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NOBLE METAL-CATALYZED HOMOGENEOUS AND
HETEROGENEOUS PROCESSES IN TREATING
SIMULATED NUCLEAR WASTE MEDIA WITH
FORMIC ACID

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Noble Metal-Catalyzed Homogeneous and Heterogeneous Processes in Treating Simulated Nuclear Waste Media with Formic Acid

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Abstract

Simulants for the Hanford Waste Vitrification Plant feed containing the major non-radioactive components Al, Cd, Fe, Mn, Nd, Ni, Si, Zr, Na, CO_3^{2-} , NO_3^- , and NO_2^- were used to study reactions of formic acid at 90°C catalyzed by the noble metals Ru, Rh, and/or Pd found in significant quantities in uranium fission products. Such reactions were monitored using gas chromatography to analyze the CO_2 , H_2 , NO, and N_2O in the gas phase and a microammonia electrode to analyze the $\text{NH}_4^+/\text{NH}_3$ in the liquid phase as a function of time. The following reactions have been studied in these systems since they are undesirable side reactions in nuclear waste processing: (1) Decomposition of formic acid to $\text{CO}_2 + \text{H}_2$ is undesirable because of the potential fire and explosion hazard of H_2 . Rhodium, which was introduced as soluble $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, was found to be the most active catalyst for H_2 generation from formic acid above ~80°C in the presence of nitrite ion. The H_2 production rate has an approximate pseudo first-order dependence on the Rh concentration. (2) Generation of NH_3 from the formic acid reduction of nitrate and/or nitrite is undesirable because of a possible explosion hazard from NH_4NO_3 accumulation in a waste processing plant off-gas system. The Rh-catalyzed reduction of nitrogen-oxygen compounds to ammonia by formic acid was found to exhibit the following features: (a) Nitrate rather than nitrite is the principal source of NH_3 . (b) Ammonia production occurs at the expense of hydrogen production. (c) Supported rhodium metal catalysts are more active than rhodium in any other form, suggesting that ammonia production involves heterogeneous rather than homogeneous catalysis.

Keywords: Nuclear waste, noble metals, rhodium, hydrogen, ammonia, reduction

Introduction

The most promising method for the disposal of highly radioactive nuclear wastes is a vitrification process in which the wastes are incorporated into borosilicate glass, the glass is poured into large stainless steel canisters, and the sealed canisters are buried in suitably protected burial sites. The use of formic acid to treat the aqueous feed for liquid-fed ceramic melters producing borosilicate waste glass was developed at the Savannah River Laboratory for mercury removal^{1,2} and for slurry rheology improvement^{2,3}; it has been implied that formic acid may also decrease glass foaming.^{4,5} In addition, melter operation and glass durability may be affected by the glass oxidation state. Formation of a conductive metallic sludge in an over-reduced melt can shorten melter lifetime. An over-oxidized feed mixture may lead to foaming and loss of ruthenium as volatile RuO₄.^{3,4,6,7} Historically, foaming in the joule-heated ceramic melter is caused by reboil and is controlled by introducing a reductant such as formic acid into the melter feed. Formic acid is also found to decrease the melter feed viscosity thereby facilitating pumping.

The use of formic acid to process nuclear wastes for vitrification plants can lead to two detrimental side reactions:

- (1) **Decomposition of formic acid into CO₂ + H₂:** The production of H₂ in nuclear waste vitrification plants is of particular concern because of the potential fire and explosion hazard.
- (2) **Generation of ammonia from the formic acid reduction of nitrate and/or nitrite:** The production of NH₃ in nuclear waste vitrification plants is of concern because of the generation of a possible explosion hazard from NH₄NO₃ accumulation in a waste processing plant off-gas system.

During the past four years we have been examining the role played by the noble metals found in uranium fission products in catalyzing these reactions with the objective of finding conditions where these reactions are minimized. Our experiments have been done with nonradioactive feed simulants containing the major nonradioactive components found in nuclear wastes, namely Al, Cd, Fe, Mn, Nd, Ni, Si, Zr, Na, CO₃²⁻, NO₃⁻, and NO₂⁻.

Experimental Approach

Feed simulants were prepared on a 1-L scale from reagent grade chemicals using the protocol summarized in Figure 1. The feed simulant containing all 12 components listed in Figure 1 is designated as UGA-12M1. Samples of these feed simulants (generally 40 to

50 mL) were treated with 88 weight % formic acid in a 550-mL closed glass reactor at 80 to 100°C. The formic acid was added at the reaction temperature at a constant rate using 10-mL plastic disposable syringes driven by a Sage Instruments syringe pump (Model 355) purchased from Fisher Scientific. The standard rate of addition of formic acid was 0.0194 ± 0.0002 mL/min (1.164 mL/h) corresponding to 0.448 mmoles $\text{HCO}_2\text{H}/\text{min}$ or 26.9 mmoles $\text{HCO}_2\text{H}/\text{h}$. The composition of the gas phase was analyzed periodically for H_2 , CO_2 , NO , and N_2O using gas chromatography. The H_2 analyses were performed using a Varian 90P gas chromatograph with a 20 cm \times 6 mm column packed with a 40/60 mesh 13 \times molecular sieve material and argon as the carrier gas. The column temperature was maintained at 80°C. The CO , CO_2 , N_2O , and NO analyses were performed using a gas partitioner (Fisher Model 1200), which separates the gases on the basis of their size and polarity by means of two columns, a 2 m 80/100 mesh Columnpak PQ and a 3.3 m 13 \times molecular sieve column mounted in series using helium as the carrier gas. The temperatures of both columns were maintained at 50°C. Sensitivity factors were determined from known amounts of pure certified samples of the gases of interest and were rechecked every week. Nitrogen dioxide could not be determined using gas chromatography because of the $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium.

After the feed simulants had been treated with the formic acid, the resulting reaction mixture was analyzed for NH_4^+ produced by NO_3^- or NO_2^- reduction. A 0.5-mL sample of the reaction mixture was diluted with 0.5 mL of distilled water and then was made strongly basic with 1 to 2 drops of 10 N NaOH in order to convert NH_4^+ to NH_3 . The NH_3 concentration was then determined using a MI-740 microammonia electrode obtained from Microelectrodes, Inc., Londonderry, New Hampshire. This electrode is designed to measure NH_3 gas and to record the NH_3 concentration as millivolts on a standard pH meter; an Orion 290A portable pH meter was used for these studies. The ammonia electrode was calibrated before each analysis using 0.1 N, 0.01 N, and 0.001 N NH_4Cl solutions made basic with 10 N NaOH.

Results and Discussion

Decomposition of Formic Acid to $\text{CO}_2 + \text{H}_2$

There is a strong precedent in the literature for the noble metal catalyzed decomposition of formic acid to H_2 . The earliest studies by Müller and Loerpabel⁸ used salts of the six platinum group metals to effect the dehydrogenation of 10% formic acid containing dissolved sodium formate. Much more recent studies have focussed on various aspects of Pd-catalyzed formic acid decomposition including work by Ruthven and Upadhye⁹ on the

catalytic decomposition of aqueous formic acid over Pd black, work by Aguild¹⁰ on the Pd(II)-catalyzed oxidation of formic acid in acetic acid solution, and work by Hill and Winterbottom¹¹ on the Pd-catalyzed decomposition of formic acid/sodium formate solutions. Soluble derivatives of other noble metals including Ru carbonyls¹² and the Rh phosphine complex Rh(C₆H₄PPh₂)(PPh₃)₂ (ref. 13) have also been shown to be active homogeneous catalysts for formic acid decomposition. However, these Ru and Rh derivatives contain carbonyl or phosphine ligands that are expected to modify greatly the underlying noble metal chemistry and are not likely to be present in the nuclear wastes being treated. Chemical processing studies of nuclear waste simulants containing Ru, Rh, Pd, and Ag produced H₂ when processing was carried out with formic acid.¹⁴

Initial studies at the University of Georgia screened the four noble metals found in uranium fission products, namely Ru, Rh, Pd, and Ag, for their catalytic activity for the decomposition of pure formic acid.¹⁵ Subsequent studies¹⁶ investigated the catalytic activity of these noble metals for formic acid decomposition in non-radioactive sludges simulating the compositions of the feed to be processed for vitrification. Other components in the sludge simulants, particularly NO₂⁻, were found to profoundly modify the catalytic activity of the noble metals of interest for formic acid decomposition. The most active catalyst precursor for H₂ evolution from the sludge simulant was found to be RhCl₃, even though it was inactive as a catalyst precursor for H₂ evolution from pure formic acid at the same temperature. Effects of changing the Rh source, Rh concentration, NO₂⁻ concentration, and temperature on the nitrite-promoted Rh-catalyzed formic acid decomposition in nuclear waste feed simulant media (Figure 1) have been examined.

Figure 2 illustrates a titration of 50 mL of the UGA-12M1 feed simulant with 88 weight % formic acid at 90°C in the presence of 14 mg of RhCl₃·3H₂O as a soluble Rh catalyst precursor. Production of H₂ began only after all of the CO₃²⁻ has been converted to CO₂ and the NO₂⁻ to NO and N₂O. This immediately suggests that one method of limiting H₂ production during the treatment of nuclear wastes with formic acid is to limit the amount of formic acid to that required to convert all of the CO₃²⁻ to CO₂ and the NO₂⁻ to NO and N₂O. A total of 1.3 mmoles of H₂ was produced in this experiment.

Insoluble Rh sources rather than soluble RhCl₃·3H₂O have also been investigated as catalyst precursors. Two rather different methods of introducing Rh in an insoluble form were investigated. In the first method, Rh was introduced into the feed simulant as hydrous Rh₂O₃ by coprecipitation in the iron fraction (Figure 1) using hydrated Rh(NO₃)₃ as the Rh source at a concentration of 0.28 g/L. Titration of 50 mL of this feed simulant with 85 mmoles of formic acid at 88±2°C led to the production of a total of 1.4 mmoles of H₂ as compared with 1.3 mmoles of H₂ in a comparable experiment in which Rh was

introduced as the soluble "RhCl₃·3H₂O." No significant differences were observed in the behavior of this system when Rh is coprecipitated with the other metal oxides in the feed simulant preparation as compared with otherwise similar experiments in which RhCl₃·3H₂O is added to the slurry immediately before the start of the experiment.

In the second method, Rh was introduced as a 5% dispersion of the metal supported on carbon or alumina using 0.1175 g of 5% Rh/C or 0.115 g of 5% Rh/Al₂O₃, respectively, corresponding to the amount of Rh in the 14 mg of RhCl₃·3H₂O used in the standard experiments. The observed behavior with these solid 5% Rh dispersions in UGA-12M1A upon titration with 85 mmol of 88 weight % formic acid at 90°C was very different from the observed behavior with RhCl₃·3H₂O in the following ways:

- (1) Only a very small amount of H₂ was produced (0.16 mmoles and 0.28 mmoles at the end of the experiments with 5% Rh/C and 5% Rh/Al₂O₃, respectively).
- (2) The initially produced NO but not the N₂O was almost entirely consumed during the course of the experiment. For example, a maximum of 9.29 mmoles of NO was measured after 216 min but only 1.25 mmoles of NO remained at the end of the experiment with 5% Rh/C.

The drastically reduced production of H₂ and the consumption of NO as the reaction proceeds suggests that Rh dispersed on carbon might be an active catalyst for the hydrogenation of NO. This is supported by the production of a relatively large amount of CO₂ in this experiment as well as by the studies on ammonia formation discussed below.

A series of six experiments was performed in which 50-mL samples of the feed simulant UGA-12M1 and 10 mL of water each were titrated at 91°C with a total of 86 mmoles of formic acid in the presence of amounts of RhCl₃·3H₂O ranging from 1.4 mg (0.0056 mmoles) to 14 mg (0.056 mmoles) in a detailed attempt to assess the minimum amount of Rh needed to catalyze H₂ evolution from formic acid. Generation of H₂ began to occur after sufficient formic acid has been added to deplete the NO₂⁻ and CO₃²⁻. The maximum rate of H₂ production was found to be pseudo first order in Rh concentration (moles per liter) according to the following equation:

$$\text{H}_2 \text{ production (mmoles/min)} = -0.92 + 8030 [\text{Rh}] \quad R^2 = 0.952 \quad (1)$$

Since NO₂⁻ has been shown to promote the catalytic activity of Rh for formic acid decomposition in feed simulant media, it was of interest to investigate the effect of NO₂⁻ concentration on the reaction rate. A series of four experiments involving titration of 50 mL of the nitrite-free feed simulant UGA-11XN1, 14 mg of RhCl₃·3H₂O, 10 mL of water, and amounts of NaNO₂ ranging from 0.6 g to 1.5 g in 0.3-g increments with 85 mmoles of

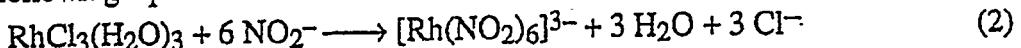
formic acid indicated that the rate of H₂ production is relatively insensitive to NO₂⁻ concentration at relatively high NO₂⁻ concentrations. The expected production of NO and N₂O was observed in all of the experiments. There were no major qualitative differences, and the amounts of nitrogen oxides appeared roughly proportional to the amount of NaNO₂ used.

Another question of interest: what is the minimum amount of NO₂⁻ needed to promote this reaction? Accordingly, 50 mL of the nitrite-free and nitrate-free feed simulant UGA-10XNN'1 mixed with 10 mL of water and 0.5 g. (5.88 mmoles) of NaNO₃ was titrated at 90°C with 85 mmoles of 88 weight % formic acid in the presence of 14 mg of RhCl₃·3H₂O (0.054 mmoles) and varying amounts of NaNO₂ ranging from 11.6 mg (0.17 mmoles) to 0.5 g. (7.24 mmoles). Considerable amounts of H₂ were produced in all of these experiments, even in the experiment using only 11.6 mg NaNO₂ (corresponding to a NO₂/Rh ratio of ~3) in which ~4 mmoles of H₂ was produced at the end of the experiment. This contrasts with the production of only 0.4 mmole of H₂ at the end of an otherwise similar experiment in which no NO₂⁻ was added. This confirms that NO₂⁻ promotes the Rh-catalyzed decomposition of formic acid but that stoichiometric amounts of NO₂⁻ corresponding to formation of a trinitrorhodium derivative suffice for catalyst promotion.

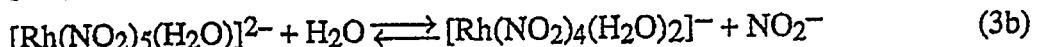
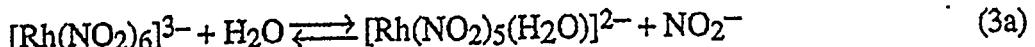
The effect of temperature on the Rh-catalyzed H₂ generation rate was also evaluated. A series of experiments was performed at temperatures ranging from 77°C to 94°C in which 50 mL of the standard UGA-12M1 feed simulant and 10 mL of an aqueous solution of RhCl₃·3H₂O (1.4 mg RhCl₃·3H₂O/mL) was titrated with a total of 85 mmoles of formic acid. As expected, the rate of H₂ production increases with increasing temperature with a H₂ production rate of 0.29 mmoles H₂/min/L feed simulant at 94°C. Hydrogen production at temperatures below ~85°C was found to be so slow that meaningful rates could not be obtained from the slope of the hydrogen production curve. It thus appears that H₂ production can be shut off at temperatures below ~75°.

The role of NO₂⁻ ion as a promoter suggests the role of soluble nitrorhodium complexes as intermediates in the Rh-catalyzed decomposition of formic acid. In this connection, RhCl₃ was reported more than a century ago¹⁷ to react with excess NO₂⁻ in boiling water to give salts of the hexanitrorhodate anion, [Rh(NO₂)₆]³⁻. Three of the six nitro groups in [Rh(NO₂)₆]³⁻ are reported to be labile upon treatment with strong oxidants¹⁸ or sulfamic acid¹⁹ indicating the feasibility of opening catalytic sites on the central Rh atom under the conditions of formic acid decomposition. These vacant sites on the central Rh atom can be used both for anchoring onto an insoluble hydrous oxide support as well as for coordination with formic acid prior to its decomposition.

The reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with NO_2^- to give $[\text{Rh}(\text{NO}_2)_6]^{3-}$ can be summarized by the following equation:



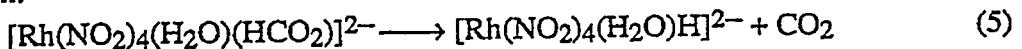
The lability of three of the six nitro groups in $[\text{Rh}(\text{NO}_2)_6]^{3-}$ can be summarized by the following equations in which nitro groups are successively replaced by more labile aquo ligands:



Formate can then displace the aquo ligands by reactions such as the following:



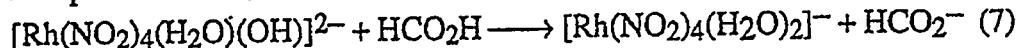
Coordinated formate can undergo a hydrogen shift from carbon to a vacant rhodium site with carbon dioxide evolution to generate a rhodium hydride according to the following equation:



Hydrolysis of the rhodium hydride, possibly acid catalyzed, can then result in the observed hydrogen evolution, i.e.,



The resulting hydroxorhodium complex can then be protonated by formic acid to give the original diaquo derivative, i.e.,



The net sum of equations 4-7 is the observed formic acid decomposition



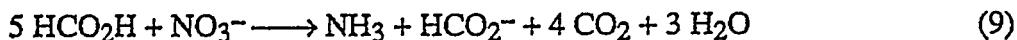
In this mechanistic scheme, NO_2^- is essential to the reaction but excess NO_2^- can inhibit the reaction by tying up catalytic sites forming $[\text{Rh}(\text{NO}_2)_6]^{3-}$ (see equation 3a). The balance between the requirement of NO_2^- to make active nitrorhodium intermediates but the ability of excess NO_2^- to inhibit the reaction can account for the observed insensitivity of the reaction rate to NO_2^- concentration.

Generation of Ammonia from the Formic Acid Reduction of Nitrate and/or Nitrite

The NH_4^+ concentrations produced by selected titrations of various nitrite and/or nitrate-containing feed simulants with 88 weight % formic acid in the presence of various noble metals were determined by NH_3 analyses as outlined above. The NH_3 analyses were performed on the residues remaining from the experiments, which had been stored in

sealed screw cap bottles at room temperature ($24 \pm 7^\circ\text{C}$) since completion of the experiments.

The results summarized in Table 1 indicate that the only experiments which produced significant quantities of NH_3 (> 1 mmole) were the runs using the Rh catalysts supported on charcoal or alumina (the 9/2/92 and 10/2/92 experiments, respectively). These experiments are also distinguished by the production of far too much CO_2 to arise solely from reactions of formic acid leading to CO_3^{2-} decomposition, MnO_2 reduction to Mn^{2+} , NO_2^- reduction to N_2O , and formic acid decomposition to H_2 . In addition the final pH in both of these experiments is much higher (6.9) than the final pH in any of the other formic acid titrations (2.9 to 4.3). Production of each mole of NH_3 by NO_3^- reduction can convert four moles of formic acid to CO_2 and neutralizes a fifth mole of formic acid to give formate, i.e.,



The observed final pH of 6.9 is outside the range of the formic acid/formate buffer (pK of $\text{HCO}_2\text{H} = 3.7$) but in the range of the carbonic acid/bicarbonate buffer (pK_1 of $\text{H}_2\text{CO}_3 = 6.4$). Thus some of the CO_2 liberated by the formic acid forms HCO_3^- and thus cannot be measured in the gas phase.

These preliminary observations suggest that NH_3 production by the Rh-catalyzed reduction of NO_2^- or NO_3^- ion by formic acid is highly dependent on the form of the rhodium. Thus, highly dispersed Rh on alumina or charcoal is a very active catalyst whereas soluble Rh compounds (such as the nitrorhodium complexes obtained from RhCl_3 and NO_2^-) are much less active catalysts. Furthermore, Rh coprecipitated with the iron fraction in the feed simulant UGA-13+Rh1 as the hydrous oxide Rh_2O_3 is not an active catalyst for NH_3 production even though the Rh_2O_3 is presumably dispersed in the other insoluble metal hydrous oxides. Since NH_3 production appears to occur at the expense of H_2 production, we suspect that the supported Rh metal catalysts are functioning as hydrogenation catalysts for NO_2^- , NO_3^- , and/or nitrogen oxides. This idea is also supported by the observed decrease in NO concentration to zero in the experiments using supported Rh catalysts producing significant amounts of NH_3 .

A question of considerable interest is whether NO_2^- or NO_3^- is the source of the NH_3 nitrogen. A feed simulant prepared according to the standard protocol but leaving out both NO_2^- and NO_3^- (UGA-10XNN'1) was titrated with formic acid in the presence of NaNO_3 as well as 5% Rh on charcoal. The amount of NH_3 produced in this experiment (1.6 mmoles) was essentially identical to the amount of NH_3 produced in an experiment using the full feed simulant UGA-12M1 containing NO_2^- . No nitrogen oxides were

observed in the experiment with the nitrite-free feed simulant indicating that Rh cannot catalyze the formic acid reduction of *nitrate* to N_2O or NO.

Two other experiments indicate the role of supported Rh metal catalysts in ammonia production from nitrogen-oxygen species and formic acid:

(1) The usual protocol for the preparation of UGA-10XNN'1 feed simulant was followed except that 0.284 g of $RhCl_3 \cdot 3H_2O$ was added to the $Al(NO_3)_3 \cdot 9H_2O$ before precipitation of the aluminum hydroxide according to the standard procedure. The presence of Rh(III) in the aluminum hydroxide precipitate was indicated by the tan color of the precipitate and a colorless supernatant liquid. Titration of this feed simulant with 85 mmol of 88 weight % formic acid at 90°C in the presence of $NaNO_3$ gave negligible amounts of NH_3 and 0.4 mmoles of H_2 . This experiment suggests that supported Rh must be the free metal (i.e., in the zero oxidation state) to exhibit high activity for the reduction of NO_3^- to NH_3 by formic acid.

(2) Negligible amounts of NH_3 were observed when the same UGA-10XNN'1/ $NaNO_3$ mixture was titrated with 85 mmol of 88 weight % formic acid at 90°C in the presence of soluble $RhCl_3 \cdot 3H_2O$ rather than the 5% Rh on carbon.

Important conclusions suggested by the experiments outlined above concerning the Rh-catalyzed reduction of nitrogen-oxygen compounds to NH_3 by formic acid include the following:

- (1) Nitrate rather than nitrite is the principal source of NH_3 consistent also with a nitrite-free test run at Pacific Northwest Laboratory.²⁰
- (2) Ammonia production appears to occur at the expense of H_2 production.
- (3) Supported Rh metal catalysts are more active than Rh in any other form, suggesting that NH_3 production involves heterogeneous rather than homogeneous catalysis.

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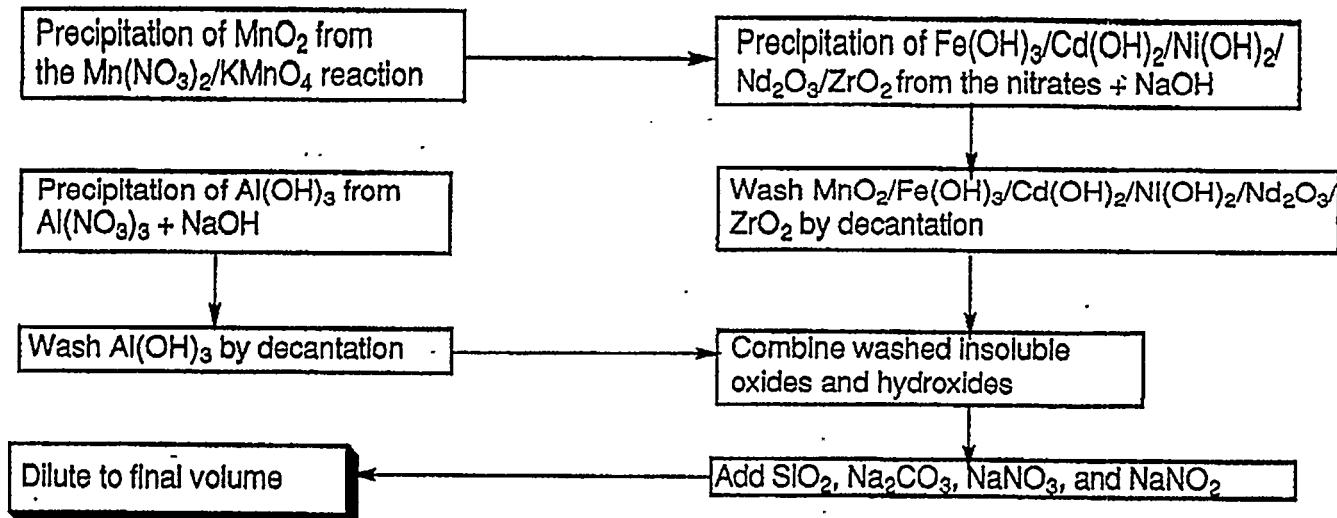
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Figure Captions

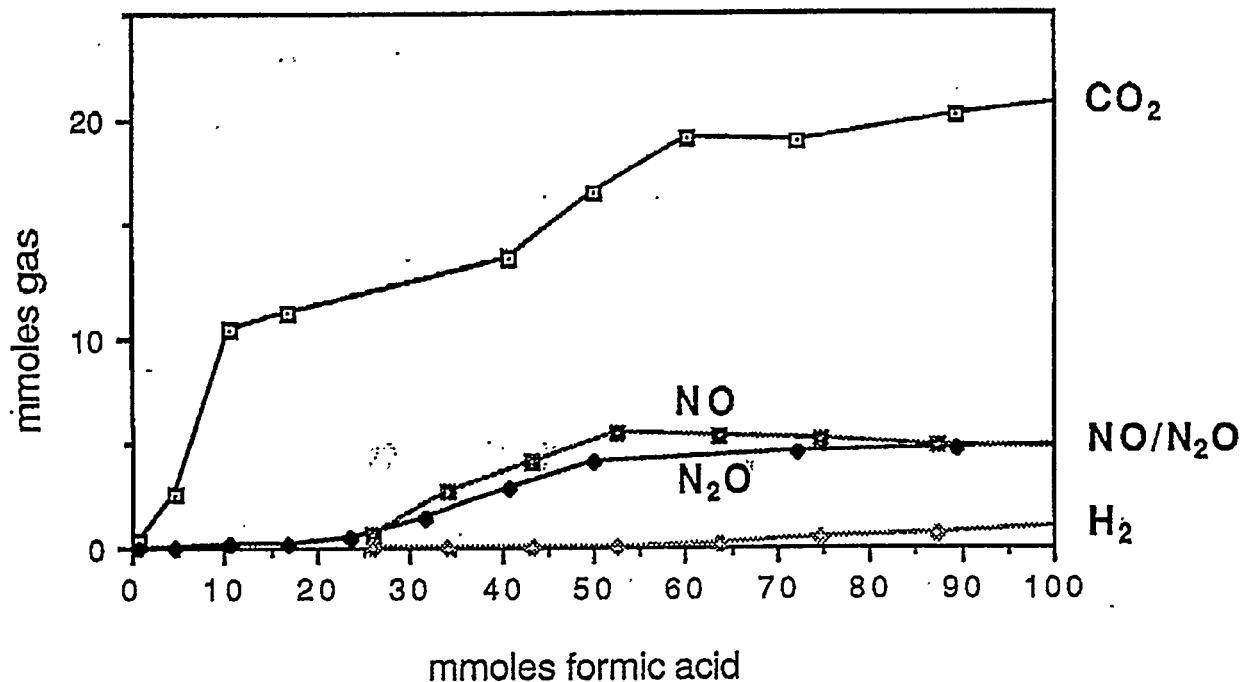
Figure 1: Preparation of the feed simulant UGA-12M1 used in this work.

Figure 2: Gas generation upon titration of 50 mL of the UGA-12M1 feed simulant with 88% formic acid at a rate of 0.0196 mL/min = 0.42 mmol/min in the presence of 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and equations for the reactions involved.



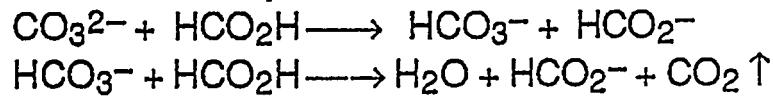
Sources of the Components of the Feed Simulant UGA-12M1

Component	Molarity	Source	g/liter	Water solubility
Al	0.226	Al(NO ₃) ₃ ·9H ₂ O	84.8 g	63.7 g/100g @ 25°C
Cd	0.03	Cd(NO ₃) ₂ ·4H ₂ O	9.2 g	215 g/100 g @ 25°C
Fe	0.45	Fe(NO ₃) ₃ ·9H ₂ O	181.8 g	"soluble"
Mn	0.0314	{ KMnO ₄ (Mn(NO ₃) ₂)·6H ₂ O	{ 2.0 g [5.4 g	{ 6.38 g/100 g @ 20°C [426.4 g/100 g @ 0°C
Nd	0.0264	Nd(NO ₃) ₃ ·6H ₂ O	11.6 g	152.9 g/100 g @ 25°C
Ni	0.0392	Ni(NO ₃) ₂ ·6H ₂ O	11.6 g	238.5 g/100 g @ 0°C
Si	0.0854	SiO ₂	5.1 g	insoluble
Zr	0.156	ZrO(NO ₃) ₂ ·6H ₂ O	52.9 g	soluble
Na ⁺	0.801	Na ₂ CO ₃ + NaNO ₃ + NaNO ₂	see below	see below
CO ₃ ²⁻	0.125	Na ₂ CO ₃	13.2 g	7.1 g./100 g @ 0°C
NO ₃ ⁻	0.116	NaNO ₃	9.9 g	92.1 g/100g @ 25°C
NO ₂ ⁻	0.435	NaNO ₂	30.0 g	81.5 g/100 g @ 15°C

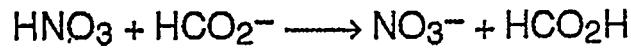
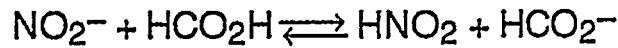


Reactions Involved

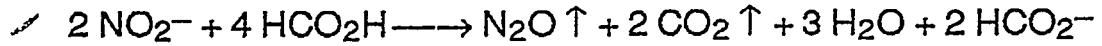
Carbonate Decomposition



Decomposition (disproportionation) of nitrous acid



Reduction of nitrite



Formic acid decomposition

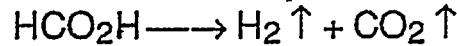


Table 1
Ammonia Analyses on Samples from Selected Titrations of Feed Simulants
with Formic Acid

Date	Sample (Amount, mL)	Catalyst (Amount, mg)	HCO ₂ H mL(added over min)	Temp °C	Final mmol H ₂	Final pH	Final NH ₃ mmoles
4/27/93	12M1(50)	RhCl ₃ ·3H ₂ O(14)	3.63(190)	89±1	1.4	4.3	0.0
9/2/92	12M1(50)	5% Rh/C(117)	3.53(190)	90±1	0.2	6.9	15.0
10/2/92	12M1(50)	5% Rh/Al ₂ O ₃ (115)	3.67(190)	88-91	0.3	6.9	5.4
9/10/92	13M+Rh1(50)	RhCl ₃ ·3H ₂ O(14)	3.53(190)	90±2	4.8	4.1	0.1
8/19/92	13M+Rh1(50)	0	3.53(190)	91±2	0.4	3.9	0.3
11/17/92	12M1(50)	RhCl ₃ ·3H ₂ O(14)	3.71(190)	70-90	1.4	3.5	0.2
12/18/92	12M1(50)	RhCl ₃ ·3H ₂ O(14)	3.40(185)	90±1	0.3	4.3	0.1
12/23/92	water(50)	RhCl ₃ ·3H ₂ O(14)	3.71(190)	90±1	6.3	2.9	0.2
	NaNO ₂ (1.5g)	CuCl ₂ (100mg)					
1/14/93	water(50)	RhCl ₃ ·3H ₂ O(14)	3.46(180)	91±1	10.0	2.6	0.3
	NaNO ₂ (1.5g)						
7/9/93	12M1(50)	RhCl ₃ ·3H ₂ O(14)	3.61(190)	91±1	1.9	4.1	0.2
9/30/92	12M1(50)	PdCl ₂ (12)	3.67(190)	90±2	0	5.4	0.4
1/8/93	water(60), NaNO ₂ (1.5g), HCO ₂ Na(6.2g)	PdCl ₂ (14)	0	92±1	0.1	10.6	0.1
1/9/93	water(60), NaNO ₂ (0.5g), HCO ₂ Na(6.2g)	PdCl ₂ (14)	0	92±2	1.4	10.0	0.8
1/13/93	water(60), HCO ₂ Na(6.2g)	PdCl ₂ (14)	0	90±2	1.4	9.6	0
5/19/93	12M1(50)	"RuCl ₃ ·3H ₂ O"(15)	3.63(190)	90±1	0	3.9	0.1