3}$  and 5% Pd/rod Ga<sub>2</sub>O<sub>3</sub>, respectively (6 times), despite the comparable surface area of their supports. The electrochemical results thus reflect the stronger interaction of the Pd with the plate than rod oxide, leading to significantly higher electrochemically active sites on the former material. However, it is noted that the nature of electrochemically metal active sites may not necessarily correspond to the same catalytically active sites for methanol synthesis as it is known that synergetic sites created at the metal-metal oxide interface may be required for both CO2 and H2 activations and catalysis.<sup>13,14</sup> On the other hand, the onset potential for the stripping process was lower for the plate form, being 0.77  $\pm$  0.006 V, and for rod 0.83  $\pm$  0.008 V with the peak<sub>max</sub> shifting 15  $\pm$  3 mV to lower voltage in the plate sample (ESI<sup>+</sup>). This earlier onset for the plate form indeed shows more chemically active form of surface Pd sites in synergy with this support material, compared to the rod form. In addition, for most supported Pd samples, adsorbed CO on Pd is totally stripped off during the first anodic scan. Interestingly, we noted here that CO stripping signals were still observed for both samples on the second and subsequent scans (higher CO stripping signals for each scan for the plate form, ESI<sup>+</sup>). Thus, the results suggest that COad can be inter-transferred between Pd and Ga2O3 sites presumably via surface carbonate/bicarbonate, resembling the reversible spillover phenomenon with strong MSI.<sup>18</sup> Clearly, Ga<sub>2</sub>O<sub>3</sub> and its energetic (002) surface with the plate morphology have an extensive influence on catalytic chemistry of Pd phase.



**Fig. 3** (a) Atomistic model showing the (002) surface of  $Ga_2O_3$  with oxygen termination (O red, Ga grey); (b) EPR spectra of rod  $Ga_2O_3$  and plate  $Ga_2O_3$ ; DOS of (002) surfaces in comparison to bulk  $Ga_2O_3$  surface; (c) O termination; (d) Ga termination.

We then carried out DFT calculations to probe the electronic properties of the energetic (002) surface, compared with bulk Ga<sub>2</sub>O<sub>3</sub> (ESI<sup>+</sup>). As stated, the (002) polar surface for plate Ga<sub>2</sub>O<sub>3</sub> has two possible terminations, namely Ga and O terminated surfaces,<sup>16,17</sup> and an atomistic model is shown in Fig. 3a. The calculations for the density of states (DOS) associated with these surfaces clearly reveal some unusual electronic properties. On both terminations, a strong modification of the DOS with respect to bulk Ga2O3 takes place. The principal effects consist of an important strong exchange splitting and distortion of the DOS towards higher energy at the top of the valence band (up-shift) due to electrostatic repulsion on the O termination (the line at 0 eV represents the Fermi level) and a downward shift of the surface conduction band on the Ga termination. As a result, the band gap becomes narrower and electrons can be promoted more easily to higher surface bands. It is noted that similar calculations over (002) ZnO and other polar metal oxide surfaces reported the narrowing of band gaps and in some cases, metallation (total disappearance of band gap) was suggested.<sup>16,17</sup> In contrast, we found that a typical (110) nonenergetic, non-polar surface shows a similar DOS to bulk Ga<sub>2</sub>O<sub>3</sub> (ESI<sup>+</sup>).

It is known that electrostatic repulsion of the same charged species within the layer on a high energy oxide surface can render instability of its structure. However, the high energetic surface may tend to seek various mechanisms for stabilization, such as selective adsorption of counter-ions, surface reconstruction and excitation of localized electrons to delocalized bands as our calculations presently indicate.<sup>16,17</sup> If the latter takes place, the excitation of electrons to higher conduction bands from localized oxygen anions would facilitate its oxygen release to create anion vacancies. We have therefore calculated the minimum energies required for the formation of an oxygen vacancy from (002) polar O terminated and (110) non-polar surfaces with active oxygen sites at the lowest coordination. Results were -0.78 eV for the polar surface and +1.74 eV for the non-polar surface, indicating that the unstable high energy oxide (002) surface is readily prone to produce oxygen vacancies and excited electrons. To verify this mechanism, electron paramagnetic resonance (EPR) studies on rod and plate Ga2O3 were thus performed. EPR profiles of plate and rod samples (Fig. 3b) clearly reveal that the plate sample gives a higher signal of unpaired electrons  $(4.728 \times 10^{16} \text{ spins per mg})$  than the rod sample

 $(2.076 \times 10^{16} \text{ spins per mg})$ . The presence and quantity of spin reflect the degree of structural defects present in the sample. The *g* value of 2.30 (plate) and 2.20 (rod) can be attributed to deep trapped electrons from oxygen defect sites near the valence band ( $O_2^-$  acts as an electron acceptor when an  $O_2$  molecule from air adsorbs on oxygen vacancy).<sup>13,14</sup> Interestingly, only plate Ga<sub>2</sub>O<sub>3</sub> gave a distinctive signal with a *g* value of 1.96, which is attributed to shallow trapped donor defects near the conduction band. The presence of such donor defects clearly reflects the occupancy of excited electrons in the conduction band. Similarly, plate ZnO also gives higher EPR signals for the deep trapped acceptors and unique shallow donors as compared to rod ZnO.<sup>13,14</sup> In addition, Yan *et al.* reported a higher degree of surface defects for plate Ga<sub>2</sub>O<sub>3</sub> than powder form by photoluminescence.<sup>15</sup>

It is therefore evident from our work that it is the instability of the (002)  $Ga_2O_3$  surface and its high propensity for electron transfer that facilitate the interaction with Pd (as a way of stabilization) at their Schottky-Mott interface (the oxide support has a higher conduction band energy than the Fermi-level of the overlying metal).<sup>11-14</sup> This can lead to higher metal dispersion and its orientation and possible (Pd–Ga) alloy formation at the materials interface,<sup>19</sup> giving higher activity and selectivity in methanol production than those of low energy surfaces.

In conclusion, we have adopted a new approach by controlled growth of nano-size  $Ga_2O_3$  crystals of different shapes and used them to host Pd. We have found a stronger MSI between Pd and polar (002) surface of plate form  $Ga_2O_3$  than other non-polar surfaces with facilitated electron transfer, giving a higher activity for methanol production from  $CO_2$  hydrogenation.

We thank Dr X. Gong of East China University of Technology for calculations and facilities, Dr T. Li of Oxford Materials and Dr Q. Lu of US Naval Research Laboratory for TEM and EPR.

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