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High-Resolution Electron Microscopy of $LaPO_4$ Catalysts

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High-resolution electron microscopy has revealed a difference in morphology of the crystallites of samples of $LaPO_4$ which are good and poor catalysts for the hydrolysis of aromatic chlorides. In the good catalysts an acicular habit is such as to expose chains of La and PO_4 ions which run parallel to the c axis of the crystal. Observations of lattice fringes include those of forbidden reflections, suggesting some modification of the structure, as well as revealing structural imperfections.

INTRODUCTION

Rare-earth phosphates containing trace amounts of copper have been shown to be effective substitutes for copper-promoted tricalcium phosphate as catalysts for the hydrolysis of aromatic chlorides (*1*). The mechanism for the hydrolysis reaction is not understood, but the presence of the copper appears to be significant. For a typical reaction, increase in the copper content from 0 to 1000 ppm gives an increase in the conversion from 13 to 32 wt%, and although the selectivity decreases from 100 to 90 wt% the yield increases from 13 to 29 wt% (*1*).

The rare-earth phosphates (represented by $LaPO_4$) are orthophosphates and exist in a hexagonal form when formed by precipitation. In the oven-dried state the preparation is hydrated and usually described as $LaPO_4 \cdot \frac{1}{2}H_2O$. The crystal structure (*2*) contains large open channels which are thought to accommodate the water and foreign ions such as the copper between chains of alternating La and PO_4 ions. On heating, the hexagonal form undergoes a rather sluggish transformation between 250 and 350°C to a monoclinic form (*3*) which is the catalytically active modification. The crystal size, as indicated by the breadth of X-ray diffraction powder pattern lines, is small and decreases with increasing copper content. Heating to 800°C gives larger crystals which are catalytically inactive.

The role of the copper is thought to be that the copper ions associated with water in the channels of the hexagonal structure inhibit the structural transformation so that a distorted or disordered monoclinic structure having the desirable catalytic properties is obtained. The catalytic activity is presumably related to the association of copper with OH^- ions on the surface of the disordered structure.

During the early stages of the commercial development of this catalyst a dif-

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ficult problem was encountered with lack of reproducibility of the catalytic properties of repeat preparations. Consecutive preparations would often vary in activity widely, as suggested in Table 1, but no differences between the catalysts could be detected by use of X-ray diffraction or by any of the several conventional analytical techniques that were tried. We have therefore applied the techniques of high-resolution electron microscopy which have recently been developed to the stage of providing structural information on an atomic level for small, stable crystals (*4*, *5*). These methods quickly provided the first tangible evidence of differences that correspond with catalytic activity. We report the observations here as an indication that high-resolution electron microscopy may well be a powerful tool for use in the development and characterization of catalysts.

METHODS

Three samples have been examined. One, labeled sample A, was a poor catalyst. Two, samples B and C, were good catalysts. The samples were prepared by precipitation from a solution of a lanthanum salt under carefully controlled pH conditions. The dried precipitates consisted of the hexagonal form of $LaPO_4$ and were activated by calcining in air at 600°C to effect at least a partial transformation to the monoclinic form. All samples contained 0.05 wt% copper.

For electron microscopy a small drop of a suspension of the powder in water was dried on a carbon micromesh grid. Electron diffraction patterns and both bright-field and dark-field images were obtained using a JEM-100B electron microscope with 100-keV electrons. Micrograph magnifications varied from 510,000 to 850,000 × in the microscope with subsequent optical magnification to form the prints reproduced in Figs. 2 to 5.

TABLE 1

Comparative Activities of $LaPO_4$ + 0.05 wt% Cu Catalysts for the Hydrolysis of Chlorobenzene to Cresol[a]

Catalyst	Conversion (wt%)	Selectivity (wt%)
A	11	96.5
B	32	98.0
C	41	97.5

[a] Temperature, 425°C; atmospheric pressure.

RESULTS

Electron Diffraction

The electron diffraction patterns from the three samples could not be distinguished. The diffraction rings were spotty and composed of rather large, extended spots consistent with the small sizes of the individual crystallites (Fig. 1). The measured *d* values were therefore inaccurate but showed reasonable agreement with those obtained from X-ray diffraction powder patterns of monoclinic $LaPO_4$ by Jaulmes (*3*) (see Table 2). Since absolute calibration of the effective camera length is difficult in an electron microscope, the spacing corresponding to the first ring, $d = 5.21$ Å, was assumed and used as a calibration.

It was concluded that the phase present was that found by X-ray diffraction to be monoclinic $LaPO_4$, space group $P2_1/a$, $a = 8.25$ Å, $b = 7.09$ Å, $c = 6.47$ Å, $\beta = 126°16'$, with a structure made up of chains of La and PO_4 ions parallel to the *c* axis.

High-Resolution Electron Microscopy

High-resolution images of the poor catalyst, sample A, showed small crystals, 50 to 150 Å in size, with irregular outline and no pronounced development in any particular direction. The ratio of maximum to minimum dimensions rarely exceeded 3 and was usually 1 to 2 (Fig. 2). Many of the crystals showed fringes correspond-

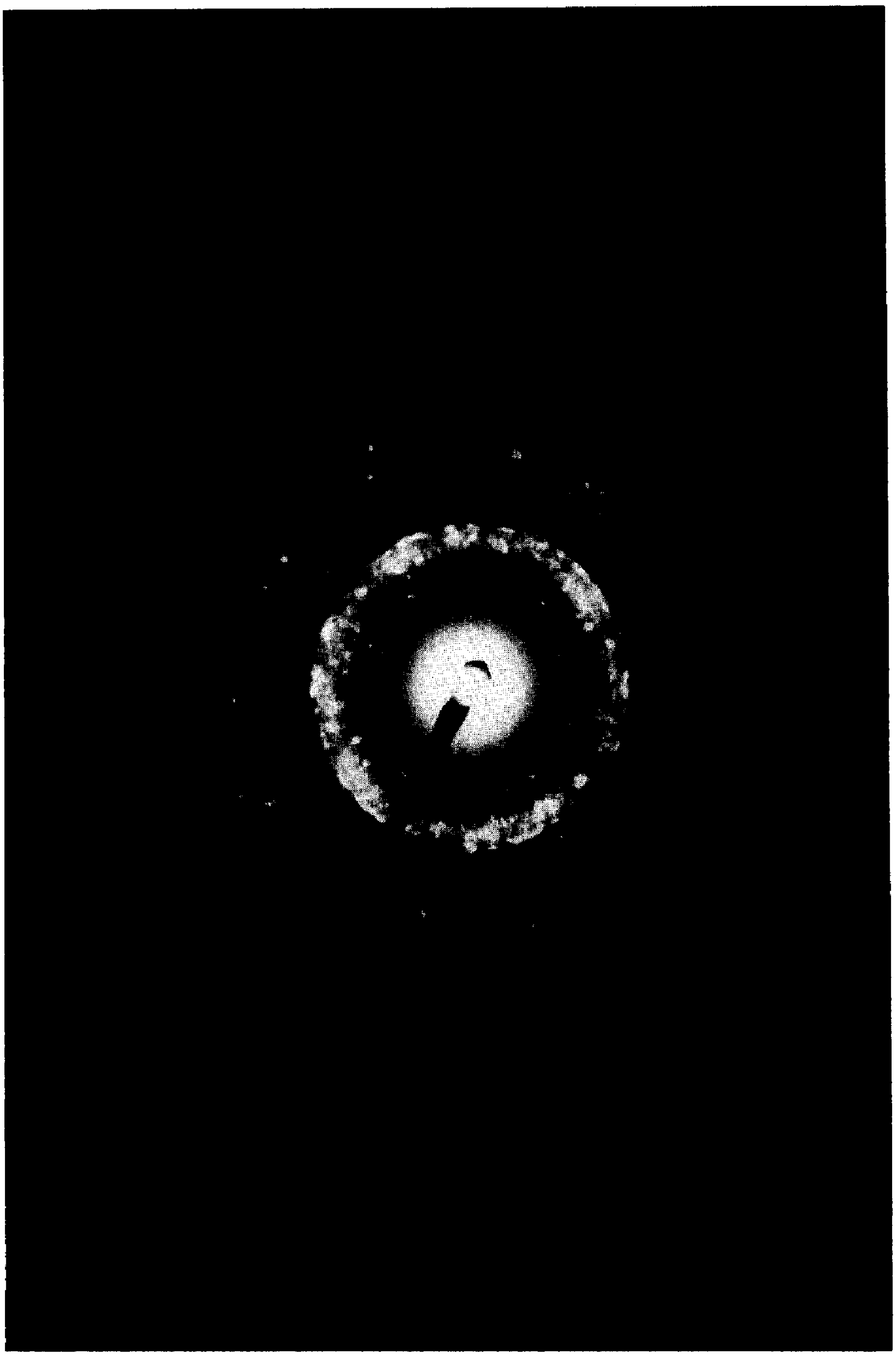

Fig. 1. Electron diffraction pattern of sample B obtained at 100 keV in the JEM-100B electron microscope from a specimen area a few micrometers in diameter.

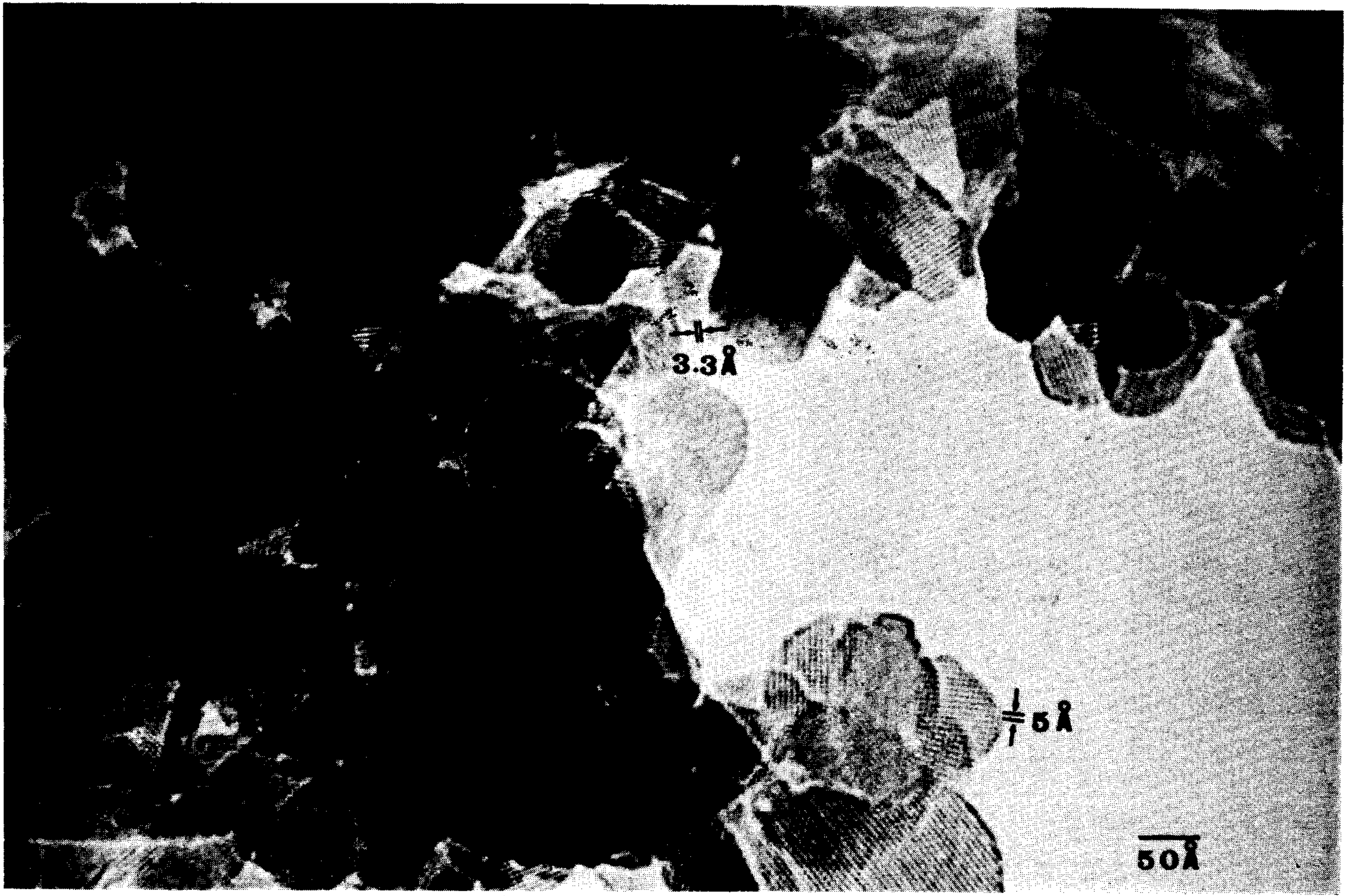

FIG. 2. High-resolution electron microscope image of sample A, the poor catalyst, showing lattice fringes with spacings in the range 3 to 5 Å; 100 keV electrons.

FIG. 3. High-resolution electron micrograph of sample B, a good catalyst, showing acicular habit of the crystals and lattice fringes including the anomalous 6.5 Å spacing (indicated); 100-keV electrons.

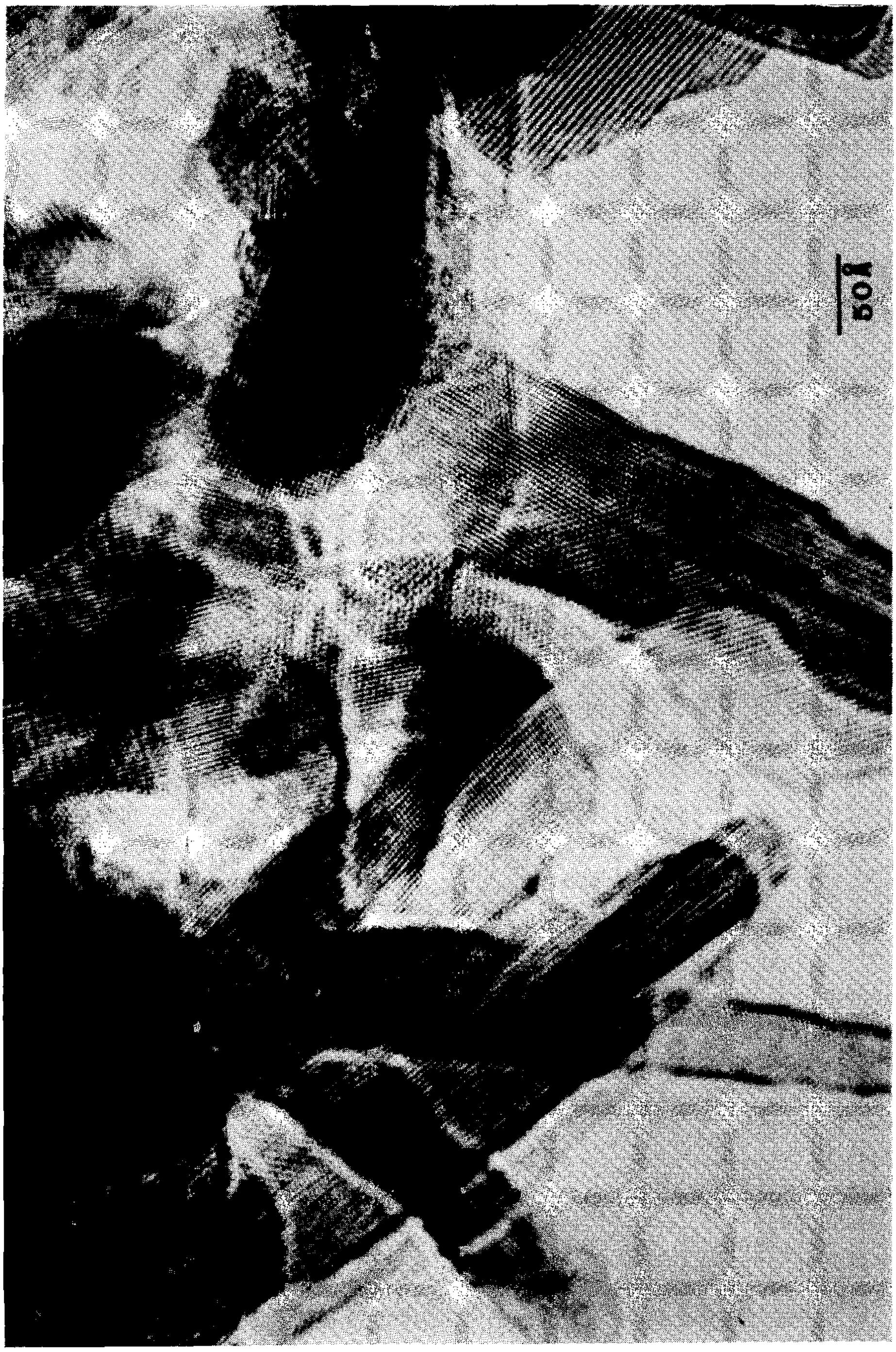

FIG. 4. High-resolution electron micrograph of sample C, a good catalyst, showing acicular habit of the crystals; 100-keV electrons.

FIG. 5. High-resolution electron micrograph of sample B after heating to 800°C in air showing the change in crystal size, shape, and degree of perfection; 100-keV electrons.

TABLE 2

Electron Diffraction Powder Pattern, Sample B[a]

Int (obs)	d (obs)	d (mono $LaPO_4$)	Int (X ray)	*hkl*
W	5.21	5.2	W	001
W	4.81	4.81	W	110
		4.69	W	$\bar{1}11$
MW	4.12	4.19	M	011
		4.12	W	$\bar{2}01$
M	3.52	3.54	S	020
M	3.35	3.31	S	200
		3.14	W	202
S	3.11	3.10	S	$\bar{1}21$
		2.99	M	111
MS	2.87	2.87	S	$\bar{1}12$
W	2.65	2.60	M	002
MW	2.41	2.45	M	012
		2.41	W	220
W	2.32	2.34	VW	$\bar{1}22$
		2.25	VW	201
M	2.16	2.20	S	131
		2.15	S	$\bar{3}21$ $\bar{2}03$
MW	1.93	1.98	S	$\bar{4}12$

[a] The d value of 5.21 was assumed for the innermost ring.

ing to lattice plane spacings in the range of 3 to 5 Å. The observed fringe spacings are listed in Table 3a. Within the limits of accuracy of measurement (a few percent) the spacings are seen to correspond to lattice plane spacings of Table 2. When patterns of crossed fringes appeared, giving two-dimensionally periodic patterns (excluding fringe sets obviously due to the formation of moire patterns from overlapping crystals) these could be assigned indices consistent with the monoclinic structure. The occurrence of the "forbidden" $0\frac{1}{2}\frac{1}{2}$ and 010 spacings may possibly be moire effects but are more likely to arise from local perturbations of the structure or (in the case of 010) from dynamical diffraction effects.

For both the good catalysts, samples B and C (Figs. 3 and 4, respectively), the small crystals show a very pronounced acicular habit with minimum dimension 50–100 Å and a maximum dimension

TABLE 3

Measured Fringe Spacings From High-Resolution Micrographs

(a)		(b)		(c)	
Spacings	*hkl*	Spacings	*hkl*	Spacings	*hkl*
Single fringe		Fringes along needles		Fringes along needles	
8.7	$0\frac{1}{2}\frac{1}{2}$				
5.7, 5.3	001	6.5, 6.4	100	6.4, 6.3	100
4.4, 4.3, 4.2	011	4.9, 4.75	110	4.8	110
3.6	020	3.15	200		
Intersecting sets of fringes		Fringes at right angles		Fringes at right angles	
Two sets					
5.2	001	5.3	001	4.95, 4.85	110
4.8	$\bar{1}10$				
4.7	$\bar{1}11$				
		Fringes at other angles		Fringes at other angles	
At 90°					
7.0	010	4.8	$\bar{1}11$	5.0	001
3.5	200	4.2	011	4.6, 4.5	$\bar{1}11$
				4.15	011

greater than this by a factor ranging from 4 to 10. The lattice fringe spacings measured for these crystals showed a very marked correlation with the morphology. The measured spacings for fringes running parallel to the needle axes, approximately perpendicular to the needle axes, and in intermediate orientations are listed separately in Tables 3b and c. These results suggest strongly that the long axes of the acicular crystals coincide with the crystallographic *c* axis, i.e., with the direction of the La–PO_4 chains in the structure. The "forbidden" 100 plane spacing recurs frequently for clearly defined sets of fringes, suggesting that in these crystals the symmetry of the crystals is not that found from the X-ray diffraction work, $P2_1/a$. Defects and disorder in the crystals are frequent, as evidenced by variations of contrast and spacing of the lattice fringes.

Portions of the good catalysts were heated for 2 hr at 800°C in air and then again examined in the electron microscope. The morphology of the crystallites was seen to have changed completely (Fig. 5). The crystals had become larger and roughly spherical with average dimensions 200–300 Å. There was considerable evidence of sintering. A smaller proportion of the crystals showed lattice fringes: This is consistent with the observation of larger and more perfect crystals. The fringe spacings measured are listed in Table 4. The single observations of the "forbidden" spacings 7.3 Å (010) and 6.5 Å (100) seem to suggest that the symmetry may not be that determined by X-ray diffraction, at least for some crystallites, but these observations may well be due to dynamical diffraction effects. There is very little evidence of disorder or defects within the crystallites.

TABLE 4

Measured Fringe Spacings for Heated Samples

Spacings	*hkl*
7.28	010
6.5	100
4.61, 4.51, 4.50, 4.48	$\bar{1}11$
4.37, 4.33	011
4.12, 4.02, 3.99	$\bar{2}01$
3.38, 3.36	020, 200

DISCUSSION

The number of independent preparations of the catalyst examined was small, but sufficient observations on each sample were made to confirm that the results reported are characteristic of the particular samples. There is a very striking difference in the morphology of the crystals for the good and poor catalysts. The good catalytic properties of the best $LaPO_4$ catalysts appear to be associated with an acicular habit with the needle axis parallel to the crystallographic *c* axis. The morphology is such as to maximize the surface exposure of *hk*0 planes. The chains of alternating La and PO_4 ions, parallel to the *c* axis, thus lie exposed on these surfaces. If the catalytic activity depends on access of the reactant molecules to sequences of Cu and OH^- ions associated with these chains, this morphology is obviously a very favorable one.

The common appearance of the "forbidden" (100) lattice plane spacing in the images of the crystals of the good catalysts suggests some deviation from the $P2_1/a$ symmetry of the structure deduced by X-ray diffraction. It is possible that this spacing might be produced by dynamical "double-diffraction" effects which are known to result in the appearance of reflections which are forbidden by the space group symmetry in kinematical scattering. Such reflections are very weak or absent when the incident beam is in special orientations in relationship to the relevant symmetry element of the crystal but may become strong in other orientations (*6*). It is characteristic of such reflections, however, that they are always very weak for thin crystals and then increase in strength with crystal thickness much more rapidly than normal reflections. No evidence of such behavior was noted in the present case except that the appearance of the forbidden reflection spacings in the thicker, more perfect crystallites of the samples heated to 800°C (Fig. 5) could well be due to this cause.

Another possible origin of these forbidden spacings could be a preferential association of copper atoms on the surfaces of the crystals with this periodicity. However, it seems unlikely that the number of copper atoms present would be sufficient to allow the observed contrast to be attributed to the contributions of copper atoms alone, especially in the presence of the much heavier lanthanum atoms in the structure. Some perturbation of the structure involving the shifting of the lanthanum atoms seems more probable. It was not clear whether any of the structural defects visible in the micrographs, Figs. 2 to 4, were associated with the presence of copper ions.

The presence of the (100) spacings in the images may be reconciled with the absence of the corresponding ring in the diffraction patterns such as Fig. 1 by consideration of the transfer function of the electron microscope objective lens. Large spacings will be imaged with much greater contrast than small spacings. For our microscope the contrast may be strongly suppressed for periodicities of less than 4 Å (*7*), i.e., for the periodicities of the strong second-order reflections which dominate the diffraction pattern.

Further information concerning the details of the structure of these catalysts could well be derived by application of the electron microscopes having better resolution, now becoming available, and by use of the microdiffraction techniques capable of providing diffraction patterns from individual small crystals in the size range occurring in these samples (*8*). Our observations to date have served the useful purpose of indicating in which directions these investigations should proceed.

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