

## Crystal Plane Dependence of Adsorption and Reaction on Zinc Oxide

It is well known that specific activity in methanol synthesis of samples of zinc oxide increases with increasing specific surface area (1). This behavior could be the result of these high area zinc oxides subtending a greater proportion of a more active crystal plane. The purpose of this note is to explore this hypothesis by examining the adsorptive and reactive properties of three samples of zinc oxide of different surface area. They are: (i) AnalaR grade zinc oxide having a total surface area  $3 \text{ m}^2\text{g}^{-1}$ , prepared by the ignition of zinc in an oxidizing atmosphere—its listed purity was 99.7%, the major carbonate impurity (0.25%) being lost by our method of pretreatment (see below); lead (0.02%) is the major metallic impurity; (ii) a high surface area material of total surface area  $36.5 \text{ m}^2\text{g}^{-1}$ , prepared by precipitation from the nitrate solution by sodium carbonate; after washing, the precipitate is calcined in air at 570 K for 6 h any residual carbonate being removed by the pretreatment method described below; the major impurity is sodium (0.016%) by X-ray fluorescence; (iii) prism face single crystal of total surface area of ca.  $0.3 \text{ m}^2\text{g}^{-1}$ —these crystals were grown from the vapor phase and were 99.9995% pure.

Transmission electron micrographs of typical crystallites of the AnalaR grade and high surface area zinc oxides, magnified 70 and 250 K respectively, are shown in Figs. 1a and b. The former are about 7000 Å in length (prism face) and 3000 Å in width (polar face) (corresponding to a surface area ca.  $3 \text{ m}^2\text{g}^{-1}$ ), while the latter are about 150 Å across (polar face) with an aspect ratio of about 1 (by X-ray diffraction line broaden-

ing). The polar faces constitute between 14 and 20% of the total surface area of the AnalaR grade zinc oxide and about 33% of the high surface area zinc oxide. Plate 1c is a light microscopy photograph (at 100 times magnification) of some of the rods of the prism face single crystal zinc oxide. The rods were relatively long (ca. 0.1 cm) and narrow ( $<1 \times 10^{-3}$  cm) from which the polar face is calculated to occupy  $<0.5\%$  of the total surface area.

The techniques used—temperature-programmed desorption (tpd) and temperature-programmed reaction spectroscopy (tprs)—were applied to each of the three samples and have been described previously (2). A description of the apparatus involved is also to be found there. The sample pretreatment and the method of dosing the adsorbates was the same for all three materials; each was pretreated in hydrogen (99.99% pure (Air Products), ca. 1 Torr pressure) at 550 K for 15 min after which the gas phase hydrogen was pumped away until the pressure reached the background level, ca.  $10^{-8}$  Torr. The hydrogen adsorbed during this process was removed by increasing the temperature to 700 K under vacuum, a fact which was confirmed by lowering the temperature thereafter to ambient and temperature programming to 700 K when no desorption of hydrogen (or any other molecule) was observed. Microreactor experiments with the AnalaR grade and high surface area zinc oxides showed that pretreatment at 500 K in a hydrogen/helium stream (5%  $\text{H}_2$  in He, 1 atm total pressure) which had been scrubbed of water by passage through a 13X molecular sieve, pro-

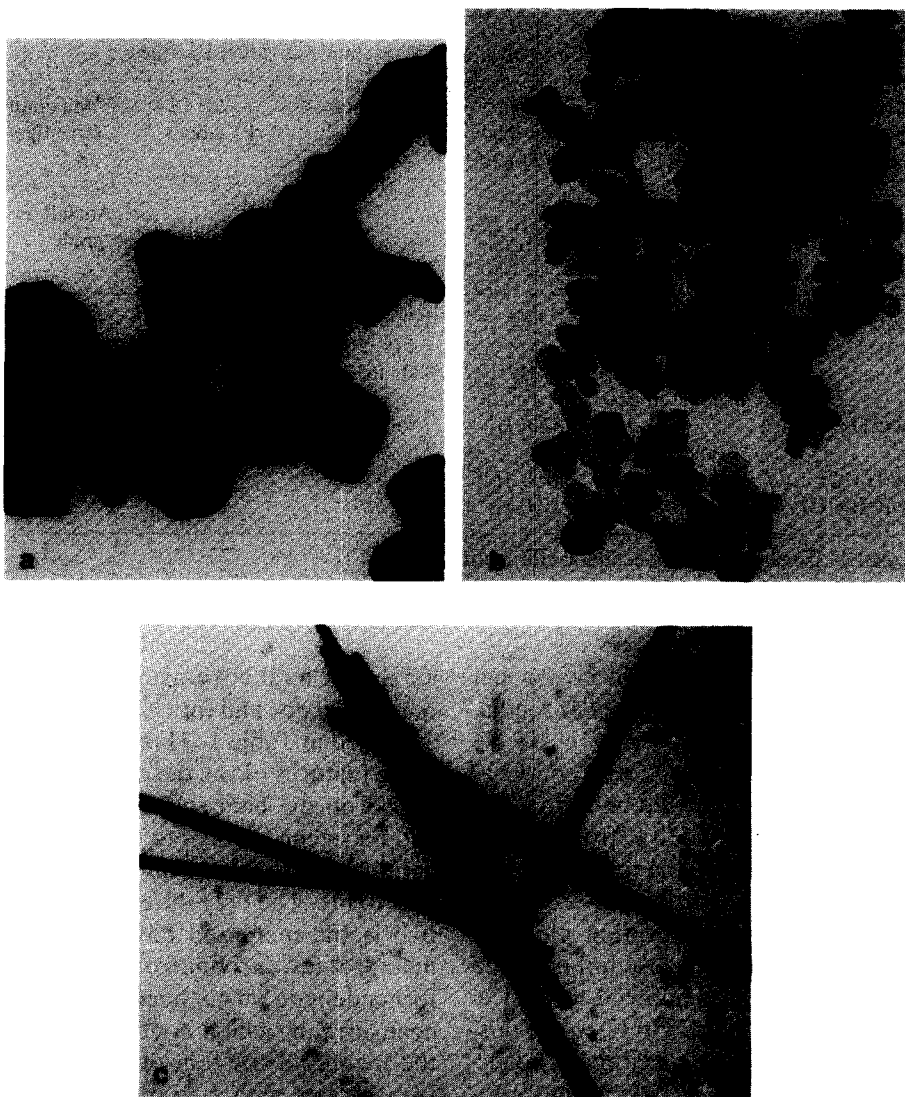


FIG. 1. (a) Transmission electron micrograph of the AnalR grade zinc oxide showing examples of the large rectangular crystallites—about 7000 Å long and 3000 Å across the end face (magnification 70K). (b) Transmission electron micrograph of the high surface area zinc oxide showing the slivers of the polar faces about 150 Å in diameter (magnification 250K). (c) Light microscopy photograph of the single crystal prism face zinc oxide ca. 0.1 cm long and ~0.001 cm in diameter (magnification 100).

duced water so that, prior to dosing the adsorbates, both of these materials will be reduced. However, as explained previously (2), the nature of the hydrogen pretreatment in the tpd apparatus precluded detection and measurement of the water produced and so these materials can only be

said to be reduced to an unspecified but reproducible extent. Since no microreactor experiments were conducted on the single crystal zinc oxide no comment can be made upon whether the hydrogen pretreatment actually reduced this material. This form of pretreatment was instituted to produce a

TABLE I  
Adsorbed Species, Coverages, and Desorption Activation Energies

Adsorbed species/ (adsorbate)	Adsorption temperature (K)	Major desorbed products	Temperatures of peak maxima (K)	$E_d^a$ (kJ mol <sup>-1</sup> )	Maximum total coverage/species cm <sup>-2</sup>	
					AnalaR grade	High surface area
CO <sub>2</sub> /(CO <sub>2</sub> )	530 (Cooled in gas)	CO <sub>2</sub>	390, 420, 510, 560	109, 117, 142, 153	1 × 10 <sup>13</sup>	1 × 10 <sup>13</sup>
H/(H <sub>2</sub> )	530 (Cooled in gas)	H <sub>2</sub>	420, 465, 540	117, 130, 150	6 × 10 <sup>12</sup> (atoms)	5 × 10 <sup>12</sup>
Formate/(CO <sub>2</sub> + H <sub>2</sub> )	530 (Cooled in gas)	CO, H <sub>2</sub>	~570	157	3 × 10 <sup>13</sup>	5 × 10 <sup>13</sup>
Formate/(H <sub>2</sub> CO)	310	CO, H <sub>2</sub>	580	160	1 × 10 <sup>14</sup>	2 × 10 <sup>14</sup>
Formate/(CH <sub>3</sub> OH)	310	CO, H <sub>2</sub>	580	160	1 × 10 <sup>14</sup>	2 × 10 <sup>14</sup>

<sup>a</sup> Calculated assuming a preexponential factor of 10<sup>13</sup> s<sup>-1</sup>.

surface condition which would bear a fair resemblance to that obtaining under methanol synthesis conditions.

The adsorbates (CO, CO<sub>2</sub>, H<sub>2</sub>, and CO<sub>2</sub>/H<sub>2</sub> coadsorption) were dosed on to the zinc oxide which was held at 530 K from a background pressure (ca. 1 Torr) for 15 min in a six-way metal cross piece (ca. 220 cm<sup>3</sup>) which comprises the adsorption chamber (2). The heating was then discontinued and the adsorbent was then allowed to cool to ambient temperature (ca. 310 K) in the dosing gas (ca. 15 min). The gas phase adsorbate was then pumped away and programmed temperature increase began when the pressure in the chamber had fallen to its background value (ca. 15 min). The method of dosing methanol and formaldehyde was the same as that just described except that the adsorption temperature was 310 K.

The results of this type of experimentation for the above adsorbates on AnalaR grade zinc oxide have been reported in some detail previously (2). The salient features of these spectra, the temperatures of the desorption peak maxima, the major products desorbing, the derived desorption/decomposition activation energies and the

maximum total coverages cm<sup>-2</sup> for each of the adsorbates and for CO<sub>2</sub>/H<sub>2</sub> coadsorption are listed in Table I. This table also lists the same features of the desorption spectra obtained on the high surface area zinc oxide and these can be seen to be virtually identical to those obtained on the AnalaR grade zinc oxide. The only difference between the two is the increased coverage of the formate species, deriving from the adsorption of formaldehyde or methanol or from CO<sub>2</sub>/H<sub>2</sub> coadsorption which is commensurate with the increased fraction of polar face of the high surface area zinc oxide. (The formate species was uniquely characterized by temperature-programmed reaction spectroscopy by the coincident desorption of CO and H<sub>2</sub> at 570 K after adsorption of methyl formate at room temperature, the methoxy species also formed in this dissociative adsorption, desorbing as methanol and formaldehyde coincidentally at 340 K (3).) No such spectra were obtained on the prism face single crystal zinc oxide in the adsorption temperature range of 300 to 550 K even though the combined gains of the electron multiplier and of the mass spectrometer were increased by a factor of 3 × 10<sup>2</sup> to

compensate for the reduction in the surface area. We conclude therefore that the adsorptions and surface reactions observed on the AnalaR grade and high surface area zinc oxide are confined to the polar faces of the zinc oxide.

This observation is in direct contrast to those of Gopel *et al.* (4) who found CO<sub>2</sub> to adsorb on the nonpolar surface of zinc oxide with an initial sticking probability  $S_0(298) = 0.6$ , giving coverages up to  $6 \times 10^{13}$  molecules cm<sup>-2</sup> having a desorption activation energy of 90 kJ mol<sup>-1</sup> and a frequency factor of  $1.6 \times 10^{14}$  s<sup>-1</sup>. This appears all the more surprising since the zinc oxide crystals used in both sets of experiments are the same, being supplied by Professor G. Heiland (Aachen). However, the desorption half-life of this state described by Gopel *et al.* is only 4 s at 310 K, which is considerably shorter than 900 s, the time during which our chamber is evacuated before temperature programming was begun. The experimental technique employed here therefore precludes any possibility of its being observed; Gopel *et al.* actually temperature-programmed in different background pressures of the dosing gas to obtain the desorption spectra. Nevertheless the marked differences between the desorption spectra of CO<sub>2</sub> from both the AnalaR and high surface area zinc oxides, and the {1010} single crystal zinc oxide (the former two are heteroenergetic and strongly held while in Gopel's work the latter shows only one weakly held state) point to the adsorption occurring only on the polar faces of the polycrystalline materials.

This view that the polar faces are the active faces for the hydrogenating properties of zinc oxide has been mooted by Grunze *et al.* (5) after their observation that only crystals of zinc oxide "exhibiting a reasonable percentage of polar faces" showed

pronounced Zn-H and O-H bands in the infrared spectrum after exposure to hydrogen.

Furthermore since the conditions of pretreatment of this zinc oxide are only slightly more reducing than those existing at steady state during methanol synthesis, we also conclude that the adsorption of hydrogen and carbon dioxide, and their surface reaction to form the formate and thence methanol all take place on the polar faces of the zinc oxide only. The role of the CO appears to be that of a reducing agent, maintaining the zinc oxide in a sufficiently anion-deficient state.

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MICHAEL BOWKER  
HILARY HOUGHTON  
KENNETH C. WAUGH

*New Science Group—Catalysis  
Imperial Chemical Industries PLC  
P.O. Box 11  
The Heath  
Runcorn  
Cheshire WA7 4QE, England*

TRACY GIDDINGS  
MINO GREEN

*Department of Electrical Engineering  
Imperial College  
Exhibition Road  
London SW7 2BT, England*

*Received January 25, 1983*