Ammoximation

II. Catalysts for the Ammoximation of Cyclohexanone

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This paper summarizes catalysts which have been screened for the newly discovered process termed ammoximation (the conversion of a ketone to an oxime by treatment with ammonia and oxygen). Because we are dealing with an entirely new process, we have had to survey a wide variety of potential catalysts. Primarily, we have dealt with large families of traditional catalysts such as metallic, nonmetallic, and amphoteric oxides, carbon, phosphates, heteropoly anions, and clays. Two significant pieces of information have been generated by this screening operation. It is readily apparent that a wide variety of "surfaces" catalyze this reaction, yet the reaction does not proceed in the gas phase, over quartz chips, or over activated carbon. Further, substantial differences in selectivity are apparent for different types of surfaces. The best catalysts, to date, are based on xerogels derived from silica–alumina with a selectivity of 68 ± 3% to cyclohexanone oxime.

INTRODUCTION

In an effort to reduce the number of process steps for the conventional synthesis of caprolactam, we have pursued a direct, selective oxidation of NH_3 to hydroxylamine as the oxime. The previous paper described our work on "ammoximation" which is the selective oxidation of ketones and NH_3 with air (*1*). Unlike the ammoxidation of propylene with NH_3 and O_2 to acrylonitrile (*2*, *3*), ammoximation [represented by Eq. (1)] is an example of a uniquely selective oxidation of NH_3 and ketone mixtures to the oxime. In the previous paper, we presented data to support our characterization of the products and the activity of two of the more active catalysts. (*4*). Because of the commercial value of caprolactam, most of our efforts focused on the reaction between cyclohexanone, NH_3, and O_2 to yield the oxime. In the previous paper, we also demonstrated that oxime from

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Ammoximation of cyclohexanone.

$$\text{(1)}$$
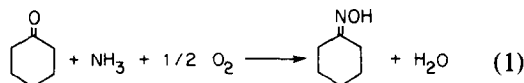
can be taken further to the lactam by the use of an acidic catalyst in a separate reaction zone after the first ammoximation catalyst (*5*). Thus, it was possible to produce both the oxime and the lactam in one pass over the appropriate catalyst(s).

$$\text{(2)}$$
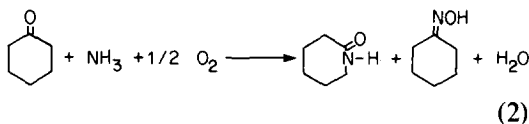
This paper will focus on classes of materials which have been tested as catalysts for Eq. (1). Because this is a process which has not been reported in the past, we tested a wide variety of potential catalysts for this reaction. As might be expected, the use of conditions which are optimum for ammoxidation (~400°C) does not lead to oxime formation due to the instability of oximes at these high temperatures. It is somewhat

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surprising that catalysts which are effective for ammoxidation of propylene are ineffective for ammoximation of NH_3 and ketones at 200°C. As this paper will demonstrate, the catalysts for ammoximation are not traditional oxidation catalysts. Currently, the best catalysts for the ammoximation of cyclohexanone are silica gels and silica-aluminas.

EXPERIMENTAL

Testing of Catalysts

The experiments summarized in this report were all performed using a similar method of gc analysis as described previously (1, 4, 6). The reactors differed somewhat in design, but basically they performed with similar selectivities on a standard run of Porasil A. The volume percentages of NH_3, O_2, cyclohexanone, and He (or N_2) were ~50, 10, 2, and 38%, respectively. The volume of catalyst (60–100 mesh) used was 1–2 cm³, irrespective of its density. The reactants were allowed to flow downward through a quartz tube (plug-flow reactor operated at 40–70% conversion). Most of the data were collected on the automated reactor systems described in the previous paper (4). Catalysts were tested at four to five different temperatures between 150 and 260°C over a period of 8–16 hr. After the experiment was terminated, the reactor tube containing the catalyst was removed from the reactor and weighed to determine the amount of residue formed, if any.

Preparation of Catalysts

Porasil A is a high-surface-area silica gel. Its physical properties were discussed in the previous paper. Since it was commercially available and gave reproducible results (with several different lots), it was used as an internal standard on a weekly basis to ensure that our systems were performing correctly.

Samples of aluminas and carbons were obtained direct from the suppliers indicated. All catalysts were dried at 125–220°C prior to testing. Some of the traditional oxidation catalysts were further activated with air at 300–400°C prior to testing at ~200°C.

SiO_2/Al_2O_3. The best formulation of a gel derived from the hydrolysis of tetramethylorthosilicate (TMOS) and aluminum sec.-butoxide (ASB) appears to be one based on a molar ratio of 5.0/1, SiO_2/Al_2O_3. The preparation of this catalyst is given in the previous paper (4).

Ga_2O_3. A commercial sample of ROC/RIC (Research Organic/Inorganic Chemicals; Belleville, N.J.) gallium nitrate hydrate (5.12 g) was heated to 350°C in air overnight in a muffle furnace. The yield of the white oxide was 2.7 g (7). Analysis for N (Dumas) indicated <1% N was present.

Attempts to impregnate various transition metals onto possible supports such as carbon, Porasil, α-Al_2O_3, etc., were often accomplished by the technique of incipient wetness. Using this technique, the metal salt was dissolved in water and/or alcohol, and the solution was added to just enough dry catalyst to yield a thick slurry. The volatile solvent was removed either by filtration or evaporation and the product dried at 125–210°C.

Surface areas were obtained on a Quantasorb (Quantachrome, Syosett, N.Y.) using N_2-BET technique. Pore volumes and pore size distributions were measured on a Quantachrome scanning mercury porosimeter.

RESULTS

A variety of materials were tested as catalysts for the ammoximation of cyclohexanone. This section summarizes the results obtained with some of these materials. At first, we tested some commercial catalysts such as Pt on Al_2O_3. When this catalyst produced small amounts of oxime, we proceeded to run the control study using only γ-Al_2O_3. To our surprise, γ-Al_2O_3 proved to be just as effective a catalyst as Pt/Al_2O_3. However, samples of α-Al_2O_3 gave only traces of the oxime. We pro-

ceeded to a variety of silica gels only to find that a large group of silicas were quite active catalysts. A sampling of the silica catalysts which were tested is given in Table 1.

The activity of a series of Porasils as ammoximation catalysts is listed in Table 2. These are a series of commercial silica gels having a limited pore size distribution with a fairly constant pore volume.

Table 3 lists a series of controlled pore glasses. These are commercial silica gels which are available from Electro-Nucleonics (Fairfield, N.J.) that display very narrow pore size distributions.

Gallium Oxide

We have been able to prepare an active form of gallium oxide (surface area = 133 m^2/g) which demonstrated a selectivity of ~44% to the oxime (see Experimental). Unlike some other catalysts which we have prepared, the activity displayed by these

oxides of gallium was very sensitive to the method of preparation. It appeared that the most active phase of Ga_2O_3 was the γ phase (having a defect, spinel structure). Different preparations of the γ phase gave slightly different selectivities to the oxime. Scanning electron micrographs of these γ forms of Ga_2O_3 revealed substantial morphological differences.

Acid- or Base-Treated Catalysts

From our previous paper, it was clear that aldolization of cyclohexanone was a significant problem during the ammoximation reaction. In an effort to redirect the ketone from aldol by-products to the oxime, a variety of catalysts were treated with acids or bases in order to modify the surface of the catalyst.

Treating Porasil A with 0.1, 0.25, or 1% KOH only reduces the selectivity slightly (with respect to the unaltered catalyst). A 10% KOH-treated Porasil A loses about

TABLE 1

Silica Catalysts for Ammoximation

Silica	Yield	Conversion	Selectivity to the oxime	Surface area (m^2/g)	Pore volume (cm^3/g)
Porasil A	24	43	55	450	1.0 (9.2 nm)[a]
CPG-105 Å	32	68	47		
Grace-07	<1	30	<1	720	
Grace-81	29	76	38	600	0.6
Grace-57	18	52	36	300	1.0
Alfa Sil-gel No. 89346	23	55	42	308	0.96 (7.4 nm)[a]
Lichrosphere[b]	<5	26	—	250	1.2
Silicalite[c]	0		0		
Hydrophobic fumed SiO_2 (Degussa, R972)	0		0		
Hydrophilic fumed SiO_2 (Cabot, EH-5)	4	50	8	390	
$TMOS^d$ + water	5	83	6	660	0.83 (6.6 nm)[a]
$TMOS^d$ + 5 N NH_4OH	17	39	43	524	
$TMOS^d$ + 50% aqueous HOAc	0	10	0		

[a] Mean pore diameter is in parentheses.

[b] From E. Merck, a porous, spherical silica gel.

[c] Prepared according to example 3 of Union Carbide's U.S. Patent 4,061,724; see Flanigen, E., Bennett, J., Grose, R. W., Cohen, J. P., Patton, R., Kirchner, R., and Smith, J., *Nature* 271, 512 (1978).

[d] TMOS—tetramethyl-orthosilicate.

TABLE 2

Porasils, Standard Conditions

Catalyst	Yield (%)	Conversion (%)	Selectivity (%)	Surface area (m²/g)	Pore volume (cm³/g)[a]
Porasil A	32	58	55	350–500[b]	1.0 (10)[a,c]
Porasil B	19	43	44	125–250	1.0 (10–20)[a,c]
Porasil C	11	39	28	50–100[d]	1.0 (20–40)[a,c]
Porasil D	4	26	14	25–45	1.0 (40–80)[a,c]

[a] Values supplied by Waters Associates.
[b] Determined as 475 m²/g in our labs.
[c] Average pore diameter measured in nm is in parentheses.
[d] Determined as 101 m²/g in our labs.

half of its selectivity to the oxime. A 2% loading of NH_4OAc; 4% of sodium metaborate; 0.5, 2, and 8% of phosphotungstic acid; or 0.1% of H_3PO_4 on Porasil A does not alter the activity of the Porasil. However, a sample of Porasil impregnated with 10% H_3PO_4 produces only traces of the oxime.

In the same manner, a series of γ-aluminas was treated with various acids or bases. When γ-Al_2O_3 (Girdler No. T-126) was treated with 2% KOH or 2% $(NH_4)_2HPO_4$ no improvement in selectivity (vs γ-Al_2O_3 alone) was observed. For a commercial series of acidic (pH = 4.0), neutral (pH = 7.5), and basic (pH = 9) aluminas [available from E. Merck (Darmstadt, Germany)], the neutral and basic aluminas showed no improvement over commercial samples of γ-Al_2O_3, while the

TABLE 3

Controlled Pore Glasses, Standard Conditions

Catalyst[a]	Yield (%)	Conversion (%)	Selectivity (%)	Surface area (m²/g)	Pore volume (cm³/g)
40 Å CPG[b]	24	49	48	198	0.3
50 Å CPG	25	60	42		
85 Å CPG	38	67	57	218	0.65
105 Å CPG	33	70	47		
120 Å CPG	26	55	47	133	0.86
122 Å CPG	32	68	47		
175 Å CPG	15	43	35		
240 Å CPG	17	39	44	102	0.89 (23)[c]
350 Å CPG	16	37	43	75	1.39
522 Å CPG	8	28	29	102	0.89
2000 Å CPG	2	18	11	10	0.80

[a] The number preceding the CPG designation corresponds to a rough approximation of the average pore size diameter of the silica; available from Electro-Nucleonics, Fairfield, N.J.
[b] A different glass composition is used to prepare CPGs with <7.5-nm pores.
[c] Average pore diameter measured in nm is in parentheses.

acidic alumina gave only traces of oxime. [These aluminas all have comparable surface areas ($\sim$110 m^2/g) and mean pore diameters (9 nm).]

Impregnated Supports

Coatings of 4% sodium borate, 0.5–8% phosphotungstic acid, 2% levels of borophosphoric or silicotungstic acid, tungstates, and a variety of transition metal salts (of Cu, V, Fe, Co, Ni, Cr, Mo, or Ag) on Porasil A, α-Al$_2$O$_3$, γ-Al$_2$O$_3$, activated carbon, or Grace-07 silica gel yielded catalysts which were no better (and sometimes less effective) than the supports themselves. Generally, impregnating oxidants such as Cu^{2+}, Mo^{5+}, Co^{2+}, Cr$_2$O$_3$, and Bi$_2$O$_3$ on Porasil or γ-Al$_2$O$_3$ reduced the selectivity to less than 15%. Further, washing Porasil A with EDTA solutions (a technique often used to remove metal ions) did not appreciably alter the S to oxime.

The following list is a summary of our results with the standard mixture of cyclohexanone, NH$_3$, and O$_2$ over a series of commercial catalysts which seemed to offer a chance of success (the comments in brackets indicate the amount of oxime produced): 2% Co on Al$_2$O$_3$ (Ketjen 76-RM-30) [trace]; $\sim$20% Cr on Al$_2$O$_3$ (Grace) [no oxime]; 10% WO$_3$ on Al$_2$O$_3$ (Strem) [S = 36%]; 10% Cu on γ-Al$_2$O$_3$ (Girdler T-317) [no oxime]; 10% Mo on γ-Al$_2$O$_3$ (Girdler T-306) [S = 11%]; WO$_3$ (Strem) [no oxime]; V$_2$O$_5$ on SiO$_2$ gel (Strem) [no oxime]; NiO on Al$_2$O$_3$ (Strem) [no oxime]; and MnO$_2$ on Al$_2$O$_3$ (Strem) [no oxime].

Attempts to mimic the black layer on the Porasil A by impregnating a variety of organic compounds (2% in water or alcohol) such as cyclohexanone oxime, caprolactam, dipyridyl, phenazine, or EDTA failed to produce a more active catalyst than the support itself. Further an induction period was still apparent.

Silica–Aluminas

A variety of molecular sieves (Linde 13X, Type L, NH$_4^+$–Y) failed to demonstrate any significant selectivity to the oxime at 200°C. A sample of a Grace zeolite (No. XZ-25) also proved ineffective as did a sample of a La^{3+}-coated molecular sieve (Linde SK-500). Other effective commercial SiO$_2$/Al$_2$O$_3$ catalysts (e.g., Grace 980-25, S = 40%) even with ratios of SiO$_2$/Al$_2$O$_3$ approaching 5.0 proved less active than that prepared from TMOS/ASB/H$_2$O. (This latter result may depend on the conditions the supplier used to activate the catalyst).

The best silica–alumina catalysts have been prepared from TMOS/ASB. The highest selectivities have been obtained with a molar ratio of 5.0/1. Table 4 displays the strong dependence of selectivity with the ratio of SiO$_2$/Al$_2$O$_3$. Controlling the temperature of the reactants (4–90°C) during the exothermic hydrolysis of the TMOS/ASB mixture led to no dramatic differences in selectivity of the resulting catalyst. The minimum amount of water should be 0.9 cm^3 for every 3 g of TMOS. While one can substitute alternative forms of alumina [fumed Al$_2$O$_3$, Al$_2$(SO$_4$)$_3$, or sodium aluminate] in place of ASB, some TMOS should be present to prepare an effective catalyst. If one substitutes colloidal silicas, sodium silicate, or SiCl$_4$ in place

TABLE 4

Vary Ratio of TMOS/ASB with 1 cm^3 Water

Moles SiO$_2$/Al$_2$O$_3$	Selectivity[a] (%)	Surface area (m^2/g)
32.0	<10	
10.4	41	
6.6	36	308
5.4	59	
5.0	69	313
4.8	59	239
4.5	50	
4.0	<10	
0.66	28	

[a] Standard conditions: 1 cm^3 of catalyst dried to 200°C, reacted with 50% NH$_3$, 2% cyclohexanone, and 10% O$_2$ at 220°C.

of TMOS, the resulting SiO_2/Al_2O_3 gel was a poor catalyst for the ammoximation of cyclohexanone. A third component was incorporated into the SiO_2/Al_2O_3 gel by dissolving the additive in the water used for the hydrolysis. Additives such as tungstates, Ga^{3+}, fluorides, Mg^{2+}, La^{3+}, Bi^{3+}, Zr^{4+}, Ti^{4+}, phosphotungstates, borates, and a variety of transition metal salts when allowed to cogel with the SiO_2/Al_2O_3 did not improve the selectivity to the oxime.

Other Potential Catalysts

The following catalysts are often used as supports and display a wide range of surface acidities (8) but show little activity as ammoximation catalysts (the amounts of oxime are indicated in brackets): montmorillonite clays (e.g., Girdler K-306) [trace]; porous, activated carbons [e.g., Amoco PX-23) [no oxime]; TiO_2 (Harshaw) [no oxime]; MgO (Harshaw) [trace]; ZnO (Kadox-25) [no oxime]; ZrO_2 (Strem) [trace]; TiO_2/SiO_2 (Girdler T-1219) [trace]; SiO_2/MgO (Grace-7-1937) [trace]; 24% ZnO on Al_2O_3 (Strem) [trace]. Most of the materials which are termed inactive showed very little conversion of the ketone.

DISCUSSION

Several silica gels are effective catalysts for the ammoximation of cyclohexanone. At the moment, there seems to be some importance in a silica having a moderately high surface area ($\sim$400 m^2/g). However, some high-surface-area silica gels are quite inactive catalysts for the ammoximation of cyclohexanone. Initially, attempts to make our own silica gels failed to yield materials as active as Porasil A. However, hydrolysis of the alkoxide (tetramethyl-orthosilicate) with 5 N NH_4OH instead of water leads to an effective silica gel catalyst. Table 1 also indicates that other types of silica such as fumed silica or silicalite (9) are ineffective catalysts. While we have not determined

exactly what type of surface constitutes an active catalyst, it is clear that the physical characteristics as well as the method of preparation of the silica are extremely crucial to obtaining a good catalyst.

Early in our work, we observed that Porasil A was a good catalyst for ammoximation. Originally it was selected because of its purity and its high surface area. The other Porasils listed in Table 2 certainly were less active catalysts, and it appeared at first glance that the pore size might play a crucial role in catalyst activity. We tested this latter concept further by screening a variety of silicas prepared from the melt. It is clear from the controlled pore glasses given in Table 3 that materials between 4 and 35 nm are all quite active when the pore volume is allowed to vary.

In addition, we observed that γ-Ga_2O_3 was a catalyst for the ammoximation of cyclohexanone. Ga_2O_3 is reported to catalyze (although somewhat differently) many of the reactions that Al_2O_3 does (10). γ-Aluminas proved to be less effective than Porasil A resulting in lower yields of the oxime (at the same levels of conversion), whereas α-alumina (of lower surface area) was ineffective. The lower activity of alumina relative to silica may be attributed to the fact that aluminas are known to be very effective catalysts for the aldolization of cyclohexanone (11). In the presence of excess NH_3 which we have during a reaction, we would expect (4,12) substantial secondary reactions of the ketone with NH_3.

Attempts to modify the surface of γ-Al_2O_3 or silica gels with various promoters (such as acids, bases, or metal salts) resulted in no improvement in activity. In some cases, the addition of strong oxidants such as Ce(IV) resulted in materials with no selectivity to the oxime. A number of different heteropoly anions were impregnated onto various supports because these anions were reported to be important catalysts for the addition of peroxides to ketones to yield the oxime (13). However, in our system

these salts proved to be ineffective co-catalysts.

A variety of commercial oxidation catalysts proved to be ineffective catalysts (or no more effective than the supports themselves). Attempts to go to lower temperatures led to less conversion while higher temperatures produced CO, CO_2, and oxides of nitrogen. Even preparations of the bismuth–molybdenum oxides (14) (reported to be active for ammoxidation of propylene) proved to be ineffective catalysts for the ammoximation of cyclohexanone at 200–250°C ($S < 5\%$; $C < 45\%$).

We tested a variety of other traditional supports as potential catalysts for ammoximation. However, a wide variety of these materials (titania, magnesia, carbons, etc.) proved to be poor catalysts.

Our initial screening of commercial silica–aluminas proved to be negative. However, when we tested a variety of SiO_2/Al_2O_3 gels prepared by hydrolyzing TMOS and ASB, we found these materials to be even more active than silica gels. The activity of these new catalysts was very dependent upon the ratio of SiO_2/Al_2O_3 and the hydrolytic reagent. With these SiO_2/Al_2O_3 gels we succeeded in preparing a catalyst (a) with double the life of Porasil A, (b) having a selectivity of 68 ± 3%, and (c) requiring only about one-half the amount of catalyst (as compared to Porasil A).

Throughout this work we found some catalysts to be very sensitive to the method of preparation employed. Preparation of gallia gave very erratic results, and we had to adhere precisely to the preparation already described. This was an indication that surface features may play a critical role in the ammoximation process. Further, we saw that silica gels with apparently similar properties (from different suppliers) gave very different results. TMOS and water yielded an ineffective catalyst, while TMOS and NH_4OH produced a catalyst comparable to Porasil A. We can only conclude that the surface features of the catalyst are extremely important in this process. These features are revealed in measurements of surface acidity as well as in the chemisorption of the reactants (15).

Wet chemical and emission analysis of these catalysts (4) indicated that these materials were quite pure. We tried to impregnate inactive silica gels with some of the very low levels of impurities found in Porasil A without obtaining any improvement in selectivity. Rinsing the Porasil A with a solution of EDTA did not alter the selectivity. Thus, it would appear that trace impurities were not the source of the catalysis. However, the presence of small amounts of Al^{3+} would be expected to impart considerable acidity to the silica gel. Further, we observed that good oxidation catalysts, even with substantial surface area, were inactive catalysts. Considering this latter result and the strength of Si–O and Al–O bonds, it would seem unlikely that lattice oxygens were required to carry out the oxidation of mixtures of NH_3 and ketones.

We have seen that the best catalysts for reaction (1) are silicas, silica–aluminas, aluminas, and gallia. These materials all have moderately high surface areas and are known to interact with ketones, ammonia, and amines (16). For the activation of such species, the availability of surface hydroxyl (17) species might play an important role.

In conclusion, the ammoximation process does not parallel the well-known ammoxidation process. The participation of lattice oxygen with the concomitant rapid and reversible change in metal valences does not appear to be important. High surface area appears to be a necessary but not sufficient condition for high selectivity. Catalysts with nearly identical bulk structures (as revealed by X-ray diffraction) have surface morphologies and catalytic selectivities that are very sensitive to preparative conditions. Further, traditional nonoxidizing materials, such as silica and SiO_2/Al_2O_3, tend to be the most effective catalysts for the ammoximation of cyclohexanone.

REFERENCES

1. Armor, J., *J. Amer. Chem. Soc.* **102**, 1453 (1980).
2. Burrington, J. D., and Grasselli, R. K., *J. Catal.* **59**, 79 (1979).
3. Keulks, G. W., Krenzke, L. D., and Notermann, T. M., *in* "Advances in Catalysis and Related Subjects," Vol. 27, p. 183. Academic Press, New York, 1978.
4. Armor, J., *J. Catal.* **70**, 72 (1981).
5. "Abstracts of the VII International Congress on Catalysis, Tokyo, Japan, July, 1980," D-14.
6. Gates, W., Zambri, P., and Armor, J. N., *J. Chromatogr. Sci.,* in press.
7. Armor, J., U.S. Patent 4,225,511.
8. Benesi, H. A., and Winquist, B. H. C., *in* "Advances in Catalysis and Related Subjects," Vol. 27, p. 97. Academic Press, New York, 1978; see comments of Deeba, M., and Hall, W. K., *J. Catal.* **60**, 417 (1979).
9. Prepared according to Example 3 of Union Carbide's U.S. Patent 4,061,724; see Flanigen, E., Bennett, J., Grose, R. W., Cohen, J. P., Patton, R., Kirchner, R., and Smith, J., *Nature* **271**, 512 (1978).
10. Carleton, F. B., Quinn, H. A., and Rooney, J. J., *J. Chem. Soc. Chem. Commun.,* 231 (1973); Davis, B. H., Cook, S., and Naylor, R. W., *J. Org. Chem.* **44**, 2142 (1979).
11. Scheidt, F. M., *J. Catal.* **3**, 372 (1964).
12. Nielson, A. T., and Horilihan, W. J., *in* "Organic Reactions" (A. C. Cope, Ed.), Vol. 16. Wiley, New York, 1968.
13. (a) Yasui, E., Kawaguchi, T., Matsubara, T., Hirose, T., and Kato, H., German Patent 1,274,124 (*Chem. Abst.* **70**, 11209w); (b) also see Hawkins, E. G. E., *J. Chem. Soc. C,* 2663 (1969).
14. Batist, Ph. A., Bouwens, J. F. H., and Schuit, G. C. A., *J. Catal.* **25**, 1 (1972).
15. Armor, J. N., and Zambri, P., *J. Catal.,* in press.
16. Curthoys, G., Davydov, V. Ya, Kiselev, A. V., Kiselev, S. A., and Kuznetsov, B. V., *J. Colloid Interface Sci.* **48**, 58 (1974).
17. Pequignot, F., Bastick, M., and Bastick, J., *Bull. Soc. Chim. Fr.* I-101 (1978); Hair, M. L., and Chapman, I. D., *J. Amer. Ceram. Soc.* **49**, 651 (1966); Hair, M. L., and Hertl, W., *J. Phys. Chem.* **73**, 4269 (1969); Hirschler, A. E., *J. Catal.* **6**, 1 (1966).