## Understanding Properties of Engineered Catalyst Supports using Contact Angle Measurements and X-Ray Reflectivity

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## **Contact Angle Measurement (CAM)**

*Theoretical Background.* The contact angle ( $\theta$ ) formed for a drop of liquid on a flat substrate is a unique property of the solid-liquid-vapor system. It is a quantitative representation of the intrinsic ability of a non-reactive liquid to spread on a plane solid surface – a measure of the underlying competition between the energy of cohesion of the liquid molecules and the energy of adhesion between the substrate and the liquid droplet. The interfacial tensions ( $\gamma$ ) are related to  $\theta$  by the Young's equation:<sup>1</sup>

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \tag{S1}$$

where  $\gamma_L \gamma_{S'}$  and  $\gamma_{SL}$  are the surface tension of the liquid, the surface tension of the solid, and the interfacial tension between the solid and the liquid. Equation 1 has only two measurable parameters:  $\theta$  and  $\gamma_L$ . To determine  $\gamma_S$  and  $\gamma_{SL}$ , indirect methods that involve a relation between these quantities must be established. Here, the contact angle approach of van Oss, Chaudhury, and Good (VOCG) is used to investigate the acid-base properties of the catalyst substrates.<sup>2-4</sup> As proposed by Dupré,<sup>5</sup> the concepts of work of cohesion ( $W^{coh}$ ) and work of adhesion ( $W^{adh}$ ) can be used to describe the relation between the  $W^{adh}$  occurring between the substrate and the liquid droplet. The Dupré work of adhesion,  $W^{adh} = \gamma(1 + \cos \theta)$ , represents the thermodynamic stability of interfaces involving different materials. Further, the free energy (G) for the solid-liquid interface can be used to describe W<sup>coh</sup> and W<sup>adh</sup> because  $\gamma$  is the free energy per unit area, as well as force per unit length; therefore,  $\Delta G_{SL}$  is expressed as:

$$\Delta G_{SL} = \gamma_{SL} - \gamma_S - \gamma_L \tag{S2}$$

Combining equations (1) and (2) yields the Young-Dupré equation:

$$-\Delta G_{SL} = \gamma_L (1 + \cos\theta) \tag{S3}$$

According to VOCG, the total surface free energy  $(\gamma_{S}^{TOT})$  is the sum of Lifshitz-van der Waals (LW) component and the acid-base (AB) component:

$$\gamma_{S}^{TOT} = \gamma^{LW} + \gamma^{AB} \tag{S4}$$

where  $\gamma^{AB}$  component is further simplified in terms of the electron-accepting ( $\gamma^+$ ) and electrondonating ( $\gamma^-$ ) components (i.e., Lewis acidity and basicity, respectively):<sup>4</sup>

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \tag{S5}$$

The solid-liquid interfacial energies are given as

$$\gamma_{SL}^{LW} = \left(\sqrt{\gamma_L^{LW}} - \sqrt{\gamma_S^{LW}}\right)^2 \tag{S6}$$

$$\gamma_{SL}^{AB} = 2\left(\sqrt{\gamma_{S}^{+}\gamma_{S}^{-}} + \sqrt{\gamma_{L}^{+}\gamma_{L}^{-}} - \sqrt{\gamma_{S}^{+}\gamma_{L}^{-}} - \sqrt{\gamma_{S}^{-}\gamma_{L}^{+}}\right)$$
(S7)

By combining equations S2 - S4 and S6 - S7, the Young-Dupré equation used for analysis of the measured contact angles is obtained:

$$(1 + \cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^{LW} \gamma_L^{W}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}\right)$$
(S8)

The Young-Dupré equation (equation S8) depicts the force-balance equilibrium for a liquid droplet on a flat substrate.<sup>5</sup> To characterize the acid-base properties of a solid surface, CAMs from at least three different liquids with known surface free energies ( $\gamma_{L}^{LW}, \gamma_{L}^{+}, and \gamma_{L}^{-}$ ) must be acquired. By convention, the liquid combination should consist of two polar (H<sub>2</sub>O and CH<sub>3</sub>NO) liquids and one nonpolar liquid (CH<sub>2</sub>I<sub>2</sub>); the surface energy components of the probe liquids are presented in Table S1.

*Contact Angle Measurement and Surface Energy Extraction.* CAMs were conducted under ambient conditions with a commercial system (Attension Theta Optical Tensiometer, Espoo, Finland) in an enclosed chamber to exclude contamination. The system is equipped with a video camera, an adjustable sample stage, and an LED light source (Figure S1). Two polar and one nonpolar liquids with known surface energy components were used for CAM (Table S1): deionized water, diiodomethane (99% purity, from Aldrich), and formamide (99.5% purity, from Aldrich). The contact angles ( $\theta$ ) for the different liquids were measured immediately after ion beam bombardment. The experimental procedure involved dispensing a small drop (0.5–1.0 µL) of the test liquid on the substrate. The drop shape and  $\theta$  profile were monitored with the digital camera during deposition and fluid evaporation process, and the drop diameter, left and right contact angles and volume were recorded. The advancing contact angles were used for the analyses. The advancing contact angle is widely considered to be a good approximation of the

Young's contact angle.<sup>6</sup> The sample stage was rotated to ensure that a clean surface was tested for each experiment. The drop images obtained were processed using the OneAttension software on the system. The Young–Laplace equation was used to mathematically describe the drop contour from which the contact angles were determined. The contact angles formed by the microdroplets of the liquids were the equilibrium values calculated as the mean of measurements from at least seven droplet experiments (Table 1).

Using the known surface energy components of the liquids,  $\gamma_{L}^{LW}, \gamma_{L}^{+}, and \gamma_{L}^{-}$ , and the measured advancing contact angles, the Lifshitz-van der Waals and the acid-base components ( $\gamma_{S}^{LW}, \gamma_{S}^{+}, and \gamma_{S}^{-}$ ) of the substrate surfaces, which are unknown, can be determined. For the three test liquids, equation S8 can be written separately as:

$$(1 + \cos\theta_W)\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right)$$
(S9)

$$(1 + \cos\theta_F)\gamma_L = 2\left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}\right)$$
(S10)

$$(1 + \cos\theta_D)\gamma_L = 2\left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}\right)$$
(S11)

where  $\theta_D$ ,  $\theta_W$ , and  $\theta_F$  are contact angles (in degrees) for diiodomethane, water, and formamide on pristine and ion beam bombarded sapphire supports, respectively. The  $\gamma_L^+$  and  $\gamma_L^-$  for the apolar liquid (diiodomethane) are both zero and thus equation S11 reduces to:

$$\gamma_S^{LW} = \gamma_L \frac{(1 + \cos \theta_D)^2}{4} \tag{S12}$$

This allows for  $\gamma_{S}^{LW}$  to be calculated from  $\gamma_{L}$  of the apolar liquid. Consequently, we are left with two equations, S9 and S10, with only two unknowns ( $\gamma_{S}^{+}$ , and  $\gamma_{S}^{-}$ ). With the mean contact angles from two polar solvents (H<sub>2</sub>O and CH<sub>3</sub>NO), the unknowns can be determined by solving equations S9 and S10 simultaneously.

The extraction of surface energy components using CAM has two main challenges:<sup>3,7</sup> (1) sensitivity of the extracted surface energy values to the selected probe liquid combination, and (2) the contact angle data scatter produces larger uncertainty for surface energy components obtained from select liquid combinations. To address these challenges, a method developed by

Clark et al.<sup>7,8</sup> was used to extract the surface energy components from equations S9 - S11. The method involved using Monte Carlo error analysis whereby both the calculated  $W_{adh}$  values and corresponding standard deviations were used to generate 1,000 individual datasets using a normal distribution. The "goodness" of the fit was ascertained using reduced chi-square values. The advantage of this approach is that it reduces the sensitivity of the surface energy components to the liquid combination by constraining the extracted energy components to adequately match each liquid or datum of  $W_{adh}$  in the dataset. In addition, the numerous datasets generated enables the simulation of the contact angle data scatter, and consequently, the direct characterization of the sensitivity of each surface energy component.

Table S1.	Liquids	$\gamma^{TOT}$	$\gamma^{\rm LW}$	$\gamma^{AB}$	$\gamma^+$	γ-	η	Surface
Components Probe Liquids	Water (polar)	72.8	21.8	51	25.5	25.5	0.010	for the at 20°C in
$mJ/m^2$ , and $Viscosities.^5$	Formamide (polar)	58	39	19	2.28	39.6	0.0376	their
	Diiodomethane (apolar)	50.8	50.8	0	0	0	0.028	



**Figure S1.** Schematic setup of contact angle measurement apparatus, consisting of a computer controlled syringe pump, high-speed camera, and sample stage. The syringe pump feeds the test fluid through tubing to a small (33 gauge) stainless steel syringe needle (inner diameter:  $\sim$ 120  $\mu$ m, outer diameter: 210  $\mu$ m).



(1) Fit XRR from controlled sapphire to extract atomic density and surface roughness





(3) Fit XRR from ion beam damaged sample using two layers on top of substrate: - Use atomic density of substrate fixed at 3.99 g/cc



Figure **S2**: Steps used to fit the X-ray reflectivity (XRR) pattern measured on multiplayer film containing damaged (via ion beam bombardment) layers on top of crystalline sapphire.

(a) X-ray diffraction (XRD) setup





(c) Relation between lattice plane and X-ray angles



(d) Extracted lattice constants (d<sub>hkil</sub>) at various degrees of damage

Accelerating voltage	2θ [degrees]	d <sub>hkil</sub> [Å]	Strain [%]
0	41.63	2.1669	0
3 kV	41.65	2.1659	0.04
5 kV	41.7	2.1634	0.16
6 kV	41.77	2.16	0.32

Figure **S3**: (a) X-ray diffraction (XRD) setup used to measure the spacing between different crystal planes of ion beam damaged sapphire. (b) XRD spectra collected from substrates damaged with different degrees of ion beam by variation in acceleration voltage from 3-6 kV. (c) Schematic representation of the relationship between incident angle ( $\theta$ ) and distance between crystallographic planes (d<sub>hkil</sub>) of c-cut sapphire, where h,k,i,l are miller indices. (d) Shift in X-ray diffraction peak with variation in ion beam acceleration voltage suggests presence of residual strain up to 0.32% in the crystalline layer below layers 1 and 2 (Figure 3).

## Section S1: Evolution of Substrate Properties during CNT Growth

In this supplementary section, we present the structural evolution of the catalyst substrate during CNT growth. To perform this, XRR was first performed on ion-beam damaged substrates and then analyzed to obtain the thicknesses and densities of Layer 1 and Layer 2 [Figure S4(a)]. These substrates were later subjected to a "dummy" CNT growth run (*i.e.*, H<sub>2</sub> treatment at 585 °C for 10 min and then a mixture of argon, H<sub>2</sub> and ethylene treatment at 760 °C for 30 min) without the use of Fe catalyst. Figure S4(b) plots thicknesses and atomic densities for the two layers after the "dummy" CNT growth. The observed decrease in damage depth after CNT growth suggests recrystallization of the damaged layer at high temperatures used for catalyst annealing and CNT growth. Atomic density for Layer 1 stays unchanged, remaining close to the stoichiometric value of 3.99 g/cc during CNT growth while the density of Layer 2 decreases. This suggests that the total porosity within the substrate remains constant during the recrystallization process (CNT growth run) and is distributed within a thinner damage layer at a higher density (which leads to lower atomic density) after the growth run. For comparison, we also measured the evolution of layer thickness and atomic density for an alumina supporting layer deposited by atomic layer deposition during the "dummy" CNT growth and observed negligible change in layer thickness (from 9.95 nm to 9.54 nm) and atomic density (from 3.11 g/cc to 2.94 g/cc).



**Figure S4.** The thickness and the density of different layers present at the surface of ion beam damaged sapphire (a) before (b) after CNT growth. The substrate is damaged at an acceleration voltage of 5 kV and for different ion doses. The data in Figure (a) is obtained by fitting XRR patterns of Figure 4(a). Figure (b) is obtained by processing similar XRR data taken after CNT growth. The dashed line shows the stoichiometric density of  $Al_2O_3$  (3.99 gm/cc).

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