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Identification by X-Ray Diffraction of MoS_2 in Used Co–Mo–Al_2O_3 Desulfurization Catalysts[1]

The nature of the molybdenum species in supported molybdena hydrodesulfurization (HDS) catalysts is still a matter of controversy. The primary controversy is whether the molybdenum exists as a monolayer across the support surface or in three-dimensional units. Of particular importance, from a practical standpoint, is the structure of the catalysts subsequent to the oxide-to-sulfide transformation caused either by treatment with a specific sulfiding agent (e.g., hydrogen sulfide or thiophene) or after use in an HDS reactor.

Massoth (*1*) has recently summarized the evidence for the structure of the sulfided catalysts. He concluded that the molybdenum monolayer present in the oxide form(s) of the catalyst is maintained upon sulfidation. Using Raman spectroscopy, Brown *et al.* (*2*) have recently suggested the presence of three-dimensional MoS_2 in a commercial catalyst of Co–Mo supported on SiO_2–Al_2O_3 after its use in a coal liquefaction reactor. X-Ray diffraction has previously been used to study sulfided Co–Mo–Al_2O_3 and Co–Mo–SiO_2 catalysts (*3*). de Beer *et al.* observed the strongest diffraction line of MoS_2, 6.15 Å, in two of the silica- and none of the alumina-supported catalysts sulfided with a mixture of H_2 and H_2S. This present note reports the results of an X-ray diffraction study of a commercial, Harshaw 0402T, Co–Mo–SiO_2–Al_2O_3 catalyst untreated, sulfided, and after use as a hydrodesulfurization catalyst for coal.

The unused catalyst contains, by weight, 3% CoO and 15% MoO_3 on silica-stabilized (5%) η-alumina. Reactor conditions were 450°C and 4000 psi pressure for a run that lasted 1068 hr, during which the catalyst was exposed to more than 12 tons of coal (*4*). Since the catalyst was not presulfided, the sulfidation occurred with sulfur from the coal matrix and under the extreme conditions of the reactor operation.

The X-ray diffraction data were collected on a Rigaku[2] horizontal goniometer using a copper X-ray tube operated at 40 kV and 35 mA. All measurements were made with a 1° divergent slit, 0.3-mm receiving slit, receiving graphite monochromator and scintillation counter with pulse-height discrimination. All samples were ground finer than about 20 μm and packed into a glass holder with an opening 16 × 8 × 0.5 mm. No binder or adhesive was needed.

Reproduced in Fig. 1 are representative diffractograms of the samples studied. Figure 1A, from the 0402T catalyst (oxide form) as received from the manufacturer, shows peaks due to η-alumina (the support), nordstrandite, [$Al(OH)_3$], and $CaMoO_4$. Molybdenum both as $CaMoO_4$ and as a monolayer species has previously been observed in this catalyst by Raman spectroscopy (*5*). Figure 1B is from the

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[2] Use of brand names facilitates understanding and does not necessarily imply endorsement by the U.S. Department of Energy.

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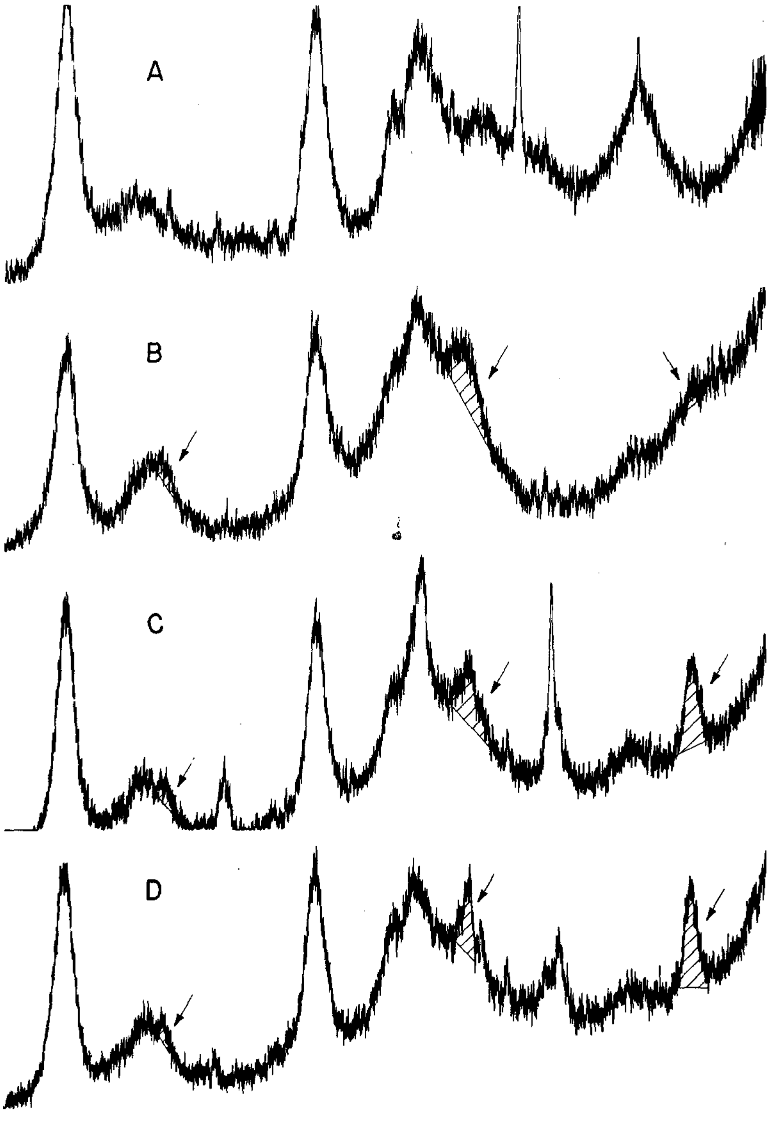

FIG. 1. Diffractogram of (A) unused Harshaw 0402T catalyst, (B) Harshaw 0402T sulfided at 440 to 450°C, with 10% H_2S in H_2, for 1 hr at 1650 to 1960 psi pressure, (C) spent Harshaw 0402T from reactor inlet, and (D) spent Harshaw 0402T from reactor outlet. Maximum intensity at top of chart for all curves was approximately 300 cps. A background subtraction setting on the ratemeter of 2.0 was used for all curves except "C," where the setting was 2.3. The use of this setting resulted in the straight-line background from 50 to 57° and 69 to 72°. Scanning speed 1° per min, chart speed 10 mm per min.

catalyst sulfided at 440 to 450°C for 1 hr with 10% H_2S in H_2 at 1650 to 1960 psi pressure, and Figs. 1C and D are diffractograms from the catalyst after use in the coal HDS reactor, removed from the inlet and outlet, respectively. The patterns for

ANGLE	D-SPACING	D	C	B	A	AA
10.00	8.838	199.	187.	228.	178.	229.
10.10	8.751	203.	187.	221.	178.	220.
10.20	8.665	198.	183.	225.	174.	223.
10.30	8.581	201.	~~181.~~	221.	173.	223.
10.40	8.499	195.	183.	226.	170.	223.
10.50	8.418	192.	181.	219.	167.	231.
10.60	8.339	186.	179.	215.	166.	235.
10.70	8.262	182.	176.	211.	168.	218.
10.80	8.185	185.	175.	216.	162.	225.
10.90	8.110	184.	172.	215.	163.	216.
11.00	8.037	180.	168.	211.	160.	228.
11.10	7.965	181.	171.	216.	159.	217.
11.20	7.894	184.	166.	214.	157.	215.
11.30	7.824	179.	166.	213.	157.	220.
11.40	7.756	177.	170.	212.	153.	210.
11.50	7.689	175.	170.	214.	154.	215.
11.60	7.622	179.	166.	206.	153.	211.
11.70	7.558	178.	161.	199.	149.	215.
11.80	7.494	173.	162.	205.	146.	206.
11.90	7.431	171.	164.	205.	147.	208.
12.00	7.369	174.	164.	200.	146.	208.
12.10	7.309	178.	160.	200.	148.	202.
12.20	7.249	171.	166.	201.	146.	204.
12.30	7.190	170.	161.	206.	147.	202.
12.40	7.132	174.	163.	203.	147.	197.
12.50	7.076	168.	157.	201.	144.	205.
12.60	7.020	172.	161.	202.	140.	201.
12.70	6.965	175.	162.	204.	147.	201.
12.80	6.910	174.	165.	201.	143.	200.
12.90	6.857	175.	165.	204.	144.	200.
13.00	6.805	178.	171.	202.	142.	195.
13.10	6.753	182.	174.	197.	143.	197.
13.20	6.702	189.	175.	196.	141.	195.
13.30	6.652	186.	179.	199.	139.	190.
13.40	6.602	191.	179.	195.	142.	194.
13.50	6.554	193.	185.	200.	139.	193.
13.60	6.506	196.	193.	199.	140.	182.
13.70	6.458	205.	194.	195.	145.	187.
13.80	6.412	213.	201.	203.	145.	189.
13.90	6.366	218.	209.	199.	143.	175.
14.00	6.321	224.	212.	197.	136.	182.
14.10	6.276	237.	212.	201.	145.	180.
14.20	6.232	238.	219.	197.	143.	176.
14.30	6.189	238.	219.	198.	143.	170.
14.40	6.146	240.	213.	197.	150.	173.
14.50	6.104	228.	214.	188.	147.	171.
14.60	6.062	222.	206.	184.	147.	171.
14.70	6.021	224.	208.	185.	146.	169.
14.80	5.981	216.	197.	177.	144.	164.
14.90	5.941	191.	184.	182.	147.	161.
15.00	5.901	179.	170.	172.	144.	160.
15.10	5.863	170.	165.	173.	147.	160.
15.20	5.824	170.	164.	177.	149.	156.
15.30	5.786	169.	159.	169.	152.	154.
15.40	5.749	163.	154.	170.	156.	156.
15.50	5.712	157.	156.	164.	156.	151.
15.60	5.676	158.	153.	165.	155.	152.
15.70	5.640	161.	150.	160.	152.	154.
15.80	5.604	153.	144.	~~160.~~	156.	146.
15.90	5.569	150.	144.	161.	157.	144.
16.00	5.535	154.	144.	160.	~~158.~~	150.
16.10	5.501	154.	144.	156.	160.	142.
16.20	5.467	152.	145.	155.	167.	140.
16.30	5.434	151.	142.	154.	159.	142.
16.40	5.401	149.	144.	158.	169.	143.
16.50	5.368	151.	141.	156.	172.	136.
16.60	5.336	149.	140.	152.	172.	136.
16.70	5.304	153.	141.	153.	175.	135.
16.80	5.273	154.	145.	147.	178.	132.
16.90	5.242	153.	142.	145.	179.	135.
17.00	5.211	150.	142.	149.	182.	136.

TABLE 1

List of *d* Spacings and Compounds Identified in Unused, Presulfided, and Spent Catalysts from the Reactor

2θ	*d* Spacings (Å)				Compound
	Unused 0402T	Sulfided 0402T	Reactor inlet	Reactor outlet	
14.2		6.2	6.2	6.2	MoS_2
18.6	4.77				Nordstrandite [$Al(OH)_3$], $CaMoO_4$
19.2		4.6	4.6	4.6	η-Al_2O_3
25.4			3.50	3.50	Anatase (TiO_2)
26.0			3.42	3.42	MoO_2
26.6			3.35	3.35	Quartz (SiO_2)
28.6	3.12				$CaMoO_4$
29.7			3.00	3.00	Pyrrhotite ($Fe_{1-x}S$)
31.3	2.86				$CaMoO_4$
31.9				2.80	Unidentified
32.4	2.76				Unidentified
33.0			2.71	2.71	MoS_2
33.6		2.67			MoS_2
34.4	2.60				$CaMoO_4$
37.0	2.43[a]	2.43[a]	2.43	2.43[a]	η-Al_2O_3, MoO_2
39.3	2.28	2.28	2.28	2.28	η-Al_2O_3, MoO_2
45.2	2.00				$CaMoO_4$
46.0	1.97	1.97	1.97	1.97	η-Al_2O_3
47.0	1.93				$CaMoO_4$
49.2	1.85[b]		1.85[c]		$CaMoO_4$, MoO_2
53.6			1.71		MoO_2
54.0	1.70				$CaMoO_4$
54.3				1.69	Unidentified
58.1	1.59				$CaMoO_4$
58.6		1.57	1.57	1.57	MoS_2
60.0	1.54	1.54	1.54	1.54	η-Al_2O_3
66.8	1.40	1.40	1.40	1.40	η-Al_2O_3

[a] Only η-Al_2O_3.
[b] Only $CaMoO_4$.
[c] Only MoO_2.

the sulfided, used inlet, and used outlet samples show the absence of nordstrandite and $CaMoO_4$, and the presence of η-alumina and poorly crystalline MoS_2. Arrows are used in Fig. 1 to indicate the broad lines due to MoS_2. Two of the lines, the (10) at 2.7 Å and the (11) at 1.58 Å overlap the broad (311) and (333) of η-alumina at 2.43 and 1.51 Å, respectively. The inlet and outlet samples also contain MoO_2. It has been suggested that the sulfided catalyst contains a mixture of MoO_2 and MoS_2 (*6*), but contrary evidence has also been presented (*7*). Table 1 lists the

FIG. 2. MoS_2 (002) reflection representative step scans from 10 to 17° 2θ at intervals of 0.1°, where each step was counted for 30 s. (AA) Harshaw 0402T catalyst sulfided at 450°C, with 10% H_2S in H_2, at atmospheric pressure, for 1 hr. (A) Unused Harshaw 0402T catalyst. (B) Harshaw 0402T sulfided at 440 to 450°C, with 10% H_2S in H_2, for 1 hr at 1650 to 1960 psi pressure. (C) Spent Harshaw 0402T from reactor inlet. (D) Spent Harshaw 0402T from reactor outlet.

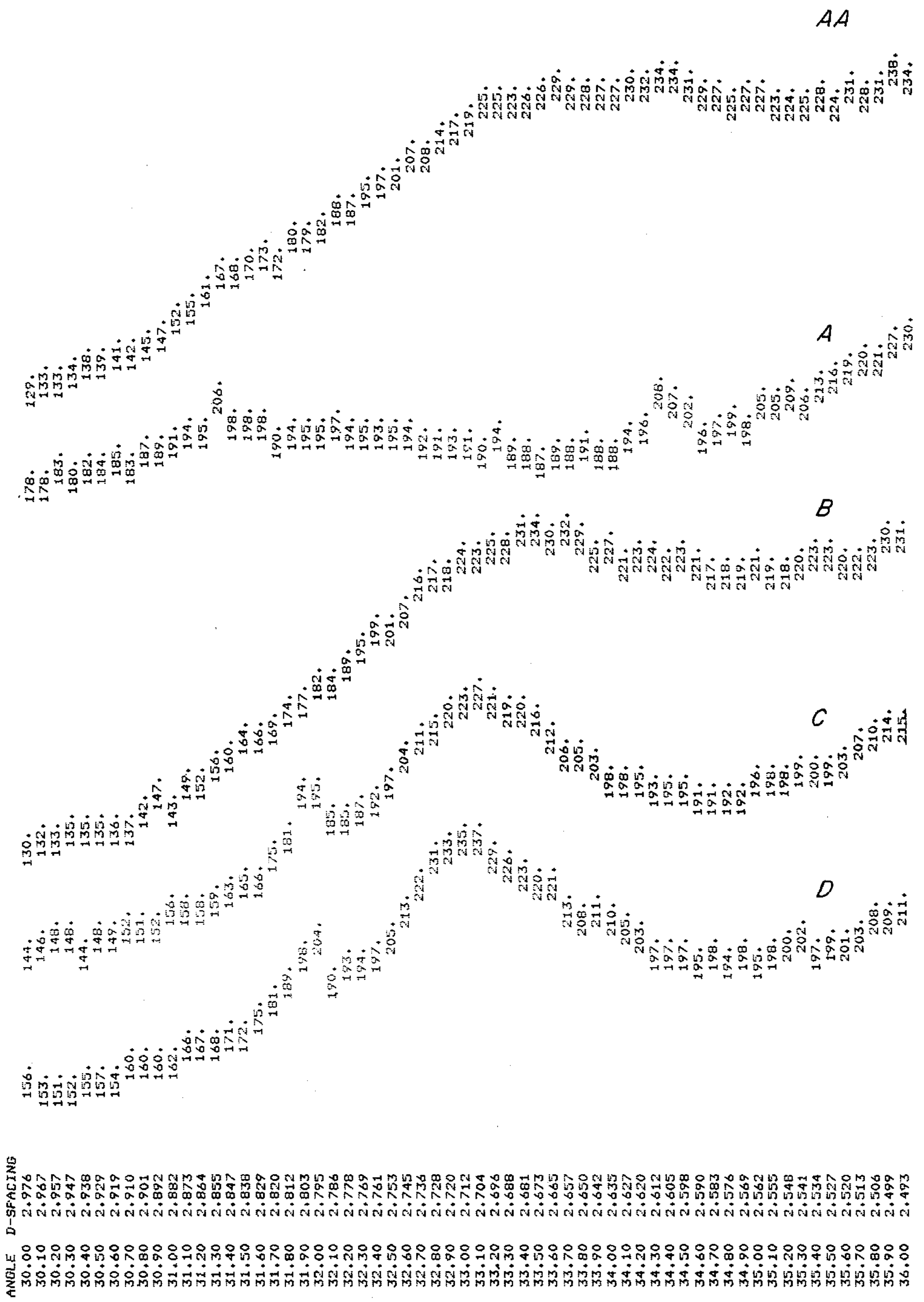
AA
A
B
C
D
ANGLE
D-SPACING

TABLE 2

Crystallite Size Estimates of MoS_2 in Presulfided and Spent Reactor Pellets

Sample	Figure designation	Crystallite size (Å)	
		L_c	L_a
Harshaw catalyst sulfided at 450°C, 1 atm, for 1 hr	2 and 3, AA	NP[a]	80
Harshaw catalyst unused	2 and 3, A	NP	NP
Harshaw catalyst sulfided at 440–450°C, 1650–1960 psi for 1 hr	2 and 3, B	57	92
Spent Harshaw catalyst from inlet of reactor	2 and 3, C	53	132
Spent Harshaw catalyst from outlet of reactor	2 and 3, D	66	142

[a] Not present.

compounds identified by X-ray diffraction. Quartz from the coal and pyrrhotite and anatase formed during liquefaction are difficult to remove completely from the spent catalysts.

The diffractogram of the catalyst sulfided at 440 to 450°C and 1650 to 1960 psi, Fig. 1B, shows a much weaker MoS_2 (002) band than that shown by the spent pellets from the reactor. A sample of catalyst was then sulfided at 450°C with 10% H_2S in H_2 at atmospheric pressure for 1 hr. This gave a diffraction pattern identical to Fig. 1B except that the weak (002) band was absent, as shown in Fig. 2AA, indicating a lack of three-dimensional growth. However, the presence of a (10) band, Fig. 3AA, and a (11) band signify the presence of two-dimensional crystallites. Wildervanck and Jellinek (*8*) produced two-dimensional MoS_2 by heating amorphous MoS_3 to 400°C, and Ratnasamy and Leonard (*9*) showed that reduction of MoS_3 in hydrogen yielded a somewhat more crystalline material at lower temperatures. Figures 2 and 3 are step scans, for all the samples studied, over the 2θ ranges of the (002) and (10) bands, 10 to 17° and 30 to 36°.

Using step scans similar to those shown in Figs. 2 and 3 the approximate crystallite dimensions of MoS_2, in the plane L_a and perpendicular to the plane of the layers L_c were determined from the width at half-maximum of the (10) and (002) reflections respectively. The following relationships were used:

$$L_a = \frac{2\lambda}{\beta \cos 16.5°}$$

and

$$L_c = \frac{0.9\lambda}{\beta \cos 7.15°},$$

FIG. 3. MoS_2 (10) reflection representative step scans from 30 to 36° 2θ at intervals of 0.1°, where each step was counted for 60 s. (AA) Harshaw 0402T catalyst sulfided at 450°C, with 10% H_2S in H_2, at atmospheric pressure, for 1 hr. (A) Unused Harshaw 0402T catalyst. (B) Harshaw 0402T sulfided at 440 to 450°C, with 10% H_2S in H_2, for 1 hr at 1650 to 1960 psi pressure. (C) Spent Harshaw 0402T from reactor inlet. (D) Spent Harshaw 0402T from reactor outlet. The peaks for (AA) and (B) occur at larger angles due to the smaller crystallite size (10). The 2.80-Å lines in (C) and (D) may be from CoS_2 or Co_3S_4.

where $\lambda = 1.5418$ Å, and β is the measured width at half-maximum converted to radians. The appropriate shape factors are 2 and 0.9 for the two- and three-dimensional lines, respectively (*10*).

The widths at half-maximum were measured on step scans made at 0.1° intervals counted for 30 or 60 s per step. Measurements were made on three samples from each treatment and each measurement was within $\pm 10\%$ of the average. Lubricant MoS_2 measured under identical conditions as the catalysts had widths at half-maximum of 0.10° for the (002) and 0.24° 2θ for the (100) reflection indicating that the instrumental broadening was small compared to that due to the size of the MoS_2 crystallites in the sulfided and spent catalysts. No attempt was made to obtain highly accurate crystallite size measurements in this preliminary study because the high background and low peak to background ratio make determination of the shape of the peaks very difficult. Table 2 shows the estimated crystallite sizes for the samples studied. These sizes, estimated to be within $\pm 30\%$ of the true value and probably on the low side, show that the MoS_2 crystallites are much larger in the plane of the MoS_2 layers than perpendicular to it. The presence of crystallites of this size is consistent with the pore volume distribution of the catalyst reported by the manufacturer. They indicate that the mercury–helium method shows that 75% of the pore volume is due to pores less than 120 Å in diameter. The number of MoS_2 layers present in these crystallites can be calculated from the measured parameters for hexagonal MoS_2 (*11*). This results in an estimate of 9 to 11 layers in the crystallites in the spent catalysts.

As noted previously, the catalyst from the reactor was not presulfided, so that the sulfiding occurred during actual reactor operation. Further, the hydrodesulfurization function of the catalyst was apparently deactivated before the termination of the run (*5*). Thus it is difficult to assess the exact role of the MoS_2 crystallites in regard to the HDS function of the catalyst. It is possible that two- or three-dimensional or amorphous MoS_2 has activity and that the noted deactivation of the catalyst occurred through a mechanism independent of the structure of the active (molybdenum) components. The molybdenum–sulfur species could still be catalytically active for HDS reactions, but are precluded from so functioning because of diffusional limitations resulting from deposited metals or mineral matter from the coal or formed intractable carbonaceous materials (coke). On the other hand, it is possible that change in the MoS_2 crystallites is symptomatic of the actual deactivation mechanism; i.e., the active two-dimensional crystallites, under the extreme conditions of operation of a coal HDS reactor, deactivate by the formation of three-dimensional crystallites with a concomitant decrease in surface area of the active components. The study of catalysts at various levels of activity (or deactivation) should permit one to more fully address these questions.

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REFERENCES

1. Massoth, F. E., *J. Catal.* **50**, 190 (1977).
2. Brown, F. R., and Makovsky, L. E., *Appl. Spectrosc.* **31**, 43 (1977).
3. de Beer, V. H. J., van der Alst, M. J. M., Machiels, C. J., and Schuit, C. C. A., *J. Catal.* **43**, 78 (1976).
4. Rogers, S. E., Mazzocco, N. J., Akhtar, S., and Yavorsky, P. M., "Coal Liquefaction in SYNTHOIL Reactor without Added Catalyst." Presented at 85th National AIChE Meeting, Philadelphia, Pa., June 4–8, 1978.

5. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50**, 385 (1977).
6. Romanowski, W., *Rocz. Chem.* **37**, 1077 (1963).
7. Richardson, J. T., *Ind. Eng. Chem. Fundam.* **3**, 184 (1964).
8. Wildervanck, J. C., and Jellinek, F., *Z. Anorg. Allg. Chem.* **328**, 309 (1964).
9. Ratnasamy, P., and Leonard, A. J., *J. Catal.* **26**, 352 (1972).
10. Klug, H. P., and Alexander, L. E., "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," 2nd ed., pp. 688, 704, Wiley, New York, 1974.
11. Dickinson, R. G., and Pauling, L., *J. Amer. Chem. Soc.* **45**, 1966 (1923).

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