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Formaldehyde Conversion to Methanol and Methyl Formate on Copper/Zinc Oxide Catalysts

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We have studied the hydrogenation of CH_2O on a Cu/ZnO catalyst at conditions of $P = 1$ atm and $380\ K < T < 420\ K$. In addition to the primary hydrogenation product CH_3OH, we observe small amounts of the decomposition products CO and CO_2, and large amounts of the disproportionation product CH_3OCHO. We propose that the small yields of CO and CO_2 show that CH_2O hydrogenation cannot be the rate-limiting step in CH_3OH synthesis on this catalyst, while the dependence of CH_3OCHO yield on CH_2O conversion suggests that the former product is likely formed in a bimolecular surface reaction between adsorbed CH_2O and CH_3O species.

INTRODUCTION

In recent years there has been a renewed interest among both academic and industrial researchers in understanding the CH_3OH synthesis reaction on Cu/ZnO catalysts (*1–4*). Discussion has touched on virtually every aspect of the reaction, including the morphology and oxidation state of the active Cu species (*5–7*), the roles of CO_2 and H_2O as reactants or promoters (*7, 8*), and (inevitably) the reaction mechanism. The latter topic has been reviewed by several authors (*1–4*), and a consensus has emerged that all of the proposed mechanisms can be classified into three groups, according to their most distinguishing surface intermediate:

I. Formyl:

$$CO_{(a)} \xrightarrow[+H_{(a)}]{} HCO_{(a)} \xrightarrow[+H_{(a)}]{} CH_2O_{(a)} \xrightarrow[+H_{(a)}]{} CH_3O_{(a)} \xrightarrow[+H_{(a)}]{} CH_3OH \quad (1)$$

II. Formate (ex CO):

$$CO_{(a)} \xrightarrow[+OH_{(a)}]{} HCOO_{(a)} \xrightarrow[+H_{(a)}]{} CH_2OO_{(a)} \xrightarrow[+H_{(a)}]{} CH_3O_{(a)} \xrightarrow[+H_{(a)}]{} CH_3OH \quad (2)$$

III. Formate (ex CO_2):

$$CO_{2(a)} \xrightarrow[+H_{(a)}]{} HCOO_{(a)} \xrightarrow[+H_{(a)}]{} CH_2OO_{(a)} \xrightarrow[+H_{(a)}]{} CH_3O_{(a)} \xrightarrow[+H_{(a)}]{} CH_3OH \quad (3)$$

All three mechanisms share the common feature of requiring the sequential addition of four H atoms to the initial CO or CO_2 reactant in order to obtain the product CH_3OH. This had led to speculation as to which of the four $H_{(a)}$ addition steps is rate limiting for the overall CH_3OH synthesis reaction (*9*).

One experimental approach to answering this question has been to determine the reaction order of the overall rate with respect to H_2 pressure, and compare this result with the values predicted by the rate expressions derived from the mechanism(s) above when each $H_{(a)}$ addition step in turn is assumed to be rate limiting. Since all of the reported rate expressions for the forward synthesis reaction at low conversions contain a factor of $(P_{CO}P_{H_2}{}^2)$ raised to some power (*1, 3, 8–10*), this approach leads to the conclusion that the fourth $H_{(a)}$ addition step is rate limiting; i.e., the desorption of CH_3OH.

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However, it is well known that caution is needed when using apparent reaction orders to infer information about the reaction mechanism. Therefore, it is desirable to have evidence of a different nature to support any conclusions regarding the assignment of the rate-limiting step (RLS). In particular, an obvious possibility is to measure the hydrogenation rate of the $CH_2O_{(a)}$ intermediate directly, by introducing gas phase CH_2O into the reactant stream. In a related study, Vedage and Klier (*11*) reported that the hydrogenation rate of CH_3CH_2CHO and several other unsaturated molecules is much faster than the CO hydrogenation rate on Cu/ZnO catalysts. However, they did not report results for CH_2O itself.

In this paper we present kinetic results for $CH_2O : H_2$ mixtures reacting on a model Cu/ZnO catalyst at atmospheric pressure. We find that CH_2O hydrogenation occurs quite rapidly at relatively low temperature (ca. 400 K). We also observe that CH_2O decomposition to produce CO or CO_2 is slower than CH_2O hydrogenation, which implies that CH_2O hydrogenation cannot be the RLS for CH_3OH synthesis at these conditions.

In addition, we observe the formation of significant amounts of CH_3OCHO, which is the product of the stoichiometric disproportionation reaction:

$$2\ CH_2O \rightarrow CH_3OCHO \qquad (4)$$

Since it has been suggested that CH_3OCHO itself might be a useful intermediate for novel alcohol synthesis routes (*12*), we also include an analysis of the CH_3OCHO formation kinetics.

EXPERIMENTAL

The Cu/ZnO catalyst used in this study was prepared by impregnation, in order to assure a large Cu particle size and therefore reduce the possible influence of metal–support interactions. The ZnO support was Kadox 25 (Gulf & Western Natural Resources), with a surface area of 8 ± 2 m^2/g, as measured using a flow BET apparatus constructed in our laboratory (*13*). A 1 wt% Cu/ZnO catalyst was prepared by saturating the support with aqueous $Cu(NO_3)_2$ solution and evaporating the solvent, followed by calcining in air at 623 K for 16 hr and then reducing in the reactor at 473 K in flowing H_2. The reduction step was monitored by observing the H_2O produced during reduction with the gas chromatograph (GC); reduction was judged complete when H_2O evolution ceased.

The Cu surface area of the reduced catalyst was 1.5 m^2/g, based on the results of a separately performed CH_3OH adsorption and temperature-programmed desorption measurement (*14*). The Cu loading was confirmed by atomic absorption analysis of a redissolved sample.

Kinetic studies were performed using the flow system shown in Fig. 1. Hydrogen and helium from cylinders are mixed and fed into a CH_2O generator. The generator consists of a tube containing ca. 1 g of paraformaldehyde powder. The generator releases a constant flux of CH_2O vapor when warmed slightly (ca. 368 K). A portion of the reactant mixture is removed at a "tee" before the reactor. The remainder of the reactant stream then enters a $\frac{1}{4}$ in tubular Cu microreactor, which contains the catalyst sample packed between two plugs of glass wool. Separate metering valves on both the reactor and bypass streams allow

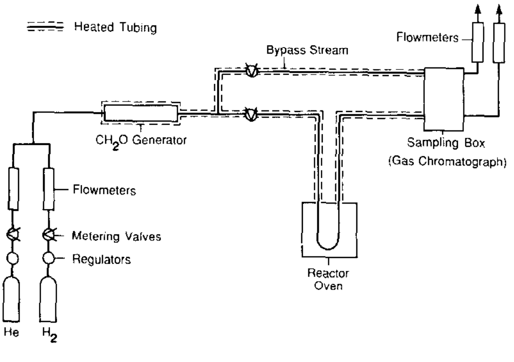

FIG. 1. Flow reactor system used for CH_2O hydrogenation kinetic studies.

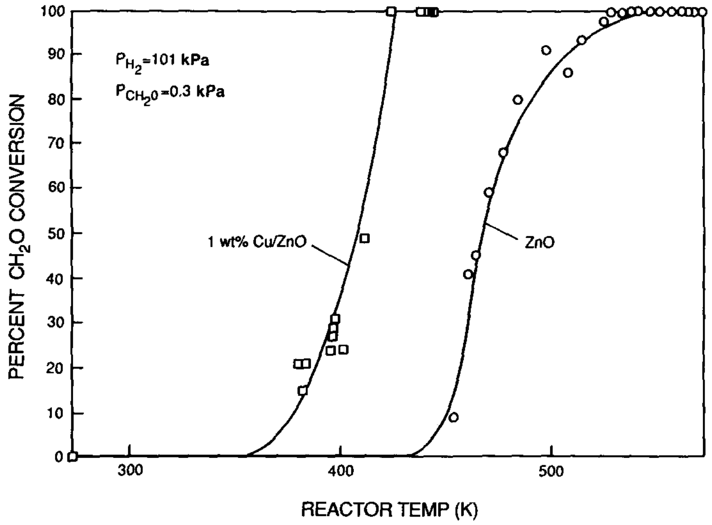

FIG. 2. CH_2O hydrogenation light-off curves. Conversion of CH_2O as a function of temperature for pure ZnO (○) and 1 wt% Cu/ZnO (□). Reactor conditions: $P_{CH_2O} = 0.3$ kPa, $P_{H_2} = 101$ kPa, $W/F_{A_0} = 106$ g hr/mole for ZnO, and 200 g hr/mole for Cu/ZnO.

us to vary the flow rate through the reactor for residence time studies without having to change the flow rate through the CH_2O generator. All of the tubing between the CH_2O generator and the GC sampling box is heated (ca. 330 K) to prevent recondensation of paraformaldehyde on the tubing walls.

The composition of both the bypass and the product streams were analyzed by gas chromatography using a 6 ft × $\frac{1}{8}$ in. Poropak T column at 413 K with a He carrier gas. A thermal conductivity detector was used to monitor the products CO, CO_2, CH_3OH, CH_3OCHO, and CH_2O. The carbon atom balance was 100 ± 7%.

RESULTS

Figure 2 compares the CH_2O conversion as a function of temperature for pure ZnO and the 1 wt% Cu/ZnO sample. The inlet composition of the reactant mixture was $P_{CH_2O} = 0.3$ kPa and $P_{H_2} = 101$ kPa, and the volumetric flow rate was 16 cm^3/min. The reactor was filled with the same volume of catalyst in each experiment, corresponding to 0.8 g of ZnO and 1.5 g of 1 wt% Cu/ZnO.

As expected, the 1 wt% Cu/ZnO catalyst is significantly more active than pure ZnO, confirming the dominating influence of the Cu component. For the reactor conditions listed above, the rate of CH_2O consumption at the 10% conversion point is 10^{-3} mole CH_2O/g catalyst/hr. The temperature required to achieve 10% conversion is below 390 K on the 1 wt% Cu/ZnO catalyst, and above 450 K on the pure ZnO catalyst. We estimate that the 1 wt% Cu/ZnO catalyst is at least two orders of magnitude more active than the pure ZnO catalyst at 450 K, based on an apparent activation energy of 24 kcal/mole for reaction on the 1 wt% Cu/ZnO catalyst. (The latter value was determined from an Arrhenius plot of the conversion vs temperature results for the 1 wt% Cu/ZnO catalyst.) We consider only the 1 wt% Cu/ZnO catalyst for the remainder of this paper.

Figure 3 shows the CH_2O conversion and CH_3OH and CH_3OCHO product yields as a function of temperature, for the same reactor conditions noted above. Yields are defined as the exit concentration of the product divided by the inlet CH_2O

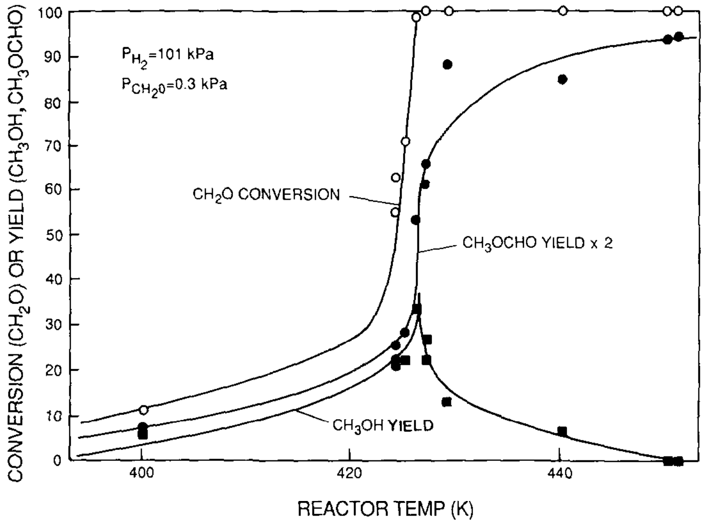

FIG. 3. Conversion of CH_2O (○) and yields of CH_3OH (■) and CH_3OCHO (●) as a function of temperature using 1 wt% Cu/ZnO. Reactor conditions are as in Fig. 2.

concentration. The yield of CH_3OCHO is shown multiplied 2×, to illustrate the carbon atom balance.

At low temperatures, where the conversion is small, comparable amounts of CH_3OH and CH_3OCHO are produced. Above 420 K the conversion increases sharply, and reaches 100% at 440 K. The absence of an asymptotic approach to the limiting 100% conversion axis suggests that the reaction may be zero order with respect to CH_2O pressure. This possibility is examined more closely below.

The second significant feature in Fig. 3 concerns the product yields. As the CH_2O conversion reaches 100%, the CH_3OH yield passes through a sharp maximum, while the yield of CH_3OCHO continues to increase, finally approaching 95% on a carbon atom basis. Superficially, this suggests that CH_3OH is a primary product in the stoichiometric reaction network, while CH_3OCHO is a secondary (i.e., sequential) product:

$$CH_2O + H_2 \rightarrow CH_3OH \qquad (5)$$

$$CH_2O + CH_3OH \rightarrow CH_3OCHO + H_2 \qquad (6)$$

To further confirm that these two products are produced in series, we next measured conversion and product yields for a series of different flow rates through the reactor, holding the reactor temperature and other parameters fixed. The results of this residence time study are shown in Fig. 4., which shows the conversion of CH_2O and yields of CH_3OH, CH_3OCHO, CO, and CO_2 as a function of W/F_{A_0}. The symbols mark the measured results, while the solid lines indicate the predictions of integrated rate expressions which are derived below.

All of the features concerning the reaction network that were suggested by the temperature variation experiments are confirmed in the residence time study. The CH_2O conversion is observed to vary almost linearly with W/F_{A_0} up to 100% conversion, which implies that CH_2O conversion obeys zero-order kinetics. At low conversions CH_3OH is the major product, but its yield has already reached a maximum below the shortest residence time studied. In its place, CH_3OCHO becomes the largest product at large values of W/F_{A_0}. This behavior confirms the series nature of reactions (5) and (6). The decomposition

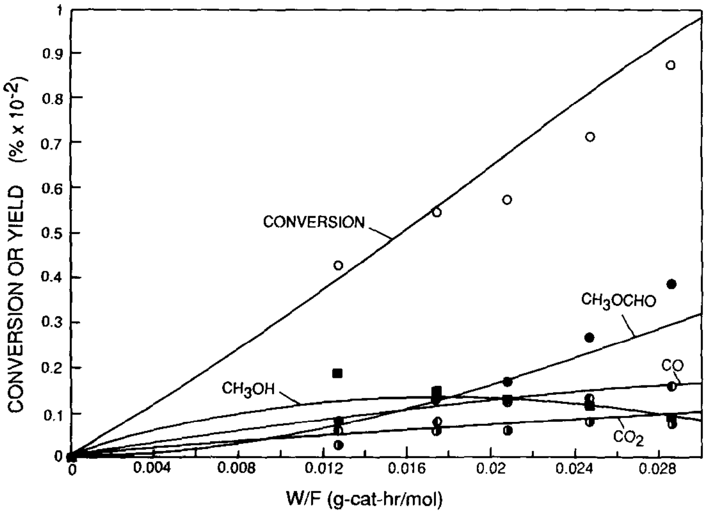

FIG. 4. Conversion of CH_2O (○) and yields of CH_3OH (■), CH_3OCHO (●), CO (◐), and CO_2 (◑) as a function of W/F_{A_0} for 1 wt% Cu/ZnO at 420 K. Solid curves show optimized predictions of Eqs. (18) and (19) (see text).

products CO and CO_2 are produced in only minor amounts. Their yields both appear to increase linearly with increasing W/F_{A_0}.

Finally, to obtain additional confirmation of the zero-order kinetics of CH_2O conversion, we performed separate experiments in which the temperature of the CH_2O generator was changed in order to vary the inlet CH_2O pressure at the reactor. The absolute rate of CH_2O disappearance (i.e., moles CH_2O/g catalyst/time) was found to be independent of inlet concentration, again confirming the presence of zero-order kinetics.

DISCUSSION

Hydrogenation of CH_2O as the RLS in CH_3OH synthesis. As stated in the Introduction, the initial goal of this study was to obtain direct evidence as to whether the hydrogenation of CH_2O is the rate-limiting step in the CH_3OH synthesis reaction. We believe our results indicate that CH_2O hydrogenation *cannot* be the RLS, based on the following reasoning.

The physical significance of the RLS for a sequential, reversible reaction mechanism at steady state (cf. reactions (1), (2), or (3)) is that it represents the elementary step whose forward and reverse rates are most dissimilar, i.e., whose ratio is most different from unity. From this definition it follows that the intermediate which is produced by the RLS will have a (reverse) decomposition rate which is slower than the forward rate of any subsequent elementary step.

In this context the most significant feature of the present results is the observation that CH_3OH is produced in greater yield than CO or CO_2. This means that the rate of CH_2O decomposition is slower than the rate of hydrogenation, which in turn implies that CH_2O must be the *product* of the RLS (or a step which follows it), and not the reactant (or predecessor) for the RLS. Thus CH_2O hydrogenation *cannot* be the RLS in CH_3OH synthesis, at least under the present reaction conditions.

We emphasize that this conclusion is *not* based on the fact that the observed rate of CH_3OH formation from CH_2O hydrogenation is several orders of magnitude faster than the rate of CO hydrogenation under equivalent conditions (the latter rate being undetectably small with our apparatus at 1 atm total pressure and 400 K). The latter line of reasoning would require additional assumptions involving the partial pressure of CH_2O in equilibrium with CO and H_2 at a particular set of reaction conditions, together with a measurement of the CH_2O hydrogenation rate at that pressure.

Since there is spectroscopic evidence that $HCOO_{(a)}$ is a major species on the surface of Cu/ZnO catalysts under $CO:H_2$ mixtures at CH_3OH synthesis conditions (*15*), we suggest that the RLS for CH_3OH synthesis will be the $HCOO_{(a)}$ hydrogenolysis step:

$$HCOO_{(a)} + 2\,H_{(a)} \rightarrow CH_2O_{(a)} + HO_{(a)} \quad (7)$$

Since reaction (7) implies a termolecular surface reaction, it may be more realistic to postulate that the reaction proceeds in two sequential steps via a $CH_2OO_{(a)}$ intermediate:

$$HCOO_{(a)} + H_{(a)} \Leftrightarrow CH_2OO_{(a)} \quad (8)$$

$$CH_2OO_{(a)} + H_{(a)} \rightarrow CH_2O_{(a)} + HO_{(a)} \quad (9)$$

Bowker and Madix (*16*) have reported spectroscopic evidence for $CH_2OO_{(a)}$ as an intermediate during CH_3OH decomposition on Cu(110) surfaces. The same authors also report that this intermediate decomposes readily above room temperature, which suggests that reaction (8) will be reversible while reaction (9) should be considered the rate-limiting elementary step.

We note that any mechanism which includes reactions (8) and (9) will yield a rate expression which is consistent with the large reaction order for P_{H_2} noted by most authors, because of the total of three $H_{(a)}$ atoms that must participate in converting the initial CO or CO_2 reactant beyond the RLS. We are not prepared to speculate regarding the nature of these $H_{(a)}$ atoms at this time (i.e., whether they are adsorbed on Cu, Zn, or O surface atoms).

Reaction mechanism for CH_3OH and CH_3OCHO formation. The second significant result of this work was the unexpected formation of large amounts of CH_3OCHO. As noted above, it appears that CH_3OH and CH_3OCHO are produced sequentially in a mixed parallel–series network (cf. Eqs. (5) and (6)). In addition, the apparent zero-order kinetics for CH_2O conversion indicates that the surface is saturated with respect to $CH_2O_{(a)}$, at least at low conversions. At higher conversions the rate of CH_3OCHO formation *increases*, despite the fact that the partial pressures of both CH_2O and CH_3OH are decreasing over the range of W/F_{A_0} values studied.

We propose that the simplest reaction network that can reconcile these observations is

$$CH_2O \underset{K_F}{\Longleftrightarrow} CH_2O_{(a)} \quad (10)$$

$$CH_2O_{(a)} + H_{(a)} \xrightarrow[k_1]{} CH_3O_{(a)} \quad (11)$$

$$CH_3O_{(a)} + H_{(a)} \underset{K_{Me}}{\Longleftrightarrow} CH_3OH \quad (12)$$

$$CH_2O_{(a)} + CH_3O_{(a)} \xrightarrow[k_2]{} CH_3OCHO + H_{(a)} \quad (13)$$

The rate expressions which follow from this network have the form

$$r_1 = \frac{k_1 K_F P_F}{(1 + K_F P_F + K_{Me} P_{Me})} \quad (14)$$

$$r_2 = \frac{k_2 K_F K_{Me} P_F P_{Me}}{(1 + K_F P_F + K_{Me} P_{Me})^2} \quad (15)$$

where r_1 and r_2 are the rates of reactions (11) and (13), respectively. In terms of overall stoichiometry, r_1 corresponds to the rate of CH_2O conversion, r_2 corresponds to the rate of CH_3OCHO formation, and the difference $(r_1 - r_2)$ corresponds to the rate of CH_3OH formation. The adsorption constants K_F and K_{Me} have their usual meaning, as does the bimolecular surface reaction rate constant k_2. We are forced to consider the rate constant for the $CH_2O_{(a)}$ hydrogenation step as a pseudo-first-order rate constant, k_1, which will be a function of the H_2 pressure. We have not performed experiments over a sufficiently wide range of H_2 partial pressures to accurately resolve the form of this dependence.

The zero-order kinetics of CH_2O conversion imply that $K_FP_F \gg 1$ over the range of CH_2O pressures studied here. The fact that the rate of CH_3OCHO formation increases with conversion implies that $K_FP_F > K_{Me}P_{Me}$, at least at low conversions. These two observations lead to further simplification of the expressions for r_1 and r_2:

$$r_1 = k_1 \tag{18}$$

$$r_2 = (k_2K_{Me}/K_F)(P_{Me}/P_F) = k_2'(P_{Me}/P_F). \tag{19}$$

The optimum values of k_1 and k_2' were determined by regression analysis of the measured product yields using integrated forms of Eqs. (18) and (19). The calculated yield vs W/F_{A0} curves for the resulting values of k_1 and k_2' are shown in Fig. 4. For completeness, we also included zero-order processes $r_3 = k_3$ and $r_4 = k_4$ to describe the formation of CO and CO_2, respectively. The optimum parameter values are

$$k_1 = 17 \text{ mole/g/hr}$$

$$k_2' = 70 \text{ mole/g/hr}$$

$$k_3 = 7 \text{ mole/g/hr}$$

$$k_4 = 4 \text{ mole/g/hr.}$$

Additional experiments using a range of H_2, CH_3OH, and CH_2O pressures would be worthwhile, in order to resolve the individual parameters k_2, K_F, and K_{Me}, and to determine the true H_2 pressure dependence of the surface hydrogenation step (reaction (11)).

SUMMARY

Our results show that phase CH_2O is hydrogenated over Cu/ZnO catalysts at 400 K and atmospheric pressure at a rate that is much faster than the rate of CO hydrogenation (the latter process being undetectably slow at the present conditions). The rate of CH_2O hydrogenation is also faster than its rate of decomposition. The latter result indicates that the rate-limiting step in CH_3OH on these catalysts cannot be the hydrogenation of CH_2O or its subsequent derivatives. Instead, it appears that the RLS during CH_3OH synthesis conditions will be the hydrogenolysis of the $HCOO_{(a)}$ intermediate, via a molecular transition state which requires several $H_{(a)}$ atoms.

The conversion of CH_2O proceeds through the rate-limiting hydrogenation of a $CH_2O_{(a)}$ intermediate which saturates the surface. At low conversions, the resulting $CH_3O_{(a)}$ intermediate is rapidly hydrogenated to produce CH_3OH. At higher conversions, where the concentration of CH_3OH product in the gas phase becomes large enough to maintain a significant $CH_3O_{(a)}$ concentration on the surface, then $CH_2O_{(a)}$ instead reacts with the latter species to produce CH_3OCHO.

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REFERENCES

1. Klier, K., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. Weisz, Eds.), Vol. 31, p. 243. Academic Press, New York, 1982.
2. Kung, H. H., *Catal. Rev. Sci. Eng.* **22,** 235 (1980).
3. Denny, P. J., and Whan, D. A., *Catalysis (London)* **2,** 46 (1978).
4. Bowker, M., *Vacuum* **33,** 669 (1983).
5. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56,** 407 (1979).
6. Fleisch, T. H., and Mieville, R. L., *J. Catal.* **90,** 165 (1984).
7. Chinchen, G. C., Waugh, K. C., and Whan, D. A., *Appl. Catal.* **25,** 101 (1986).
8. Klier, K., Chatikavanij, V., Herman, R. G., and Simmons, G. W., *J. Catal.* **74,** 343 (1982).
9. Agny, R. M., and Takoudis, C. G., *Ind. Eng. Chem. Prod. Res. Dev.* **24,** 50 (1985).
10. Saida, T., and Ozaki, A., *Bull. Chem. Soc. Japan.* **37,** 1817 (1964).
11. Vedage, G., and Klier, K., *J. Catal.* **77,** 558 (1982).
12. Tonner, S. P., Trimm, D. L., Wainwright, M. S., and Cant, N. W., *Ind. Eng. Chem. Prod. Res. Dev.* **23,** 384 (1984).
13. Nelson, F. M., and Eggerston, F. T., *Anal. Chem.* **30,** 1387 (1958).
14. Roberts, D. L., and Griffin, G. L., to be submitted.
15. Edwards, J. F., and Schrader, G. L., *J. Phys. Chem.* **89,** 782 (1985).
16. Bowker, M., and Madix, R. J., *Surf. Sci.* **95,** 190 (1980).