An investigation of catalytic activity in mixed metal oxide nanophase materials

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Abstract. We present preliminary evidence for catalytic activity by unsupported mixed metal oxide nanocrystalline materials. The results of this study show that a nanophase form of Li-MgO has begun to exhibit catalytic activity by 300 °C. This is at least 200 degrees below the temperature at which conventional Li-MgO catalysts exhibit comparable activity. Furthermore, at higher temperatures, the same nanophase composition shows enhanced activities and somewhat improved hydrocarbon selectivities over conventional Li-MgO catalysts.

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1. Introduction

In recent years, nanometer-dimensional clusters have received increasing attention as possible building blocks for a new generation of materials exhibiting unique or improved electronic, magnetic, optical, mechanical, and/or chemical properties [1-4]. Nanometer-sized clusters themselves possess several unusual and potentially useful properties in this regard. These include unusually high surface areas, a high degree of geometrical surface defects, enhanced nonlinear optical properties, and electronic and therefore chemical reactivity properties which are inherently different from both their corresponding atoms and molecules and from their bulk forms. Likewise, consolidated nanophase materials also exhibit properties different from those of conventional bulk materials. Transmission electron microscopy has been used to examine the grain structures in nanophase materials, and it has shown that stable, discrete nanocrystallite domains are preserved within the consolidated materials even after compaction [5-7]. This results in a high fraction of grain boundary interfaces, leading to fast diffusivities in these materials. Nanophase materials have also been found to exhibit improved mechanical properties, including indications of unusually high ductilities for some ceramic compositions [8-11].

Our explorations of nanophase material applications have thus far focused on heterogeneous oxidation catalysis, utilizing the mixed metal oxide Li-MgO as a prototype system. In its bulk conventional form, lithium promoted magnesium oxide is the well known Lunsford catalyst [12,13] used in the oxidative conversion of methane to higher hydrocarbons. In the mechanism proposed by Lunsford and coworkers [13-16], activation of methane occurs by the abstraction of hydrogen atoms by [Li^+O^-] active sites on the catalyst surface to produce surface hydroxide anions and methyl radicals which are released into the gas phase. The methyl radicals then couple to produce higher hydrocarbon products while the catalytic site is regenerated via elimination of water and interaction with gas phase molecular oxygen which had been introduced along with the methane. Lunsford and coworkers [14] examined the reaction kinetics of this process using EPR to measure methyl radical concentrations and concluded that the rate limiting step appears to be the heterogeneous step involving the formation of methyl radicals on the catalyst surface.

To maximize activity, it is desirable to utilize catalysts with very high surface areas since the critical step in this process appears to occur at the surface . Given their intrinsically high surface areas, unsupported nano-particles of mixed metal oxides are particularly well-suited for this purpose. The only alternative high surface area catalysts are molecular sieves such as zeolites and supported nano-particles, the former being inappropriate for this application and the latter exhibiting smaller active surface areas per mass than unsupported nano-particles. Conventional metal oxide catalysts typically possess surface area-to-mass ratios on the order of $1m^2/g$ (typical particle diameters of ~1μm). For spherical particles, this ratio

should scale as $\sim D^{-1}$, where D is the particle diameter. The size regime of nanophase particles lies between the particle sizes of conventional oxidation catalysts and those of isolated atoms and molecules. Within this size regime, D can vary over three orders of magnitude, yielding surface area-to-mass ratios up to about three orders of magnitude larger than conventional catalysts. With such high surface areas, nanometer particles may display significantly enhanced activities over conventional catalysts. In addition to this surface area effect, other intrinsic properties of nanometer dimensional particles may make them desirable catalysts. The large number of surface geometrical defects in these systems may have important effects on catalytic selectivity, and their unique electronic properties may lead to attractive reactivity characteristics for these particles.

While the area of unsupported nanophase catalysis is relatively new and unexplored, some success has already been achieved. The first report of unsupported nanometer dimensional particles being used as catalytic materials was apparently by Hayashi who used ultrafine particles of nickel to effect the preferential hydrogenation of cyclooctadiene [17]. Work in this area continued with the investigations of Stencel, Eklund, and coworkers who employed iron-based nanophase catalysts for coal liquefaction [18], with our own studies of mixed metal oxide nano-clusters [19], and with the work of Beck and Siegel who used TiO_2 nanophase materials for the decomposition of hydrogen sulfide in a H_2 environment [20]. Here, we follow up our earlier efforts by reporting the first evidence for catalytic activity in an unsupported nanophase oxidation catalyst.

2. Preparation of Nanophase Catalyst Samples

Samples of unsupported nanophase Li-MgO powders were generated using our inert gas condensation-based Smoke Source [21] with minor modifications to facilitate sample collection. This method of nanophase powder generation is very general as indicated by the ability of this device, when operated as an ion source, to generate intense cluster ion beams from a wide variety of materials including metals, alloys, semiconductors, alkali halides, and metal oxide ceramics [22,23]. In this device, the material of interest is evaporated from a radiation shielded crucible region. Vapor effusing from this region then enters a condensation cell region typically containing 0.1-10.0 torr of helium maintained at a constant temperature which can range from -196 °C to 25 °C. The evaporated material supersaturates in this cool environment and nucleates to form a dilute smoke composed of nanometer-sized clusters. For the preparation of nanophase samples, a cooled collection plate is often inserted into the condensation cell. Convection currents within the source transport a substantial portion of the clusters to the collection surface. When this device is operated as an ion source, the condensation cell is coupled to high vacuum by a small (1.0 mm diameter) aperture, creating a flow of helium which entrains the clusters and transports them into a high vacuum region where they are ionized by a negatively biased hot filament (in the presence of suitable magnetic fields) and subsequently mass analyzed. Nanophase powders are also generated during ion source operation. Thus, this device can be used for *in situ* mass spectral monitoring of nanophase powder particle size distributions during sample preparation.

Nanophase metal oxide ceramics can be produced by three principle methods: direct evaporation of the ceramic material, reactive evaporation of the condensing metal vapor with a small partial pressure of oxidant in the helium quench gas, and post-oxidation of preformed metal nano-clusters. The latter two approaches were used to prepare the Li-MgO samples in these studies. Two nanophase powder samples have been tested for catalytic activity thus far. Both samples were prepared by coevaporating Li and Mg metals from a single multicompartment stainless steel crucible at 700 °C into ~ 800 mtorr of quench gas maintained at 15 °C. The amounts of the Li and Mg charges were adjusted to give a target composition of roughly 5% Li in MgO by weight in the final material, although the single crucible design made control of stoichiometries difficult. One of the samples (denoted Nanophase 1) was generated by evaporating the metals into pure helium gas. The Li-Mg nanophase powder was subsequently oxidized at room temperature for 12 hours in a He/O_2 mixture containing $\sim 20\%$ O_2 by weight. The sample was then collected and baked in air at ~ 100 °C for 1 hour. The other sample (denoted Nanophase 2) was produced by reactive evaporation of the metal vapors into a He/O_2 mixture containing $\sim 1\%$ O_2 by weight. This sample was then allowed to sit in air for 12 hours, after which the nanophase powder was collected and baked in air at ~ 100 °C for 1 hour. During the collection of sample Nanophase 2, it was noticed that a large fraction of the Mg metal charge had not been evaporated. This seemed to be due to the presence of a thin MgO layer over the metal charge which presumably formed by reaction of the magnesium melt with the O_2 reactant gas, and suppressed the evaporation of Mg. No oxide layer was observed over the lithium charge, resulting in a highly Li rich nanophase powder sample. Elemental analysis of this sample revealed that it contained comparable amounts of Li and Mg by weight. By contrast, elemental analysis of Nanophase 1 showed this sample to be much closer to the target composition, containing $\sim 10\%$ Li by weight.

Both scanning electron microscopy and mass spectrometry were used to estimate particle size, and thus

surface area-to-mass ratios, for the nanophase samples. The nanophase samples were each examined using scanning electron microscopy before catalytic activity tests were carried out. The samples were shown to consist of distinguishable particles with ≤ 40 nm diameters. It is important to point out, however, that this was an instrumentally limited measurement and represents only an upper limit to the particle sizes in these nanophase samples. A better estimate of the true particle sizes in these samples was obtained from mass spectrometry by examining the cluster size distributions produced under conditions closely mimicking those under which the nanophase samples were produced. Conditions for the Nanophase 1 sample showed an average mass of ~7,000 amu for Li_xMg_y clusters. Assuming weighted bulk densities, an average diameter of ~5.2 nm is implied with a surface area-to-mass ratio of ~750 m^2/g. Conditions for the Nanophase 2 sample showed an average mass of ~3,000 amu for $Li_xMg_yO_z$ clusters, implying an average diameter of ~2.8 nm with ~1,400 m^2/g. The particles in the actual nanophase samples were probably somewhat larger than those implied by the mass spectrometric measurements since they were generated in the absence of a gas flow, and would therefore have had longer residence times for nucleation. In addition, the post-oxidation process probably increased the particle sizes, but only by a small amount as was observed by Siegel for the oxidation of Ti nanophase particles [5]. Despite these increases in particle size, the surface area-to-mass ratios of the nanophase samples were still likely to have been extraordinarily high as compared with those of conventional oxidation catalysts.

3. Searches for Catalytic Activity

Catalytic activity searches were performed on 0.1 g quantities of each sample material in a narrow quartz reactor. Each sample was exposed to a 50-50 methane-air gas mixture at 1 atm total pressure over temperatures ranging from 300-700 °C. Reaction products were identified in the effluent by gas chromatography. In addition to the two nanophase samples, a conventional Li-MgO catalyst was prepared and tested for activity. The conventional catalyst (denoted ACC Conventional) was prepared by impregnating MgO with Li_2CO_3 to give ~2% Li by weight in the final material. As controls, additional blank runs were carried out at several temperatures in the absence of any catalyst to examine the extent of background reactions. The results of these tests are summarized in Table 1. Results previously reported by Lunsford and coworkers (denoted Lunsford Conventional) are shown for comparison [13]. Methane flow rates are expressed as WHSV (Weight Hourly Space Velocity). This quantity represents the mass flow rate of

feed (CH_4) per mass of catalyst sample, and thus has units of hr^{-1}. It should be noted that the lower the WHSV value, the longer the exposure time of the CH_4 to the catalyst surface. Therefore, for a given sample, lowering the WHSV would be expected to result in an increased methane conversion percentage. The product of the WHSV and the percent methane conversion is defined as the catalytic activity (ie. the mass flow rate of reaction products per mass of catalyst sample).

The results in Table 1 reveal that the behavior exhibited by Nanophase 1 at 300 °C was markedly different from that of the conventional sample. Although no hydrocarbon products were generated, a significant amount of CH_4 was converted to CO_2 at a temperature where conventional catalysts show no activity. The possibility that the CO_2 was not produced by catalytic activity but was evolved by the nanophase sample itself, can be eliminated. Any CO_2 within the nanophase sample would have been present in the form of Li_2CO_3 which would not have decomposed to give CO_2 until substantially higher temperatures had been reached [24]. Accordingly, no CO_2 was observed for the ACC Conventional sample which contained Li_2CO_3 from its synthesis. In addition, the reaction of CH_4 with any residual water vapor which may have been present in the reactor to yield CO_2 and hydrogen does not explain this result either since ΔG for this process is positive at 300 °C by over 13 kcal mol^{-1} [25]. The only other plausible alternative explanation to catalytic activity is the reaction of CH_4 with peroxide or ozonide centers in the nanophase sample. This is unlikely, however, since the production method used for Nanophase 1 tends to yield samples which are slightly oxygen *deficient*, as was observed by Siegel for TiO_2 nanophase materials [5]. Thus, this result suggests that a nanophase form of Li-MgO exhibits catalytic activity at least 200 degrees below the temperatures at which conventional Li-MgO catalysts exhibit comparable activity. This result further suggests the possibility that the process temperature for oxidative methane coupling may be lowered by a corresponding amount. This is attractive since lowering the temperature would lead to a significant reduction in the extent to which nascent hydrocarbon products are pyrolyzed.

Upon heating above 300 °C, both nanophase samples were observed to change color from black to white and to coalesce to smaller volumes within the reactor. In contrast, the ACC Conventional sample remained white, and was stable throughout the test. This suggests that the nanophase samples were initially comprised of very small particles which sintered above 300 °C. Scanning electron microscopy revealed that both nanophase samples consisted of 300 nm diameter particles after the activity tests,

Table 1. Results of catalytic activity test on Li-MgO samples

Temperature (°C)	Catalyst	CH_4 WHSV[1]	% CH_4 Conversion	% Selectivity to:					
				C_2H_6	C_2H_4	C_3H_8	C_3H_6	CO	CO_2
300	Nanophase 1	10	1.0	0	0	0	0	0	100
	ACC Conventional	5	0.0	0	0	0	0	0	0
400	Nanophase 1	10	0.2	0	0	0	0	0	100
	Nanophase 2	5	0.04	4	5	13	78	0	0
	ACC Conventional	5	0.2	0	0	0	0	0	100
500	Nanophase 1	10	0.5	0	0	0	0	0	100
	ACC Conventional	5	0.3	0	0	0	0	50	50
	Empty Tube	same flow	0.0	0	0	0	0	0	0
560	Lunsford Conventional	0.8	0.1	0	0	0	0	0	100
600	Lunsford Conventional	0.8	0.7	38	0	0	0	5	57
	Nanophase 1	10	7.7	8	1	0	0	13	78
	Nanophase 2	5	1.2	12	7	0	0	44	36
	ACC Conventional	5	3.0	2	1	0	0	34	64
	Empty Tube	same flow	0.0	0	0	0	0	0	0
700	Nanophase 1	10	8.9	43	16	2	1	3	35
	Nanophase 2	5	6.4	33	13	0	1	15	39
	ACC Conventional	5	6.1	34	9	1	1	7	49
	Empty Tube	same flow	0.1	91	9	0	0	0	0

confirming the sintering process. The size dependence of the melting and sintering behavior of clusters has been considered both experimentally [26-28] and theoretically [29-31]. A description of this behavior is provided by a thermodynamic model which predicts the melting temperatures of clusters to be reduced relative to those of their corresponding bulk materials and to scale linearly as R^{-1}, where R is the cluster radius. Accordingly, metal oxide nanophase materials may prove to be superior to many other nanophase materials for applications in which it is desirable to avoid sintering, since many bulk metal oxide ceramics possess very high melting temperatures. For pure MgO clusters of the sizes employed here, the expected melting temperature based on size scaling to the bulk melting temperature is ~950 °C [32]. It is probable that the high Li concentrations in the nanophase samples played a major role, in addition to size effects, in contributing to sintering at lower temperatures than expected. While the addition of a small percentage of a low melting point dopant such as Li should depress the melting point, it may still be possible to synthesize a nanophase Li-MgO catalyst which is stable in the operating temperature range (600-850 °C) of the conventional material by utilizing significantly lower

levels of Li than those used here. Also, the use of lower lithium concentrations may have the concurrent positive effect of increasing activity. This effect can be seen by comparing the two conventional catalysts at 600 °C in Table 1. The ACC Conventional sample (2% Li) showed greater methane conversions than those reported by Lunsford and coworkers for their conventional catalyst (7% Li) despite the much lower WHSV used in evaluating the latter.

Once the Nanophase 1 sample sintered, it behaved more like the ACC Conventional sample, although it still showed improved performance. This can be seen at each temperature from 500-700 °C in terms of methane conversion, and at 600 °C and 700 °C in terms of hydrocarbon selectivity. A better quantitative measure of the actual enhancement in the performance of Nanophase 1 relative to the ACC Conventional sample, however, is obtained by comparing the activities of the two catalysts. Over the temperature range from 400-700 °C, the activity of the Nanophase 1 sample was consistently higher than that of the ACC Conventional sample, being 3.3 times greater on average. The expected activity increase from the greater surface area of the nanophase sample, based on its post-sintering particle sizes, is approximately a factor of 6. The

reason for the entire increase not being realized may lie in the fact that the lithium concentration of the Nanophase 1 sample (~10% by weight) was substantially higher than that of the ACC Conventional sample (~2%).

In considering the performance of the Nanophase 2 sample, it should be again noted that the lithium concentration of this sample was much higher than the target concentration, and furthermore, much higher than those utilized in conventional lithium-magnesia oxidation catalysts. Nevertheless, this nanophase sample also exhibited catalytic methane conversion. The activity of this sample, however, was smaller than that of the ACC Conventional sample at 400 °C and at 600 °C, and was only slightly higher at 700 °C. The hydrocarbon selectivities of the Nanophase 2 sample were better than those of the ACC Conventional sample at 600 °C, and were comparable at 700 °C. At 400 °C, however, the nanophase sample showed a striking selectivity for hydrocarbons alone. This is a rather tantalizing result, but in light of the very low conversion, it should be taken with caution.

We have presented results demonstrating unusual catalytic activity by unsupported mixed metal oxide nanocrystalline materials. We are encouraged by these preliminary results, especially since they were achieved with nanophase samples having compositions which were probably not near being optimized. Our only reservation stems from the fact that we have only had the opportunity to evaluate two nanophase samples thus far. Clearly, additional data is needed, and in future experiments, nanophase catalysts having better specified compositions will be evaluated.

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