Development of Magnetic Nanoparticles as Microwave-Specific Catalysts for the Rapid, Low-Temperature Synthesis of Formalin Solutions

Mark Crosswhite, Jacob Hunt, Taylor Southworth, Kyle Serniak, Anthony Ferrari, and A. E. Stiegman*

Department of Chemistry and Biochemistry, Florida State University, Tallahassee Florida 32312, United States

S *Supporting Information*

ABSTRACT: A series of heterogeneous catalyst materials possessing good microwave absorption properties were investigated for their activity as oxidation catalysts under microwave irradiation. These catalysts, a series of nanoscale magnetic spinel oxides of the composition MCr_2O_4 (M = Cu, Co, Fe), were irradiated in aqueous methanol solution (1:1 $MeOH:H_2O$ v:v). This resulted in rapid conversion of methanol to formaldehyde, directly generating aqueous formalin solutions. The catalytic reaction occurred under relatively mild conditions (1 atm O_2, 60 °C), with irradiation times of 80 min converting 24.5%, 17.7%, and 13.2% of the available methanol to formaldehyde by the Cu, Fe, and Co chromite spinel catalysts, respectively. Importantly, reactions run under identical conditions of concentration, time, and temperature using traditional convective heating yielded dramatically lower amounts of conversions; specifically, 1.0% and 0.21% conversions were observed with Cu and Co spinels, and no observable thermal products were obtained from the Fe spinels. This work provides a clear demonstration that microwave-driven catalysis can yield enhanced reactivity and can afford new catalytic pathways.

KEYWORDS: *microwave synthesis, microwave catalysis, alcohol oxidation, methanol oxidation, formalin, formaldehyde*
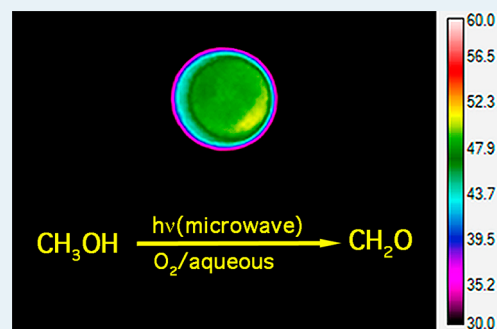
INTRODUCTION

The use of microwave radiation instead of conventional thermal heating can result in large increases in the reaction rates for certain chemical reactions.[1−7] In the particular case of heterogeneously catalyzed reactions, where the solid catalyst is itself microwave-absorbing, the use of microwave heating can produce both particularly dramatic enhancements of reaction rates and also changes in selectivity that differ from those produced by convective thermal heating.[8,9] These microwave-specific effects arise, in part, from the fact that microwaves can selectively heat the catalyst to temperatures much higher than the surroundings. This can rapidly activate substrates that strike the surface and allow the products to be ejected into the cooler medium.[10−12]

In a recent study by Bogdal et al., the magnitude of this selective heating was directly measured for a CrO_2 oxidation catalyst using thermal imaging techniques. The temperature of the catalyst was found to be significantly higher than that of the surrounding medium. In addition, it has also been reported that if this set of conditions is optimized (i.e., with a very hot catalyst and cool surroundings), product selectivity can favor the kinetic product over the thermodynamic one, an observation that is especially true for gas−solid reactions.[7,9]

In addition to selective heating, other microwave-specific effects that can have a strong impact on microwave-driven catalysis have now been well demonstrated, most notably the selective interfacial heating of molecules adsorbed at the surface.[13−15] The latter effect can give rise to changes in the adsorption−desorption properties and activation of substrates at the active site, which can accelerate chemical transformations at the surface. These various microwave-specific processes are shown schematically in Figure 1. Taken together, these fundamental, microwave-specific effects suggest that catalysts selected or designed for their microwave-absorbing properties may show dramatic acceleration of known reactions, or, possibly, facilitate chemical transformations not possible through conventional thermal processes. Because of these potential advantages, the development of microwave-specific, catalytic materials is of some importance.

Our approach to this is to identify classes of materials that show some level of thermal activity toward a specific chemical transformation and, at the same time, are strongly microwave-absorbing. Among the materials that meet these requirements are magnetic spinel nanoparticles. Their suitability arises from the fact that they have significant microwave absorption cross sections arising from loss processes associated with interactions of the electromagnetic field with the unpaired electrons in the spinel.[16−18] In addition, they have high surface areas and are known oxidation catalysts that have been shown to oxidize alcohols.[19]
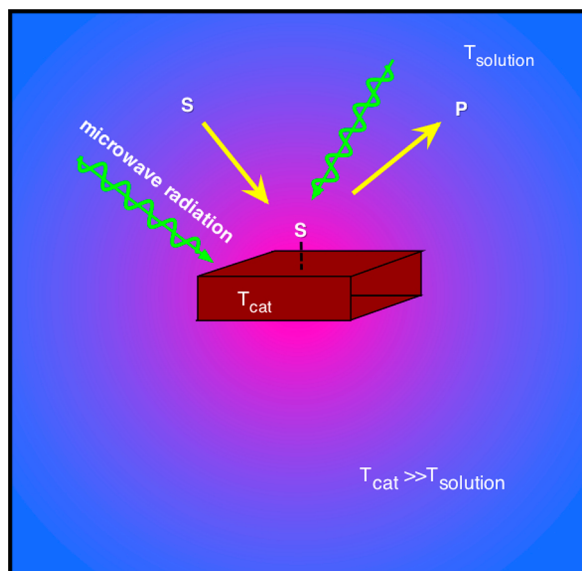
Figure 1. Schematic showing specific microwave interactions with a microwave-absorbing, heterogeneous catalyst system where S is the substrate and P is the product of the catalytic reaction.

In terms of catalytic oxidations, the conversion of methanol to formaldehyde is one of the most challenging; at the same time, it is one of the most useful chemical transformations, as formaldehyde is an essential C-1 building block that is used in a myriad of products. Industrially, its synthesis is carried out by the oxidation of methanol, which is heterogeneously catalyzed by either silver metal or an iron molybdate metal-oxide catalyst as a gas–solid reaction.[20,21] Because of its high volatility and reactivity, formaldehyde is generally produced as an aqueous solution of formalin.[20] We report here the development of a highly microwave-specific catalyst, based on magnetic spinel nanoparticles, that provides rapid, direct, low-temperature, solution-phase synthesis of formalin solutions directly from aqueous methanol.

RESULTS AND DISCUSSION

The catalytic materials that were initially synthesized and screened for activity toward methanol oxidation were a range of ferrite (MFe_2O_4) and chromite (MCr_2O_4) spinel materials where M is a divalent, first-row transition metal ion. The catalysts were made using the precipitation technique, which generates nanoscale particles ($\sim$6−14 nm) with surface areas ranging from $\sim$30−60 m^2/g (see Supporting Information).[22] As a whole, the ferrite series was largely inactive, with the exception of magnetite, Fe_3O_4, which showed modest reactivity. The ferrites tended not to be crystallographically phase pure, when generated through precipitation, which may have been a contributing factor in their performance, though it might simply be that spinels based on Fe^{3+} are inherently less reactive. In contrast to that, the chromite series proved to be phase pure and showed significant microwave-driven methanol oxidation, with the most active of the series being those with the late first-row dications Fe^{2+}, Co^{2+}, and Cu^{2+} (see Supporting Information). For this reason, the chromite series is the focus of the study.

Microwave Heating Properties of the Reaction Solutions. For a microwave-driven, heterogeneously catalyzed reaction system, it is important to understand the microwave-absorption properties of the catalyst and of the other constituents of the medium. For a gas–solid reaction, Debye-type heating of molecules in the gas phase does not occur; therefore, it is the heating of the catalyst and the interaction between the microwaves and adsorbed species on the surface of the catalyst that lead to the observed reactivity. For the liquid–solid catalytic system where the liquid medium, in addition to the catalyst, is microwave-absorbing, the magnitude of the absorption processes of both needs to be considered in analyzing the contribution of the catalyst to the reaction solutions.

Microwave heating of solid dielectric catalyst materials arises from loss processes, which are determined by measuring the real and imaginary part of the dielectric constant (eq 1a), with the loss tangent (eq 1b) computed from those values, typically used to indicate the magnitude of the loss process. The dielectric heating process in solids arises largely from space–charge (interfacial) polarization, which is typical for solid dielectric materials.[23] For the case of magnetic spinels, analogous

$$\varepsilon = \varepsilon' + i\varepsilon'' \tag{1a}$$

$$\tan \varphi_\varepsilon = \frac{\varepsilon''}{\varepsilon'} \tag{1b}$$

$$\mu = \mu' + i\mu'' \tag{2a}$$

$$\tan \varphi_\mu = \frac{\mu''}{\mu'} \tag{2b}$$

to the chromite materials used here, the loss process that leads to heating occurs primarily through the imaginary part of the permeability (eq 2a) and its associated loss tangent (eq 2b), as opposed to the permittivity that is more often observed in solid oxides (eq 2b).[24,25]

The mechanism of the loss processes in magnetic oxides has been treated theoretically by Tanaka et al., who have shown that microwave heating is caused by nonresonant coupling of the magnetic field of the microwave to electron spins in the unfilled 3d orbitals of the metal.[16] The nonresonant coupling was found to cause large changes in the internal energy of the materials through exchange interactions. For the case of magnetic oxide nanoparticles, with a large surface area, we also have to consider that defects and interfacial processes will contribute to heating though dielectric loss mechanisms.

The catalytic reactions reported here are run in strongly microwave-absorbing, aqueous methanol solutions that can potentially attenuate the microwaves and reduce the amount of radiation absorbed by the catalyst itself. The absorption of microwaves by a medium is typically described in terms of an attenuation factor that decreases the intensity of the incident radiation as it propagates though the medium.[26] The magnitude of the attenuation factor is a function of the real and imaginary components of the permittivity (eq 1a) and permeability (eq 2a), and it falls off exponentially in the direction of the radiation flows. For a heterogeneous catalyst–solution system with both components absorbing, the attenuation factor will be related to the attenuation factor for the methanol–water solution plus the catalyst, weighted by their fraction of the total composition. Such attenuation, if significant, would cause a decrease in microwave heating across the radius of the reaction vessel, thereby creating heterogeneity by restricting the reactivity to an annulus around the sides of the reaction vessel. While such attenuation would not be expected (or would be expected to be small) in a well-stirred solution, it is useful to confirm, at least

qualitatively, the homogeneity of the solution under reaction conditions. This can be done qualitatively, by thermal imaging of the solution under reaction conditions.

As can be seen in Figure 2a, the thermal images of the surface of the stirred solution under irradiation show relatively uniform
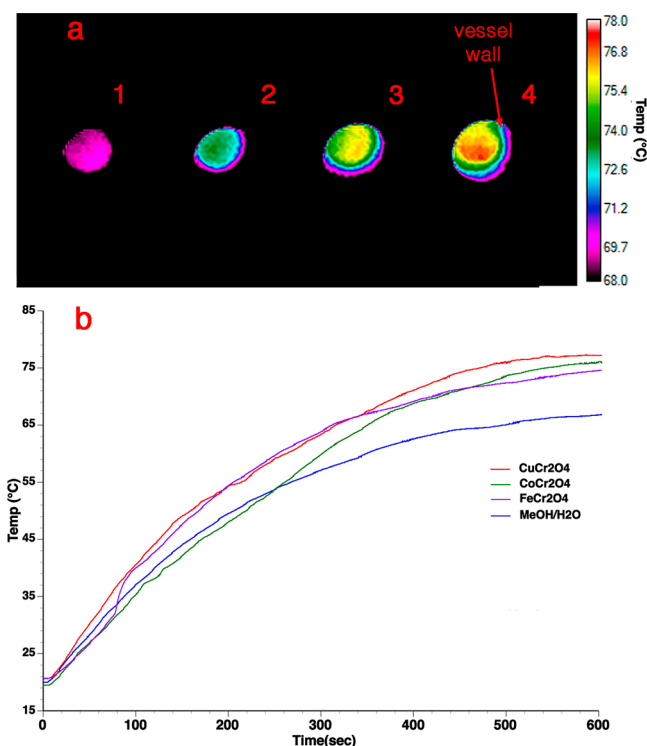

Figure 2. (a) Thermal imaging of the surface of stirred 6 mL MeOH:H$_2$O (1:1 v:v) solution containing (1) no catalyst and 166 mg of (2) FeCr$_2$O$_4$, (3) CoCr$_2$O$_4$, and (4) CuCr$_2$O$_4$ at steady-state temperature. (b) Heating curves for the same solutions irradiated in the microwave at 5 W constant applied power.

temperatures across the surface of the solution. The images shown were collected when the system had reached steady state and, as would be expected, lower temperatures are observed at the edges of the vessel where convective heat flow out of the system is occurring. More importantly, while there are variations in the temperature across the surface because of agitation of the solution, there is no systematic decrease in the temperature, and, in fact, the center of the solution is generally hotter than the edges, suggesting that the reaction solution is being homogeneously heated.

To assess the contribution that the catalyst makes to the absorption of microwaves by the reaction solution, heating curves at fixed applied power (5 W) for 6 mL of a methanol/water (1:1 v:v) solution containing no catalyst and 166 mg of the three spinel catalysts were measured using an internal fiber-optic thermometer (Figure 2b). The observed heating curves generally follow the established trajectory for microwave heating in lossy solution where there is a rapid, relatively linear, initial increase in the temperature as microwave power is applied, followed by a plateau as steady-state conditions are attained (the heat flow out of the reaction vessel matches the heat generated in the solution by the microwave).[27]

Notably, however, there are significant variations along the individual curves that can be observed as the system heats. The most notable of these is that the heating curve for the CuCr$_2$O$_4$

catalyst, which at places along the heating curve generates less heat than the FeCr$_2$O$_4$ catalyst, ultimately surpasses it as steady state conditions are reached. Similarly, the CoCr$_2$O$_4$ catalyst shows one of the lowest initial heating rates, even falling below the pure solvent but becomes the second highest generator of heat as steady-state conditions are achieved. It is important to note that this and other nonuniform variations in the heating behavior are completely reproducible over multiple independent runs. The observed variation of the heating curves along their trajectories arises in part from the temperature dependence of the microwave-absorption cross section for the constituents of the reaction. In particular, the methanol/water reactant/solvent system will become less absorbing as it heats because of the inverse temperature dependence of the dielectric loss, as indicated in the Debye equations.[27,28] Similarly, the metal oxide catalysts will also show a temperature dependence. For dielectric heating of nonmagnetic metal oxides, the absorption usually increases with temperature (for bulk solids, this typically occurs at much higher temperatures than are attained here).[29,30] For a magnetic metal oxide, particularly one that is a nanoparticle, the temperature effects have not, to the best of our knowledge, been investigated.

Finally, since this is a strongly interacting catalytic solution, interfacial effects may alter the absorption cross section over time, and since, as will be discussed, the reaction is exothermic, heat will be generated that will contribute to the observed temperature of the solution. Regardless of the variation in the specific trajectories of the heating curves, the systems reach steady-state conditions at temperatures close to where the catalytic reaction will be run. Specifically, the steady-state temperature reached by the methanol/water mixture is 66.8($\pm$.4) °C, while the Cu, Co, and Fe chromite catalyst systems reach higher steady-state temperatures of 77.2($\pm$.6), 76.0($\pm$.4), and 74.5($\pm$.4) °C, respectively. The difference between the steady-state temperature of the pure solution and those of the solutions containing the catalyst is caused by the additional heat being put into the solution by the catalyst; this heat arises from convective heat transfer from the irradiated catalyst and from any heat generated from chemical processes occurring at the surface. From the energy balance equations (see Supporting Information) for microwave heating of the methanol–water solvent system in presence and absence of the catalyst, the percent contribution of the catalyst to the total heat of the solution, estimated from the ratios of the steady-state temperatures, was found to be 19%, 17%, and 15% for Cu, Co, and Fe, respectively (Supporting Information, eqs S1−S5).

Catalytic Oxidation of Methanol. Initial microwave reaction studies of the active catalysts were carried out using a fixed set of conditions. In particular, reaction mixtures composed of 6 mL of a 12.3 M aqueous methanol (1:1 v:v MeOH:H$_2$O) solution and 166 mg of the spinel catalyst were heated to a temperature of 60 °C, with samples withdrawn for analysis every 20 min during the 80 min of total reaction time. The reactions were carried out in a closed Pyrex cell with constant stirring under 1 atm of O$_2$ with the temperature monitored internally using a fiber-optic thermometer.

The production of formaldehyde as a function of irradiation time is shown in Figure 3. As can be seen, all three catalysts show good efficiency, converting between ~13% and 26% of the methanol to formaldehyde over the 80 min of reaction time, depending on the catalyst. From the number of moles of formaldehyde generated over the reaction time and the Brunauer−Emmett−Teller (BET) nanoparticle surface area
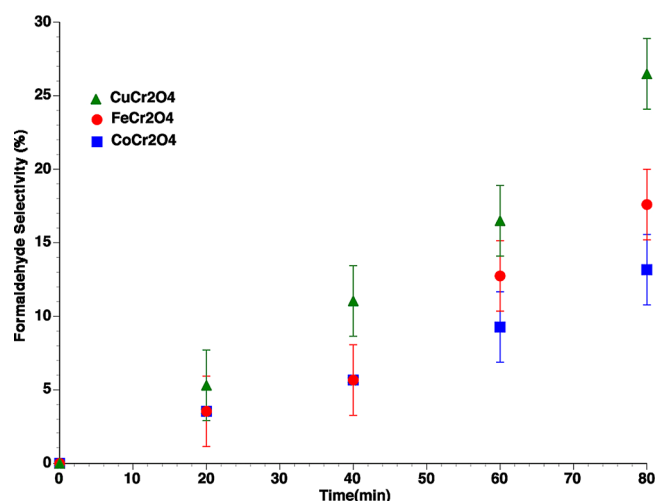
Figure 3. Percent methanol converted to formaldehyde as a function of reaction time at a temperature of 60 °C (i.e., microwave irradiation time) for the catalysts (▲) $CuCr_2O_4$, (●) $FeCr_2O_4$, and (■)$CoCr_2O_4$.
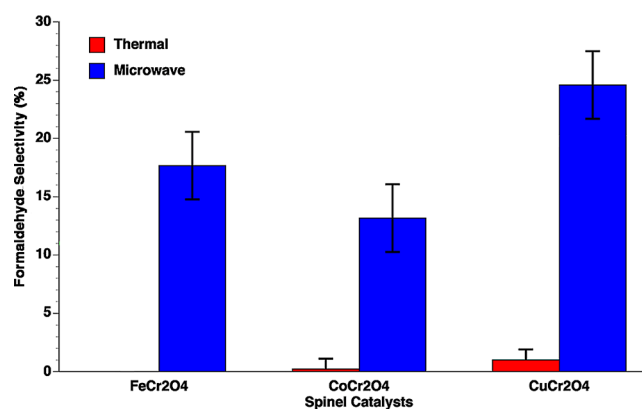

Figure 4. Percent conversion of methanol to formaldehyde for the three spinel catalysts after 80 min of reaction time (6 mL of 1:1 $MeOH:H_2O$ v:v, 166 mg of catalyst) at 60 °C under (blue) microwave and (red) convective heating.

measurements, the values for the turnover frequencies were determined to be 0.01, 0.15, and 0.37 mmol/sec m^2 for the Co, Fe, and Cu catalysts, respectively. As indicated by the data in Figure 3 and the turnover frequencies, even with its smaller surface area the $CuCr_2O_4$ is the most efficient catalyst, while the Fe and Co chromites are similar in activity and have somewhat lower efficiency. Notably, this relative ordering is consistent with the heating curves, which show the Cu to generate the most heat in the reaction solution at steady state. For the Co and Fe, the formaldehyde formation data indicate that Fe has greater reaction efficiency than does Co, while the heating curves indicate that Co makes a greater contribution to the heat of the solution than does Fe. This may suggest that Fe is a better catalyst even though it contributes less heat to the solution (possibly suggesting a lower activation energy); however, methanol production for both the Co and the Fe is similar, generally within experimental error, making such analysis speculative at best.

Of central interest in this investigation is the degree to which the reaction is microwave-specific. To evaluate this, the reactions were carried out under identical conditions (i.e., stirred, closed container; 1 atm of O_2; internal temperature monitoring) but using a regulated thermal bath to maintain a temperature of 60 °C (see Supporting Information). After 80 min of reaction time, the conversion of methanol to formaldehyde was measured.

The results are shown in Figure 4 as the percent methanol oxidized to formaldehyde. What is most significant is that the reaction is almost uniquely microwave-specific, with only a limited conversion to formaldehyde (≤4% of the microwave conversion) being observed during conventional thermal heating for $CuCr_2O_4$. Even increasing the thermal temperature to 80 °C for $CuCr_2O_4$ results in only a 10.2% conversion after 80 min. This establishes quite clearly that microwave-driven catalysis has unique characteristics that can result in dramatic enhancements in reaction rates.

Selectivity. The evolution of the microwave-driven oxidation as a function of microwave irradiation time was monitored by ^1H NMR spectroscopy. As indicated by the spectra (Supporting Information, Figure S5) shown for the $CuCr_2O_4$ catalyst, the reaction is very selective, with no

evidence of any other organic products other than formalin (4.8 ppm) within the detection limits of the NMR.[31] Importantly, this also includes formic acid, a typical side product of methanol oxidation, which would have exhibited a methyl resonance at 6.45 ppm. Finally, gc analysis of the head space over the reaction indicates that no measurable amount of CO or CO_2 was detected, which would be the product of more complete oxidation of the methanol.

Nature of the Oxidation Process. The net oxidation of methanol as it is carried out commercially over iron molybdate catalyst is an exothermic oxidation process that consumes oxygen and produces water (rxn. 1).[20] The reaction over iron molybdate is thought to take place by a Mars−van Krevelen mechanism, where oxidation of methanol occurs through removal of the lattice oxygen of the catalyst. The reduced catalyst is subsequently reoxidized with O_2.[32,33] Isotopic labeling studies have indicated that the rate-limiting step is the cleavage of the methyl C−H bond on methanol at the active site.[33,34] Similar results have been reported by Wachs et al. for methanol oxidation over another oxide system.[35,36]

$$CH_3OH + 1/_2O_2 \xrightarrow{FeMoO_4} CH_2O + H_2O$$
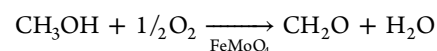
$$\Delta H = -159\ kJ/mole \qquad (1)$$

It might be anticipated that the microwave-driven oxidation over magnetic oxides would proceed via the oxidation process in rxn. 1.

Consistent with this expectation, we observe a pronounced effect of applied O_2 pressure across the series of catalysts (Figure 5). Specifically, under the same conditions of reaction temperature, solution concentrations, and amount of catalyst, the percent conversion of methanol under 1 and 3 atm of applied O_2 was measured. It was found that the amount of methanol converted increased by a consistent factor of 1.49 (±0.09) for all the catalysts in going from 1 to 3 atm. Notably, the strong O_2 dependence argues against a Mars−van Krevelen mechanism, which typically occurs at high temperatures and exhibits a zero- or low-order O_2 pressure dependence.

A quantitative determination of the stoichiometry of the reaction can be obtained from the disappearance of O_2 during the course of irradiation (Figure 6). Specifically, the pressure change during the course of the reaction, for the vessel used, corresponds to 5.91×10^{-3} moles of O_2 being consumed. At
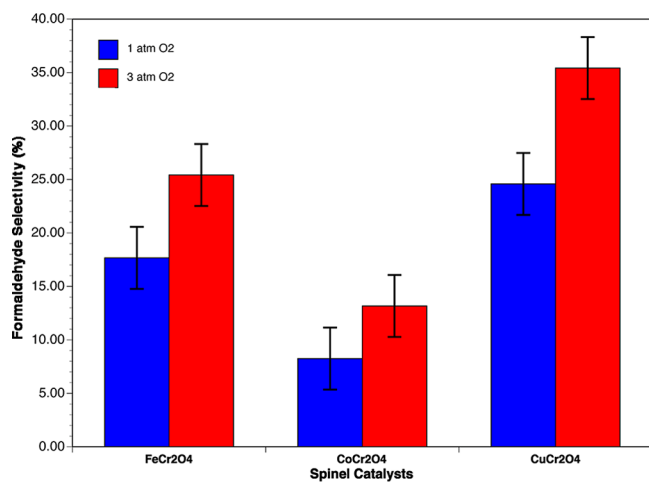
Figure 5. Methanol conversion (%) for the three spinel catalysts at a starting O₂ pressure of (blue) 1 and (red) 3 atm. Experimental conditions were 6 mL of 1:1 v:v MeOH:H₂O, 0.166 mg of catalyst, 80 min at 60 °C.
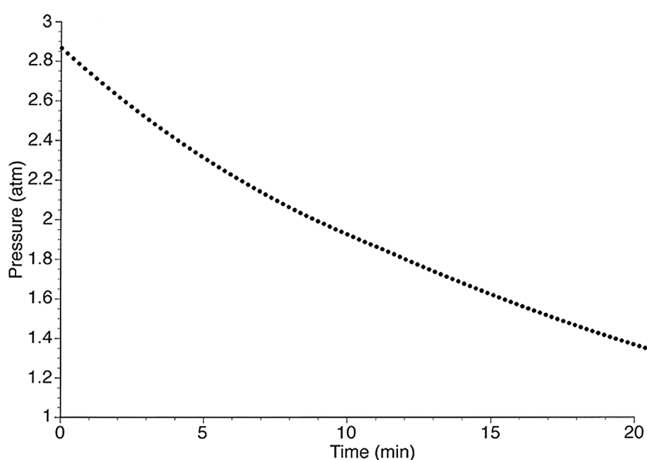

Figure 6. Consumption of oxygen during the conversion of methanol to formaldehyde over $CuCr_2O_4$ catalyst at 60 °C.

the end of the 20-min period, the amount of formaldehyde produced was determined to be 1.21×10^{-2} moles, yielding a stoichiometry of ~2:1 MeOH:O₂, consistent with rxn. 1.

Industrially, methanol oxidation is carried out as a gas−solid reaction at temperatures between 300−440 °C, wherein a vaporized methanol and oxygen mixture reacts over the catalyst. Although there are some disagreements in the literature, the iron−molybdate catalyst used in the industrial reaction is generally considered to be water-sensitive, and the desired formalin solutions are generated at the end of the reaction by addition of water.[20,33] For this reason, the fact that microwave conversion occurs in high yield in aqueous solution is somewhat notable. Commercial formalin solutions are typically 37 wt % formaldehyde in water, which are inhibited by methanol in amounts ranging from 1−15 wt %. Under the reaction conditions described above (166 mg of CuCr₂O, 12.3 M MeOH, 80 min at 60 °C), we produce 0.0173 mols of formaldehyde, yielding a formalin solution that is 9.37 wt % formaldehyde in a solution that is, after the reaction, approximately 37 wt % in methanol. Obviously, we would expect to see more formaldehyde formed by increasing the amount of catalyst or the temperature or duration of the

reaction. However, as one of the more interesting aspects of this reaction is that it is efficient in aqueous solution, and with the goal of making directly solutions with higher formalin and lower final methanol concentrations, we investigated what effect the amount of methanol had on the production of formalin. Using the same conditions described above, reactions were run with MeOH:H₂O ratios of 1:3.2, 1:1, and 1:0.5.

The percent conversion obtained from these reactions is shown in Figure 7. As indicated by the data, both Fe^{2+} and Co^{2+}
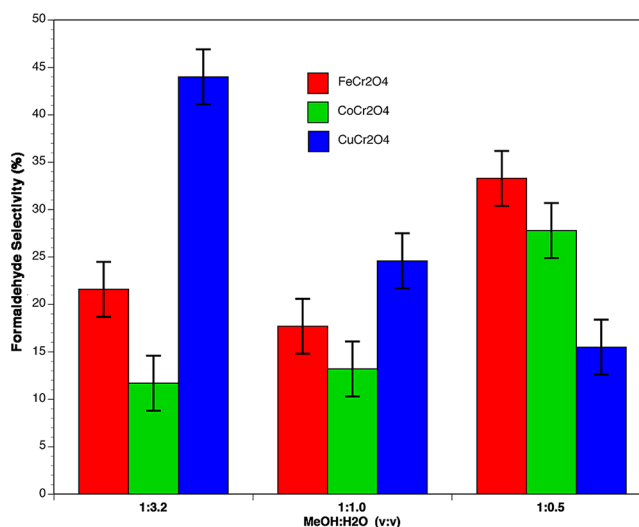

Figure 7. Conversion of methanol to formaldehyde after 80 min at 60 °C under 1 atm O₂ for the three spinel catalysts under varying MeOH:H₂O ratios.

chromites tend to show an overall increase in conversion efficiency in solutions that are high in methanol. Obviously, we do not know specifically what the active sites are on these catalysts; however, the strong dependence of the reactivity on the nature of the M^{2+} ion suggests that it plays a key role. All three of these spinels are normal, and consequently, in the bulk, the M^{2+} ions will occupy tetrahedral sites.[37] On the surface, they will likely be coordinatively unsaturated, and, in an oxide lattice and an aqueous methanol environment, would be in a weak ligand field environment. This suggests that aspects of their relative reactivity can be interpreted by considering ligand substitution processes. Under these conditions, Fe^{2+} and Co^{2+} are relatively labile (significantly more labile than Cu^{2+}), suggesting that the observed trend is likely due to the decreased competition for binding to the active site as the amount of water decreases.[38] What is not as easily reconciled is the fact that $CuCr_2O_3$ appears to be inhibited in solutions that are high in methanol. In fact, it has a very high conversion efficiency (>40%) in aqueous solutions that are low in methanol. The cause of this is not completely clear but may have to do with the high acidity of the Cu^{2+} sites in the aqueous environment.[38] Detailed studies of methanol binding to metal oxide surfaces in the gas phase have shown that two types of sites form: simple coordinated methanol (M−OHCH₃) and methoxy sites (M-OCH₃).[39,40] The formation of the methoxy sites necessarily requires the loss of a proton, which will be enhanced with a strongly acidic metal such as Cr^{2+}. In the gas phase, the proton will be trapped on the oxide surface; however, in solution it will be solvated, depending on the nature of the solvent.[39] This suggests that the concerted effect of the acidic Cu^{2+} site coupled with the aqueous environment may significantly drive

the formation of the methoxy species, which could account for the enhanced reactivity under conditions of high water. Obviously, while this provides a reasonable explanation of the observed trend for $CuCr_2O_4$, it has not been verified, and other explanations exist such as interfacial, microwave-specific effects that result from changes in the surface composition as a function of methanol concentration, with hydrated surfaces being more selectively heated and, therefore, becoming more reactive. From a synthetic standpoint, however, this indicates that, as with traditional thermal catalysis, microwave-driven catalysis will be very dependent on the composition of the reaction mixture. As such, evaluation of catalysts under different conditions will facilitate the optimization of a particular reaction.

In conclusion, we believe the most significant aspect of this study is that it reports the catalysis of a difficult and important oxidation process, the oxidation of methanol, which is almost exclusively microwave-driven. An important aspect of the work is that the catalysts were developed specifically for their microwave-absorption characteristics. The catalyst systems, which are a series of chromite nanospinels, generate form-aldehyde (formalin) directly from aqueous methanol with good efficiency (~ 25% conversion of a 12.4 M solution) under very mild conditions (60 °C, 1−3 atm O_2) when under microwave irradiation. To the best of our knowledge, there are no thermal counterparts to these catalysts that produce formaldehyde under similar conditions and with equal efficiencies. Taken together, the results suggest that a rational approach to the development of catalysts specifically for microwave-driven processes is potentially useful.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Catalyst preparation and characterization, determination of formaldehyde concentrations, energy balance equations, ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: stiegman@chem.fsu.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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