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Emission of Pollutants from Glycine–Nitrate Combustion Synthesis Processes

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Four ceramic powders were produced using the glycine–nitrate process: lanthanum-doped barium cobaltite, ceria, magnesia, and strontium-doped lanthanum chromite (LSC). Glycine-to-nitrate ratios from 0.25 to 1 were investigated. During the combustion synthesis process, careful collection of process off-gas was followed by detailed gas analyses to determine product gas composition. All of the synthesis processes produced pure phase ceramic powders, but also produced criteria pollutant emissions levels that were significant enough (up to 4500 ppm of NO_x and 9000 ppm of carbon monoxide) to warrant consideration. Equilibrium and chemical kinetic computations are used to determine the implications of the current findings.

I. Introduction

THE glycine–nitrate process (GNP) of combustion synthesis was detailed by Chick *et al.*¹ in 1990; it has since been highly valued and heavily used for synthesizing mixed rare-earth oxides. The process itself is fairly simple: a precursor solution containing the desired cation stoichiometry of the target mixed-cation oxide is prepared by (1) dissolving metal nitrates in water, (2) adding glycine as a complexing agent and combustion fuel, and (3) heating the solution to remove the water until the precursor solution spontaneously ignites.¹ The ash resulting from the combustion reaction is the desired mixed-metal oxide, usually with ultra-fine particles and high purity.^{2–7} The GNP synthesis technique has been used for the synthesis of oxides for many applications, notably exotic mixed-metal oxides for use in solid oxide fuel cells and catalysts.^{2,4,8}

The GNP technique has been billed as “environmentally compatible” by previous researchers.^{1,6,9} This assertion stems from the reaction equations that have been proposed for the process, which have cations, nitrate, and glycine as reagents/reactants, and metal oxides, nitrogen, water, and carbon dioxide (CO₂) as products. These equations assume that the lowest energy products possible are favored and achieved in the reaction process. However, combustion reactions often take place under conditions that are highly unfavorable to the formation of equilibrium products. The duration of exposure to high-temperature environments may be short, leading to kinetic limitations of the combustion reactions. Additionally, depending upon the temperatures at which the overall combustion reaction proceeds, and the rates of temperature increase and quench, products of complete combustion (PCC) may not even be thermodynamically preferred. For example, the thermodynamic equilibrium composition of typical GNP chemistry, at the elevated

temperatures at which reactions are expected to proceed, always includes carbon monoxide (CO).¹⁰

The present work was undertaken after GNP reactions carried out in house were noted to form and emit a visible brown haze suspected to be NO₂. This has also been observed by other researchers, although the species speculated to cause the brown haze was not discussed in their publications.⁶

II. Background

The reaction equation that is generally written⁵ to describe glycine–nitrate combustion synthesis is

This equation assumes that the only products of the reaction are the desired oxide and PCC. The equation can also be written with oxygen as a reagent or product in order to balance the equation.

The reaction equation may also include products of incomplete combustion (PIC). This equation is somewhat more complicated, with additional products as follows:

The additional products NO, NO₂, and CO are of particular interest as they are known to be environmentally harmful PIC. They are toxic and smog-forming chemicals, and their emissions are strictly regulated. Because of their noxious nature, they are also potentially a hazard for laboratory personnel.

If the nitrogen is bound in the fuel, it is possible that nitrogen oxides will form readily and cannot be easily avoided. Because nitrogen is present both as an oxidizer and in the glycine complexing agent and carbon is present in the glycine, it is expected that nitrogen oxides will be formed from both sources as intermediate species, as will other nonequilibrium intermediate nitrogen and carbon compounds. What fraction of these intermediates remains at the completion of the reaction and after quenching of the products is the primary subject of this work.

It has been hypothesized that the glycine nitrate combustion synthesis process proceeds in three major steps. The first step is evaporation of water, dehydrating the precursors. The second step is the decomposition of precursors to form flammable gases such as NO₂ and CO. The third step is a self-sustaining rapid reaction resulting in the production of ceramic powder and gaseous combustion products.^{1,11}

The formation of the gaseous intermediates NO and NO₂ is potentially problematic. It is well known that the reaction of NO

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to N_2 and O_2 is typically kinetically limited in combustion reactions, where quenching of the combustion reaction may not allow sufficient time at temperature to allow these reactions to proceed.¹⁰

III. Experimental Procedure

To determine the product gas composition from GNP procedures, a reaction apparatus was set up to continuously sample the gas composition in each reaction studied. Product gases from five varying glycine-to-nitrate group ratios, for four compositions of metal-oxide precursors, were measured using GNP combustion synthesis reactions under air. The standard method of predrying mixtures and hot plate heating until spontaneous combustion occurs—generally reported in the literature^{1,9}—was also used in this work.

The gaseous products from each GNP reaction were analyzed using a Horiba PG-250 exhaust gas analyzer (Irvine, CA) that had been calibrated in the highest ranges of CO and NO_x (5000 and 2500 ppm, respectively). The Horiba PG-250 uses an infrared absorption technique to measure CO and CO_2 , and a chemiluminescence detector coupled to an ozone generator to measure NO or NO_x separately. Simultaneous measurement of both NO and NO_x is not possible, and because total NO_x includes all species of interest, this instrument mode was used in this work. Sampling of the gaseous products of each GNP reaction was accomplished using a noncooled stainless steel sampling probe and Teflon sampling line through which the gas sample was drawn by a positive displacement pump at a flow rate of 0.6 L/m under ambient pressure. Measured concentrations of CO, CO_2 , and NO_x from the exhaust gas analyzer were recorded in real time using a PC with a LabVIEW virtual instrument written for this purpose. A diagram of the set up is shown in Fig. 1.

The metal nitrate precursors chosen were magnesium nitrate for MgO , cerium ammonium nitrate for CeO_2 , barium, lanthanum, and cobalt nitrates for lanthanum-doped barium cobaltite (BLC), and finally strontium, lanthanum, and magnesium nitrates for strontium-doped lanthanum chromite (LSC). The wide variety of metal nitrates and glycine-to-nitrate ratios were chosen to confirm that the characteristic emissions of the GNP reactions are shared across many different precursor formulations, and are not peculiar to any specific formulation.

A wide range of glycine-to-nitrate group ratios ranging from 0.3 to 1.0 were tested to ensure that the results from this work are comparable to other GNP-related work,^{1,9} and to investigate the influence of the ratio on PIC formation and emission. The “stoichiometric” glycine-to-nitrate ratios for each of the compositions calculated assuming only PCCs in the product gas are 0.37 for ceria, 0.53 for BLC, 0.55 for MgO , and 0.55 for LSC, respectively.

The ceramic powders synthesized were also verified to be consistent with anticipated phases using X-ray diffraction

Fig. 2. Emissions measured from the product stream for glycine-nitrate process synthesis of ceria at a glycine-to-nitrate group ratio of 0.4. This profile exhibits saturation at the instrument limit of 2500 ppm NO_x .

(XRD, Siemens/Bruker D5000, Madison, WI) analysis of calcined product powders.

IV. Results

Contrary to the assumptions of Eq. (1), the levels of PICs measured for all cases were very high. As the gas sample was extracted from a loosely sealed glass beaker, the total mass of the PICs in the product gas cannot be accurately quantified, but there is no question that they are present at a significant level.

In many of the cases, levels of NO_x in excess of 2500 ppm were observed (Fig. 2). In these cases, the actual concentration was even higher than the instrument's upper detection limit, leading to measurement saturation for a period of time. In all cases, high concentrations were observed for a period of about 100 s with peak concentrations, followed by a gradual decline back to zero as the process air inside the beaker was exchanged with ambient air (Fig. 3). In cases when the peak concentration exceeded the maximum instrument capability, an estimate of the peak level of NO_x emission was developed by linear extrapolation of the linear portions of the rising and falling concentration trends; a period of 10 s before saturation and a window of 20 s following saturation were utilized, with the point of intersection designated the peak concentration.

Fig. 3. Emissions measured from the product stream for glycine-nitrate process synthesis of ceria at a glycine-to-nitrate group ratio of 0.5. This profile does not exhibit saturation in either species.

Fig. 1. Glycine-nitrate process exhaust monitoring equipment schematic.

Fig. 4. Peak measured NO_x concentrations (concentrations over the detector limit were estimated). Note that the glycine-to-nitrate group ratio versus emissions trends are different for each formulation.

The actual or estimated peak values of CO and NO_x versus glycine-to-nitrate ratio are plotted in Figs. 4 and 5 for all of the formulations of precursors, for each of the GNP reactions investigated. Figure 4 shows that peak NO_x production and emission is minimized for ceria, magnesia, and LSC production for glycine-to-nitrate ratios in the range of 0.5–0.8. On the other hand, peak NO_x production and emission monotonically decreases with increasing glycine-to-nitrate ratio for BLC production. Figure 5 shows that CO production and emission is typically higher at higher glycine-to-nitrate ratios for all of the GNP reactions tested, with the exception of BLC. Note that CO emissions are significantly higher for ceria and LSC production than for magnesia and BLC.

Fig. 5. Peak carbon monoxide concentrations (concentrations over the detector limit were estimated).

As detailed in Table I, the reactions that tended to proceed more slowly (i.e., those with a higher glycine-to-nitrate ratio) tended to produce and emit lower peak NO_x levels and higher peak CO levels. The exceptions are that the BLC synthesis tended to produce lower CO at high glycine-to-nitrate ratios and magnesia synthesis tended to produce higher NO_x levels at higher glycine-to-nitrate ratios. Typical combustion reactions exhibit a similar behavior, with increased CO production and decreased NO_x production as the combustible mixture becomes more “fuel rich.” The reactions that proceeded the fastest took place when the glycine-to-nitrate ratio was near 0.4, except for ceria, which only showed a decrease in reaction rate with increased glycine. The fastest reaction rate and lowest emissions were

Table I. Summary of Experimental Results

	Glycine-to-nitrate ratio				
	0.3	0.4	0.5	0.75	1
Ceria					
Measured NO_x peak	2500	2500	2300	2500	2500
Estimated NO_x peak	3400	3400	2600	3100	3200
Measured CO peak	1200	450	200	4500	5100
Estimated CO peak	—	—	—	—	8600
Reaction rate	Very rapid	Very rapid	Rapid	Less rapid	Less rapid
BLC					
Measured NO_x peak	2300	2500	1800	950	200
Estimated NO_x peak	2500	2650	—	—	—
Measured CO peak	1000	800	1000	200	500
Reaction rate	Less rapid	Rapid	Rapid	Very slow	Very slow
MgO					
Measured NO_x peak	2500	2500	2050	1900	2500
Estimated NO_x peak	3600	2600	—	—	3100
Measured CO peak	1700	1700	1450	1300	3150
Reaction rate	Less rapid	Rapid	Less rapid	Slow	Very slow
LSC					
Measured NO_x peak	2500	2500	2500	2500	2500
Estimated NO_x peak	†	4250	3850	3400	3800
Measured CO peak	1650	4600	3750	5150	5150
Estimated CO peak	—	—	—	7400	‡
Reaction rate	Slow	Rapid	Rapid	Less rapid	Very slow

All values in ppm (parts per million). Reaction rates were designated “very rapid” if the reaction took less than 1 s, “rapid” if the reaction took 1–2 s, “less rapid” if the reaction took 2–4 s, “slow” if the reaction took 4–10 s, and “very slow” if it took longer than 10 s to complete. † NO_x profile measured did not allow for reasonable extrapolation of true peak NO_x values. ‡CO profile measured did not allow for reasonable extrapolation of true peak CO values.

Table II. Estimated Maximum Mass of NO_x and CO Emissions from Each GNP Reaction Investigated

Ceramic powder	Estimated NO _x molar (%)	Estimated CO molar (%)	Mass fraction of NO _x (%)	Mass fraction of CO (%)
Ceria	0.34	0.86	0.29	1.25
BLC	0.26	0.10	0.22	0.14
MgO	0.26	0.31	0.22	0.45
LSC	0.42	0.74	0.36	1.07

BLC, lanthanum-doped barium cobaltite; GNP, glycine–nitrate process; LSC, strontium-doped lanthanum chromite.

not apparently dependent on the “stoichiometric” composition, especially in the case of ceria. The peak NO_x values for most of the synthesis processes investigated as exhibited relatively low NO_x production under these conditions, although the lowest NO_x values tended to appear near glycine-to-nitrate ratios slightly >0.4 (around 0.6, corresponding to a slightly fuel-rich condition). This is counter-intuitive compared with typical combustion processes, under which equilibrium conditions tend to produce more thermal NO_x near the stoichiometric condition due to higher flame temperatures. This trend implies that NO_x production in the combustion reaction is not a thermal NO_x mechanism but rather a mechanism that produces NO_x that is not fully reacted in the combustion reaction.

Typical XRD patterns of the ceramic powders after calcining showed that the desired pure phase compounds were achieved in this work. Figure 6 presents a representative XRD pattern for the ceria powder that was prepared by GNP synthesis experiments in this work. Note that the expected phase (JCPDS file # 34-394) was achieved with no evidence of significant impurity or intermediate phases.

While peak production and emission values for NO_x and CO indicate the propensity to form and emit these PICs, they do not provide the quantity of the total mass of PICs produced. If the total mass of PIC emissions is significant in comparison with the mass of PCCs (i.e., metal oxides, N₂, CO₂), then the relative amounts of precursors required to achieve the desired oxide phase may be affected by the current PIC production discovery. To assess this, an estimate of the mass fraction of NO_x and CO emissions has been made for each of the GNP reactions tested by conversion of measured volume fractions to mass fractions using formula weights (Table II). Note that even though the measured concentrations of NO_x and CO are significant from an emissions perspective, they do not significantly alter the overall chemistry of the GNP reaction.

Fig. 6. Typical X-ray diffraction pattern and the library fit for ceria powder synthesized in this work by GNP and then calcined for 2 h at 700°C.

V. Discussion

From the results obtained in this work, it may be concluded that the GNP reactions fail to produce only PCC (N₂ and CO₂) as commonly reported. On the contrary, high levels of PICs (NO_x and CO) are produced and remain as products of typical GNP reactions.

The formation of NO₂ as a product of the decomposition of metal nitrates has been well characterized in both oxidizing and inert environments.^{12,13} It was observed that the decomposition of the nitrate groups usually resulted in the formation of NO₂, a process step that was anticipated to occur in the GNP process as well. However, it is apparent that large quantities of NO₂, as well as CO, remain after the combustion event is complete. To investigate the reasons for the observed significant amount of unreacted CO and NO₂ in the combustion products, modeling of the chemical equilibrium and chemical kinetics related to GNP reactions was conducted in this work. Chemical equilibrium modeling was conducted using NASA's equilibrium code,¹⁴ while chemical kinetic calculations were accomplished using Chemkin^{®15} with the GRI-Mech¹⁶ chemical kinetic mechanism (Berkeley, CA).

For the simple case of MgO synthesized by combustion of Mg(NO₃)₂ and glycine, a balanced “stoichiometric” reaction equation is written below (theoretically requiring no additional oxygen on reagent or product sides of the equation)

Based on these product gases, at the temperatures of reaction reported by Chick *et al.*¹ of between 1000 and 1700K, equilibrium calculations predict that these gases would never spontaneously produce appreciable concentrations of NO or NO₂. Note that the CO concentration expected at equilibrium is fairly significant, even at equilibrium, at these temperatures. This implies that the NO_x measured in the exhaust must be a retained intermediate species.

Alternately, if the reaction is assumed to produce mostly NO₂ from the nitrate group and CO from the glycine, another reaction equation could be written as

Using these product gases and the temperatures reported by Chick *et al.*,¹ it was found that the equilibrium code predicts that the mixture will equilibrate to a mixture of identical composition to the equilibrium concentrations presented above, as expected.

Fig. 7. Calculated equilibrium concentrations of carbon monoxide and NO for gaseous species in the range of reported reaction temperatures.

Fig. 8. Kinetic limitation of reaction of carbon monoxide (CO) and NO for a quench from 1700 to 500K over 0.25 s.

While these levels of PICs are significant from the standpoint of emissions, equilibrium calculations alone cannot explain the observed high levels of NO_x and CO measured in this work (Fig. 7).

The high levels of PICs observed may be due to the kinetics of the reactions during the entire reaction time, and the temperature history associated with the GNP reaction. The reaction time and the temperature history results from a complex set of physical and chemical features of the process including the effects of mixing, heat supply from the hot plate and the reaction heat, heat transfer, and quenching of the reaction.

To model the effects of chemical kinetics during the time-temperature history profile of a GNP reaction, a representative history that includes thermal quenching was developed and simulated in Chemkin[®]. NO_2 and CO were assumed to be the intermediate species that form by the GNP reactions in Eq. (4). These intermediate species were considered to be the initial reactants in a homogeneous set of chemical reactions subjected to constant pressure, and constant quench rate conditions in Chemkin[®]. Various quench rates were investigated.

Figure 8 presents the results from chemical kinetic calculations that used a quench rate that led to cooling of the reacting mixture from a starting temperature of 1700–500 K in 0.25 s. At temperatures near the initial temperature of 1700 K, NO_2 is quickly reacted to form NO. For the profiles and formulas modeled, all NO_2 present in the initial gas mixtures decomposed to NO within the first time step, and so it is omitted from the profile in Fig. 8. The NO and CO, however, end up being unable to react further to produce the equilibrium products that are desired under these conditions. The NO and CO are said to be “frozen” into the gas mixture at these quench rates. For the temperatures reported for most GNP reactions, it is expected that thermal NO_x formation rates are very small (insignificant). The thermodynamic driving forces suggest that only very small amounts of NO_x can be produced from heating of air at 1700 K. The only NO_x production mechanism that can explain the levels that we measured is the fuel-bound nitrogen oxide production mechanism. The formation of NO from NO_2 can occur very quickly at the temperatures we expect in GNP reactions, and reasonable quenching rates for the process can lead to significant quantities of NO that remain in the gaseous GNP products.

The results of the chemical kinetic calculations presented in Fig. 8 suggest that significant NO and CO concentrations can be achieved for these conditions. These levels of NO and CO are higher than those observed during the GNP experiments, but because no measurement of temperature transients was made, it was not possible to simulate the exact temperature profile of the

reaction. Note finally that the results of Fig. 8 also show that the reduction of nitric oxide to nitrogen and oxygen and oxidation of CO to CO_2 , while favored by equilibrium at low temperatures, have kinetic rates that are relatively small, leading to the “frozen” concentrations as shown. This is consistent with observations made in numerous combustion studies.¹⁰

The observations in this work are also consistent with the need for additional calcining that is typically required to produce pure phase compounds using the GNP. The need for additional calcining indicates that the GNP reactions do not bring the as-synthesized metal oxides to the equilibrium states as typically reported in the literature. If the GNP reactions have fully proceeded to equilibrium conditions throughout the final products, no subsequent calcining treatment would be needed. It has been widely reported that the ash from the GNP combustion reaction contains unreacted carbon species. Therefore, it is not surprising that the gaseous products of combustion are also not those predicted by equilibrium models.

VI. Conclusions

If the GNP technique is to be used on an industrial scale, the potential for producing and emitting nitrogen oxides and CO demonstrated in this study must be addressed. Additionally, laboratory bench-top use of GNP processes should be carried out with care to avoid emission and exposure to any noxious NO, NO_2 , and CO products.

The high levels of PICs observed during the GNP could affect the methodology used to calculate the “stoichiometric” ratio for these reactions. If PCC are not produced, the desired metal oxide composition may be significantly altered. In the current experiments, the total mass of PIC emissions was estimated to comprise between 1% and 2% of the products.

Although some trends have been observed for the amount of PICs measured in the combustion process exhaust, there do not appear to be general trends that one can use to predict the levels of PICs quantitatively. The trends appear to be highly dependent on the individual precursor sets, which may merit additional investigation.

In industrial processes that produce large amounts of NO_x , the effluent stream can be reduced to N_2 and O_2 by use of selective catalytic reduction treatments or other established methods for the treatment of exhaust gases. It must be recognized that the existing reactions proposed for the glycine–nitrate combustion technique for synthesis of oxide powders has the potential to produce significantly high, even hazardous, levels of PIC that should be controlled by some means. Despite these concerns, GNP approaches remain an attractive means of producing highly uniform, complex oxide ceramic powders with precisely controlled stoichiometry.

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