

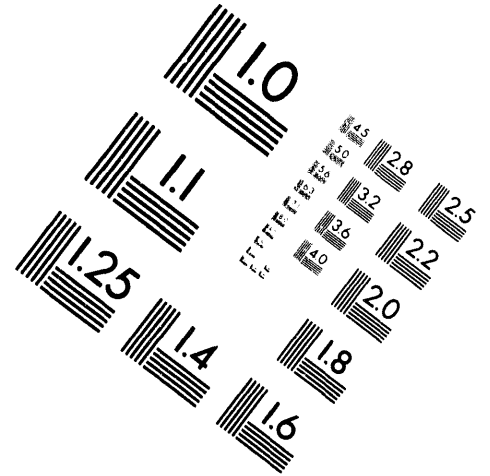
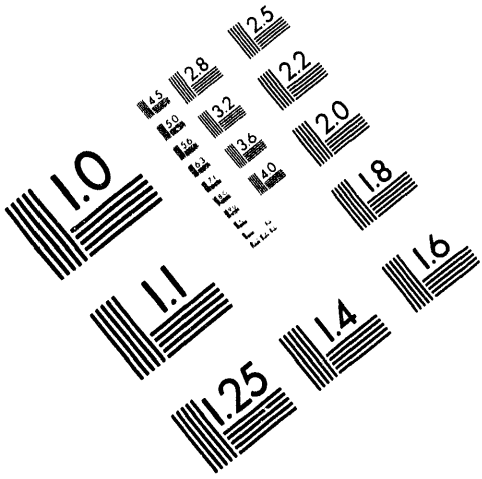


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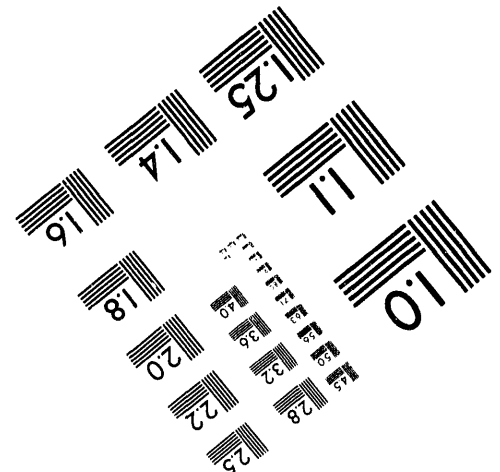
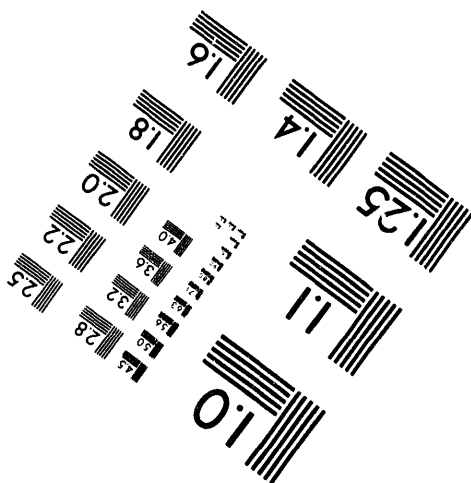
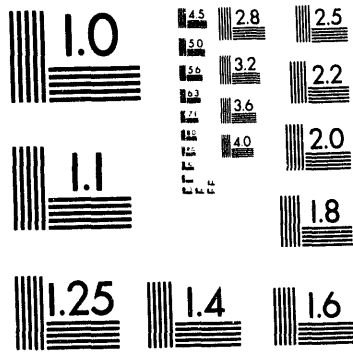
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NOBLE METAL CATALYZED HYDROGEN GENERATION
FROM FORMIC ACID IN NITRITE-CONTAINING SIMULATED
NUCLEAR WASTE MEDIA

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August 1994

Presented at the
9th International Symposium on Homogeneous
Catalysis
August 21-26, 1994
Jerusalem, Israel

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Noble Metal Catalyzed Hydrogen Generation from Formic Acid in Nitrite-Containing Simulated Nuclear Waste Media

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Abstract

Simulants for the Hanford Waste Vitrification Plant (HWVP) 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 as media to evaluate the stability of formic acid towards hydrogen evolution by the reaction $\text{HCO}_2\text{H} \longrightarrow \text{H}_2 + \text{CO}_2$ catalyzed by the noble metals Ru, Rh, and/or Pd found in significant quantities in uranium fission products. Small scale experiments using 40–50 mL of feed simulant in closed glass reactors (250–550 mL total volume) at 80–100°C were used to study the effect of nitrite and nitrate ion on the catalytic activities of the noble metals for formic acid decomposition. Reactions were monitored using gas chromatography to analyze the CO_2 , H_2 , NO , and N_2O in the gas phase as a function of time. 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 hydrogen generation from formic acid above ~80°C in the presence of nitrite ion in accord with earlier observations. The inherent homogeneous nature of the nitrite-promoted Rh-catalyzed formic acid decomposition is suggested by the approximate pseudo first-order dependence of the hydrogen production rate on Rh concentration. Titration of the typical feed simulants containing carbonate and nitrite with formic acid in the presence of rhodium at the reaction temperature (~90°C) indicates that the nitrite-promoted Rh-catalyzed decomposition of formic acid occurs only after formic acid has reacted with all of the carbonate and nitrite present to form CO_2 and $\text{NO}/\text{N}_2\text{O}$, respectively. The catalytic activities of Ru and Pd towards hydrogen generation from formic acid are quite different than those of Rh in that they are inhibited rather than promoted by the presence of nitrite ion. Palladium is also an active catalyst for the reductions of nitrate and NO to N_2O in feed simulant media.

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 for disposal (Figure 1). 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} and it has been implied that it may also decrease glass foaming.^{4,5} The operation of the glass melter and durability of the glass may be affected by the glass oxidation state. Formation of a conductive metallic sludge in an over-reduced melt can result in a shortened 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 introduction of a reductant such as formic acid into the melter feed. Formic acid is also found to decrease the melter feed viscosity thereby facilitating its pumping.

A drawback to the use of formic acid in nuclear waste processing is its potential for decomposition into carbon dioxide and hydrogen according to the following equation:



Possible formic acid decomposition catalysts include the noble metals Ru, Rh, and Pd present in the wastes as uranium fission products.⁸ In this connection there is a strong precedent in the literature for the noble metal catalyzed decomposition of formic acid to hydrogen. The earliest studies by Müller and Loerpabel⁹ 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 Upadhye¹⁰ on the catalytic decomposition of aqueous formic acid over Pd black, work by Aguilò¹¹ on the Pd(II)-catalyzed oxidation of formic acid in acetic acid solution, and work by Hill and Winterbottom¹² on the Pd-catalyzed decomposition of formic acid/sodium formate solutions. Soluble derivatives of other noble metals including Ru carbonyls¹³ and the Rh phosphine complex Rh(C₆H₄PPh₂)(PPh₃)₂ (ref. 14) 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.

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. The other components in the sludge simulants, particularly nitrite ion, were found to modify profoundly the catalytic activity of the noble metals of interest for formic acid decomposition. Thus RhCl_3 was the most active catalyst precursor for hydrogen evolution from the sludge simulant under the conditions of interest even though it was inactive as a catalyst precursor for hydrogen evolution from pure formic acid at the same temperature. The studies addressed in this paper examine in detail the effects of important variables, including the Rh source, Rh concentration, NO_2^- concentration, and temperature on the nitrite-promoted Rh-catalyzed formic acid decomposition in nuclear waste feed simulant media containing Al, Cd, Fe, Mn, Nd, Si, Zr, Na, CO_3^{2-} , NO_3^- , and NO_2^- . Information on the catalytic activity for formic acid reactions of the other noble metals of interest, namely Ru and Pd as well as various mixtures of Ru, Rh, and Pd is also presented.

EXPERIMENTAL APPROACH

Feed simulants were prepared on a one-liter scale from reagent grade chemicals listed in Table 1 using the protocol summarized in Figure 2. 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 80–100°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 composition of the gas phase was analyzed periodically for H_2 , CO_2 , NO, and N_2O using gas chromatography.

Feed Simulant Preparation

The feed simulant composition (Table 1) was chosen to contain the major ($\geq 3\%$) components present in a typical Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) feed, namely the nine metals Al, Cd, Fe, Mn, Nd, Ni, Na, Si, and Zr and the three anions NO_2^- , NO_3^- , and CO_3^{2-} . In order to distinguish this feed simulant from other feed simulants in which one or more components were omitted or additional components added, this feed simulant was given the code name UGA-12M1, with the "12" corresponding to the 12 components, the "M" indicating that the components

are the major components. Different batches of the feed simulants of the same nominal composition were distinguished by designations such as UGA-12M1, UGA-12M1A, UGA-12M1B, etc. Variations of this feed simulant were also studied in which the anions NO_2^- , NO_3^- , and CO_3^{2-} were deleted. In the feed simulant prepared without the addition of NO_3^- ion as sodium nitrate the metal ions were still introduced as their nitrate salts but the water washing of the oxide/hydroxide precipitates can be assumed to remove at least most of the NO_3^- introduced with the metal ions. Nitrite-free feed simulant is designated as UGA-11XN1 and feed simulant prepared without added NO_2^- or NO_3^- is designated as UGA-10XNN'1. In most of this work the noble metals of interest were added as their chlorides to individual aliquots of the feed simulant immediately before carrying out the hydrogen generation studies.

The commercially available inorganic salts used as sources of the 12 components of the feed simulant UGA-12M1 are listed in Table 1. Analyzed reagent grade chemicals except for $\text{Nd}(\text{NO}_3)_3$ and $\text{ZrO}(\text{NO}_3)_2$ were used as sources of the metals and ions. Neodymium and zirconyl nitrates were not available as reagent grade chemicals but were purchased from Aldrich Chemical Company, Milwaukee, Wisconsin as 99.9% $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively.

Formic Acid Reactions

The reactions were conducted in glass reaction vessels of ~550 mL total capacity equipped with a threaded plug and O-ring adapter. A pressure gauge was attached to the system. The two side-arms of the vessel near the top were capped with rubber septa through which needles could be inserted to flush the system or to sample the gas phase. The reaction vessel had two thermocouple wells. A thermocouple attached to a cycle heater was placed in one well to maintain a constant temperature. The other well was used to check the temperature of the reaction mixture independently with a second thermocouple. Magnetic stirring was used.

In typical experiments a reaction vessel of the above type was charged with a measured 40 to 50 mL of the feed simulant and a weighed quantity of the noble metal compound or a known volume of an aqueous solution of a noble metal compound. After flushing the mixture with argon, the system was closed and the gas phase analyzed using the system described below. The solution was warmed to the desired reaction temperature (typically 80–100°C) and kept there using a temperature controller. Formic acid was then added below the surface of the feed simulant from a 10 mL plastic syringe driven by the syringe pump. The standard rate of addition of formic acid was 0.0194 ± 0.0002 mL/min

(1.164 mL/hr) corresponding to 0.448 mmoles HCO₂H/min or 26.9 mmoles HCO₂H/hr. The setting on the syringe pump to achieve this rate of addition was checked weekly with either formic acid or distilled water. In a typical run, 88 weight % formic acid was added at this rate for a total of 190 minutes corresponding to a total of 85.1 mmoles of formic acid. A pressure gauge was used to monitor the pressure buildup from the gases produced during the experiment and to assure the absence of leaks. Pressures in excess of 30 psig were frequently found to cause leaks. High pressures therefore were avoided by limiting the amount of feed simulant used. Gas samples were withdrawn periodically at the reaction temperature using a Pressure-Lok syringe inserted into one of the rubber septa; these samples were analyzed immediately using gas chromatography as indicated below.

The experiments using Ru or Pd (Figures 13 and 14 later in this paper) were conducted somewhat differently in that all of the formic acid was introduced at the beginning of the experiment as 88 weight % formic acid using a smaller reaction vessel of ~250 mL total capacity. The reaction mixture was then brought to the desired reaction temperature similar to the experiments described in an earlier report.¹⁶

In order to minimize weighing errors, a stock aqueous solution of 1.4 mg/mL of RhCl₃·3H₂O was prepared. In many runs 14 mg. of RhCl₃·3H₂O was used corresponding to 10 mL of this stock solution. In order to keep the total volume the same in all of the experiments using the syringe pump, 10 mL of water was always added even if this Rh stock solution was not used.

Gas Analyses

Hydrogen analyses were performed using a Varian 90P gas chromatograph (Varian Corporation, Sunnyvale, California). The hydrogen was eluted on a 20cm × 6mm column packed with a 40/60 mesh 13× molecular sieve material obtained from Varian Corporation. Argon was used as the carrier gas. The column temperature was maintained at 80°C. Carbon monoxide, carbon dioxide, nitrous oxide, and nitric oxide were monitored using a gas partitioner (Fisher Model 1200). The gases were separated on the basis of their size and polarity by means of two columns, a 2m 80/100 mesh Columnpak PQ and a 3.3m 13× 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.

Table 1
Sources of the Components of the Feed Simulant UGA-12M1

Component*	Molarity	Source	Amount‡	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

* The insoluble components are present as Al(OH)₃, Cd(OH)₂, Fe(OH)₃, MnO₂, Nd₂O₃, Ni(OH)₂, SiO₂, ZrO₂.

† The nominal Na⁺ concentration in the simulant is 0.88 M because the NaOH precipitant was incompletely washed from the oxide/hydroxide precipitates.

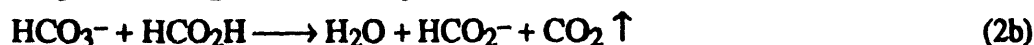
‡ Amount of source chemical for a one-liter batch.

§ The water solubility figures for these salts are taken from the *CRC Handbook of Chemistry and Physics*.

RESULTS

Experiments in the Absence of Noble Metals

Figure 3 summarizes the evolution of the gases CO₂, NO, and N₂O as a function of time when 50 mL of the feed simulant UGA-12M1 was titrated at 90°C with 2.3 mL (~49 mmoles) of 88 weight % formic acid added over a period of 118 minutes in the absence of added noble metals. Hydrogen was not observed in the absence of noble metals. In the first stage of the reaction CO₂ is generated from the carbonate ion by the two-stage reaction:



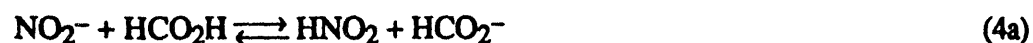
In this regime CO₂ is produced without any accompanying nitrogen oxides. The apparent production of ~9 mmoles of CO₂ in this regime is more than that expected by decomposition of the 50mL × 0.125 M = 6.25 mmoles of carbonate present in the feed simulant used by the first 12.5 mmoles of formic acid introduced. However, an additional 50 × 0.03 M = 1.5 mmoles of CO₂ can be produced by rapid formic acid reduction of the 0.03 M/liter of Mn^{IV}O₂ present in the feed simulant to Mn⁺² in this initial regime by the following equation:



Thus a total of 6.25 + 1.5 = 7.75 mmoles of CO₂ is expected from reaction of formic acid with the carbonate and MnO₂ present in 50 mL of the UGA-12M1 feed simulant.

After decomposition of the carbonate in the feed simulant to give CO₂ by equation 2 is complete the additional formic acid decomposes the nitrite according to the following reactions:

Decomposition (disproportionation) of nitrous acid:



Reduction of nitrite:



Since nitrous acid (pK = 5.22) is a stronger acid than the bicarbonate ion (pK = 6.38)¹⁷ generation of nitrous acid from nitrite is only expected to occur after all of the bicarbonate ion has been converted to CO₂ (equation 2b).

Experiments in the Presence of Rhodium

Figures 4 and 5 illustrate a titration of 50 mL of the UGA-12M1 feed simulant with formic acid in the presence of 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ under conditions otherwise identical to those shown for the experiment summarized in Figure 3. Hydrogen production is seen to begin only after all of the CO_3^{2-} has been converted to CO_2 (equations 2a and 2b) and the NO_2^- to NO and N_2O (equations 4 and 5). This immediately suggests that one method of limiting H_2 production during the treatment of nuclear wastes with formic acid is to limit the amount of formic acid to that required for conversion of all of the CO_3^{2-} to CO_2 and the NO_2^- to NO and N_2O . A total of 1.3 mmoles of H_2 was produced in this experiment.

Effect of the Type of Rhodium Source

Some studies were performed using insoluble Rh sources rather than soluble $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. Two rather different methods of introducing Rh in an insoluble form were investigated.

In the first method Rh was introduced into the feed simulant by coprecipitation in the iron fraction (refer to the standard feed simulant preparation procedure described in Figure 2) using hydrated $\text{Rh}(\text{NO}_3)_3$ 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 $88 \pm 2^\circ\text{C}$ led to the production of a total of 1.4 mmoles of H_2 as compared with 1.3 mmoles of H_2 in a comparable experiment in which Rh was introduced as the soluble " $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ " (e.g., Figure 5). The usual production of NO and N_2O was observed in this experiment. Furthermore the CO_2 production from CO_3^{2-} and the $\text{NO}/\text{N}_2\text{O}$ production from NO_2^- was essentially complete before onset of H_2 production. Thus, there appear to be no significant differences in the behavior of this system when Rh is coprecipitated with the other metal oxides in the feed simulant preparation or when $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 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 (Figure 6) or alumina using 0.1175 g. of 5% Rh/C or 0.115 g. of 5% Rh/ Al_2O_3 , respectively, corresponding to the amount of Rh in the 14 mg. of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ used in the standard experiments. The observed behavior with these solid 5% Rh dispersions in UGA-12M1A upon titration with 88 weight % formic acid at 90°C was very different from the observed behavior with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the following ways:

- (1) Only a very small amount of H_2 was produced (0.16 mmoles and 0.28 mmoles at the end of the experiments with 5% Rh/C and 5% Rh/ Al_2O_3 , 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 minutes 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.

Effect of Rhodium Concentration

A series of six experiments (Table 2) was performed in which 50 mL samples of the feed simulant UGA12M1 and 10 mL of water 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. Hydrogen evolution as a function of time for the four experiments producing H₂ is depicted in Figure 7. The H₂ generation is initiated after sufficient formic acid has been added to deplete the NO₂⁻ and CO₃²⁻. In Figure 8 the H₂ production rate in mmoles/min during the time that the catalyst is active is plotted against the rhodium concentration. Within the considerable experimental errors of experiments of this type the rate of H₂ production appears to be pseudo first order in Rh concentration (moles per liter) according to the following equation:

$$\text{H}_2 \text{ production (mmoles/min)} = -0.92 + 8030 [\text{Rh}] \quad R^2 = 0.952 \quad (6)$$

The starting pH in these experiments (Table 2) before addition of formic acid fell in the range 10.7 to 11.2. The pH after completion of the formic acid treatment (Table 2) was found to be rather insensitive to the amount of Rh used and the amount of H₂ produced. This relates to the fact that the maximum amount of H₂ produced in these experiments (1.3 mmoles) was a small fraction of the ~86 mmoles of formic acid introduced in each experiment.

Table 2
Effect of the Amount of Rh on H₂ Production from HCO₂H
 50 mL UGA12M1 feed simulant; 10 ml water; 86 mmoles HCO₂H

mg RhCl ₃ ·3H ₂ O	mmoles at end of experiment				final pH
	H ₂	CO ₂	N ₂ O	NO	
1.4	~0	17.5	4.75	8.57	3.57
2.8	~0	18.16	5.97	4.23	4.18
5.6	0.25	18.07	5.27	5.77	3.57
8.4	0.63	18.00	4.54	7.57	3.64
11.2	1.14	19.46	5.05	5.94	3.79
14.0	1.31	20.22	4.99	6.70	3.67

Effect of nitrite concentration

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. In this series of four experiments (Figure 9), 50 mL samples of the nitrite-free feed simulant UGA-11XN1 were treated with various amounts of NaNO₂ and 14 mg of RhCl₃·3H₂O in 10 mL of water in the usual ~550 mL closed glass reactor before being titrated with 85 mmoles of formic acid. The composition of the gas phase was analyzed using gas chromatography in the usual manner. The experiment with the largest amount of NaNO₂, namely 1.5 g. NaNO₂, corresponds to the concentration of NO₂⁻ present in the complete feed simulants UGA-12M1.

These data indicate that the rate of H₂ production is relatively insensitive to NO₂⁻ concentration at relatively high NO₂⁻ concentrations (0.5 to 1.5 g/60 mL). 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 is the minimum amount of NO₂⁻ needed to promote this reaction. Accordingly, 50 mL of the nitrite-free feed simulant UGA-10XNN¹, 10 mL of water, and 0.5 g. (5.88 mmoles) of NaNO₃ was titrated at 90°C with 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) (Figure 10: top). Considerable amounts of H₂ were produced in all of these experiments, even in

the experiment with only 11.6 mg NaNO_2 (corresponding to a NO_2^-/Rh ratio of ~ 3) where ~ 4 mmoles of H_2 was produced at the end of the experiment. This contrasts with the production of only 0.4 mmole of H_2 at the end of a similar experiment where no NO_2^- at all was added (Figure 10: bottom). This confirms that NO_2^- is a promoter for the Rh-catalyzed decomposition of HCO_2H but that stoichiometric amounts of NO_2^- corresponding to formation of a trinitrorhodium derivative suffice for catalyst promotion.

Effect of Temperature

In order to evaluate the effect of temperature on the Rh-catalyzed H_2 generation rate from HCO_2H , 50 mL of the standard UGA-12M1 feed simulant and 10 mL of an aqueous solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.4 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{mL}$) was titrated with a total of 85 mmoles of HCO_2H using the syringe pump. The composition of the gas phase was analyzed using gas chromatography in the usual manner. Results from five experiments of this type at temperatures ranging from 77°C to 94°C are depicted in Figure 11. As expected the rate of H_2 production increases with increasing temperature with a H_2 production rate of 0.29 mmoles $\text{H}_2/\text{minute}/\text{liter}$ feed simulant at 94°C . Hydrogen production at temperatures below $\sim 85^\circ\text{C}$ was so slow that meaningful rates could not be obtained from the slope of the hydrogen production curve. It thus appears that H_2 production can be shut off at temperatures below $\sim 75^\circ$.

A practical question is whether the activity of the Rh catalyst system for hydrogen generation from HCO_2H can be destroyed by treating the reaction mixture with formic acid at a temperature below which no H_2 generation takes place and then heating the mixture further at such a temperature before bringing the mixture to 90 – 100°C to complete the reaction. In order to test this possibility 50 mL of the feed simulant UGA-12M1, 10 mL of water, and 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was treated at 70°C with 85.3 mmoles of formic acid over 190 minutes using the syringe pump. In five experiments the reaction mixture was held at 70°C for various periods of time ranging from the 190 minutes required for the formic acid addition to 25 hr. before heating to 90°C . Figure 12 shows the H_2 generation at 90°C for such reaction mixtures pretreated at 70°C for 190 min, 6 hr, and 9 hr before heating to 90°C . Hydrogen generation begins after a few minutes of heating at 90°C and the rate of hydrogen generation appears to be the same in all three cases irrespective of the pretreatment time. Experiments in which the mixture was kept at 70°C for 12 hr and for 25 hr shows no H_2 generation after heating to 90°C for at least five hours. Thus, pretreatment of the reaction mixture at 70°C has some promise as a method for inhibiting the unwanted

H₂ generation provided that this pretreatment is carried out for a sufficiently long time (e.g., ≥ 12 hr).

Experiments with Ruthenium

Figure 13 compares the H₂ generation from formic acid catalyzed by Ru in the presence (top) and absence (bottom) of NO₂⁻ using the feed simulants UGA-12M1 and UGA-11XN1, respectively. No H₂ production occurred in the presence of NO₂⁻ (Figure 13: top). However, in the absence of NO₂⁻, production of H₂ (~0.4 mmoles) was observed (Figure 13: bottom) indicating that NO₂⁻ is an inhibitor for the Ru-catalyzed production of H₂ from formic acid in feed simulant media. Ruthenium appears to be incapable of catalyzing the reduction of *nitrate* to NO or N₂O as indicated by the absence of these gases in the experiment with the UGA-11XN1 feed simulant containing NO₃⁻ but not NO₂⁻ (Figure 13: bottom).

Experiments with Palladium

Figure 14 compares the hydrogen generation from formic acid catalyzed by Pd in the presence (top) and absence (middle and bottom) of NO₂⁻ using the feed simulants UGA-12M1 and UGA-11XN1, respectively. Negligible amounts of H₂ (0.23 mmoles) were observed in the presence of both NO₃⁻ and NO₂⁻ (Figure 14: top) and only very small amounts of H₂ (0.63 mmoles) were observed in the absence of NO₂⁻ but the presence of NO₃⁻ (Figure 14: middle). More dramatically, the production of N₂O was observed when NO₂⁻ was absent but NO₃⁻ was present indicating that Pd can catalyze the reduction of nitrate to N₂O by formic acid. Significant H₂ generation (a total of 2.6 mmoles) was observed upon HCO₂H treatment of a NO₂⁻-free feed simulant without added NO₃⁻ (UGA-10XNN'1) in the presence of Pd (Figure 14: bottom) indicating that both NO₃⁻ and NO₂⁻ inhibit the catalytic activity of Pd for H₂ production from formic acid.

Mixed Metal Experiments

In order to get a better idea as to the material balance when feed simulant is titrated with formic acid in the presence of noble metals as well as any synergistic effects from mixtures of noble metals, a carbonate-free feed simulant UGA-11M1DXC was prepared using the standard protocol but leaving out the carbonate. Samples of this feed simulant were titrated at $90 \pm 2^\circ\text{C}$ with 88 weight % formic acid adding 72 to 82 mmoles steadily over

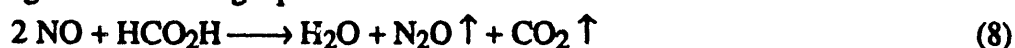
a period of 162 to 182 minutes using the syringe pump. Experiments were performed using all eight possible combinations of the noble metals Rh, Ru, and Pd ranging from no noble metals to all three noble metals in a single experiment (Figures 15 and 16). The noble metal sources in these experiments were the usual chloride salts.

In such experiments with carbonate-free feed simulant, the only source of CO₂ is formic acid oxidation. In the absence of noble metals, the expected reactions of the feed simulant with formic acid are disproportionation of nitrous acid (equation 7a) and reduction of nitrite (equation 7b):

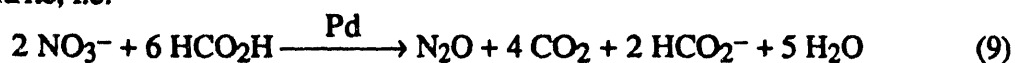


In the gas phase, reaction 7a produces only NO, whereas reaction 7b produces a 2:1 CO₂/N₂O mixture. At the end of the experiment using no noble metals (Figure 15a) a total of 8.2 mmoles of CO₂ and 4.0 mmoles of N₂O was present in agreement with this 2:1 ratio within estimated experimental error. The results with added Ru were very similar to those with no noble metals at all indicating that Ru has no significant effect on the formic acid/nitrite chemistry. Thus, at the end of the experiment with added Ru (Figure 15c) a total of 7.8 mmoles of CO₂ and 3.6 mmoles of N₂O was present still in reasonable agreement with the ideal 2:1 ratio.

Addition of Pd to the system (Figure 15d) did not result in hydrogen evolution from formic acid but resulted in complete consumption of the originally formed NO. The stoichiometry of this reaction is consistent with the Pd-catalyzed reduction of NO to N₂O according to the following equation:



In this reaction each mmole of NO gives 0.5 mmole each of N₂O and CO₂. In the experiment with added Pd (Figure 15d) the maximum amount of NO (9.5 mmoles) was present at 122 minutes; at this point 8.9 mmoles of CO₂ and 3.6 mmoles of N₂O were present corresponding to a CO₂/N₂O ratio of 2.5 rather than the ideal 2.0 from equation 7b. This CO₂/N₂O ratio of 2.5 could arise from some Pd-catalyzed reduction of *nitrate* rather than nitrite, i.e.



Thus reduction of NO₃⁻ to N₂O (equation 9) produces 4 mmoles of CO₂ for each mmole of N₂O whereas reduction of NO₂⁻ to N₂O (equation 7b) produces only 2 mmoles of CO₂ for each mmole of N₂O. The ability of Pd to catalyze the reduction of NO₃⁻ to N₂O is indicated by the production of N₂O when the NO₂⁻-free feed simulant is treated with formic acid in the presence of Pd (Figure 14: middle). Thus, a CO₂/N₂O ratio of 2.5

suggests that 75% of the N_2O is produced from NO_2^- reduction (equation 7b) and 25 % of the N_2O is produced from NO_3^- reduction (equation 9). Between 122 minutes and the end of the experiment all of the 9.5 mmoles of NO were consumed with the production of an additional 4.4 mmoles of N_2O ; the observed $\text{NO}/\text{N}_2\text{O}$ ratio is $9.5/4.4 = 2.2$, which is reasonably close to the "ideal" 2.0. However, the amount of CO_2 is much too high for it to arise only from formic acid reduction of NO_2^- and NO to N_2O since reduction of NO_2^- to the observed 3.5 mmoles of N_2O in the early stages of the reaction is expected to yield 7.0 mmoles of CO_2 by equation 6b and reduction of NO to the observed 4.4 mmoles of N_2O in the late stages of the reaction is expected to yield 4.4 mmoles of CO_2 by equation 8 for a total of $7.0 + 4.4 = 11.4$ mmoles of CO_2 in contrast to the observed 17.0 mmoles of CO_2 .

A similar analysis of the gas phase compositions can be done on the experiment using a mixture of Pd and Ru (Figure 16c) since the experiment with Ru alone (Figure 15c) was shown to be essentially similar to the experiment with no noble metals at all suggesting that the addition of Ru has no effect on these reactions in the presence of NO_2^- . In this experiment, the maximum amount of NO (9.6 mmoles) was measured after 107 minutes; at this time 7.2 mmoles of CO_2 and 3.1 mmoles of N_2O were present corresponding to a $\text{CO}_2/\text{N}_2\text{O}$ ratio of 2.3 rather than the "ideal" 2.0 (equation 7b). Between 107 minutes and the end of the experiment these 9.6 mmoles of NO were consumed with the production of an additional 5.0 mmoles of N_2O ; the observed $\text{NO}/\text{N}_2\text{O}$ ratio is 1.9 which is within estimated experimental error of the "ideal" 2.0. Again, however, the amount of CO_2 is much too high for it to arise only from formic acid reduction of NO_2^- and NO to N_2O since reduction of NO_2^- to the observed 3.1 mmoles of N_2O in the early stages of the reaction is expected to yield 6.2 mmoles of CO_2 by equation 6b and reduction of NO to the observed 5.0 mmoles of N_2O in the late stages of the reaction is expected to yield 5.0 mmoles of CO_2 for a total of $6.2 + 5.0 = 11.2$ mmoles of CO_2 in contrast to the observed 16.5 mmoles of CO_2 .

Addition of Rh to the feed simulant leads to H_2 production upon titration with formic acid whether or not the other noble metals are present. In the experiment in which only Rh is added to the CO_3^{2-} -free feed simulant (Figure 15b), 10.7 mmoles of CO_2 , 3.7 mmoles of N_2O , 8.2 mmoles of NO , and 0.8 mmoles of H_2 are present at the end of the experiment. If all of the N_2O is assumed to arise from NO_2^- reduction (equation 7b), the expected amounts of CO_2 are 7.4 mmoles from NO_2^- reduction to 3.7 mmoles of N_2O and 0.8 mmoles from formic acid decomposition to a total of 0.8 mmoles of H_2 for a total of $7.4 + 0.8 = 8.2$ mmoles of CO_2 , which is less than the observed 10.7 mmoles of CO_2 . Possibly rhodium is catalyzing the reduction of NO_2^- or NO_3^- to ammonia; evidence of

this was found in NH_3 analyses at PNL of reaction mixtures obtained after treatment of the full UGA-12M1 feed simulant with formic acid in the presence of Rh.

The effects of the three noble metals in experiments conducted with noble metal mixtures (Figure 16) indicate that the specific effects of the individual noble metals in the nitrite-containing feed simulant are additive. Thus, Ru does not contribute to the gas phase composition, Rh leads to H_2 production, and Pd leads to reduction of NO to N_2O in the late stages of the reaction regardless of the other noble metals.

DISCUSSION

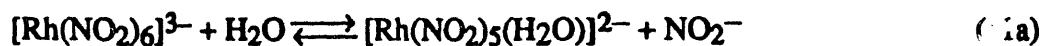
The experiments discussed in this report confirm earlier observations¹⁶ that Rh is the most active catalyst for formic acid decomposition in feed simulant media in the presence of NO_2^- . Attempts to obtain definitive mechanistic information on this system have been complicated by the presence of solid oxide/hydroxide phases as well as the large number of components in this system. For this reason, even the question as to whether the observed NO_2^- -promoted Rh catalysis of formic acid decomposition is a homogeneous or heterogeneous process has been difficult to resolve. Attempts to determine the rate dependence on Rh concentration yield ambiguous results unless the experimental conditions are very carefully controlled including use of the same batch of feed simulant and careful control of the reaction temperature. However, the apparent first order dependence of the reaction rate on Rh concentration provided by the data summarized in Figures 7 and 8 suggest that the observed NO_2^- -promoted Rh catalysis of formate decomposition is a homogeneous process involving a soluble Rh complex as an intermediate.

The role of NO_2^- ion as a promoter suggests the role of soluble nitrorhodium complexes as intermediates in the Rh-catalyzed decomposition of formic acid. In this connection RhCl_3 was reported more than a century ago¹⁸ to react with excess NO_2^- in boiling water to give salts of the hexanitrorhodate anion, $[\text{Rh}(\text{NO}_2)_6]^{3-}$. Three of the six nitro groups in $[\text{Rh}(\text{NO}_2)_6]^{3-}$ are reported to be labile upon treatment with strong oxidants¹⁹ or amidosulfuric acid²⁰ indicating the feasibility of opening up 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:



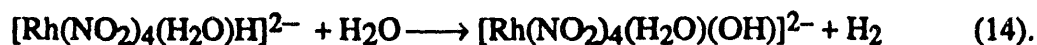
Formate can then displace the aquo ligands by reactions such as the following:



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 12–15 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 11a). 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.

The nitrorhodium catalysts involved in formic acid decomposition appear to have a limited lifetime decomposing to give much less catalytically active metallic Rh under the reducing reaction conditions created by the formic acid. The presence of the insoluble metal oxides and hydroxides in the feed simulants appears to increase the lifetime of these nitrorhodium catalysts as indicated by the much shorter lifetimes of a catalyst obtained by treating aqueous $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of excess NaNO_2 with formic acid at 90°C in the absence of any insoluble metal hydroxides or oxides (Colletti, L. P., unpublished results at the University of Georgia). This could be a consequence of the stabilization of the catalytically active nitrorhodium species by chemical bonding to the surface hydroxyl groups of the insoluble hydrous oxides of Fe, Al, Cd, etc., present in the feed simulant.

The role of NO_2^- as a promoter for the Rh-catalyzed formic acid decomposition is contrasted by its role as an inhibitor for the Ru-catalyzed (Figure 13) and Pd-catalyzed (Figure 14) decompositions of formic acid. In the case of Ru, the presence of NO_2^- could convert the metal to less catalytically active ruthenium nitrosyl derivatives; this possibility has not yet been explored. Palladium is of interest since it is even capable of catalyzing reductions of *nitrate* to N_2O (Figure 14) and NO to N_2O (Figure 15d). This suggests that the inhibitory role of NO_2^- and even NO_3^- in the Pd-catalyzed generation of H_2 from formic acid may relate to their sacrificial reduction in the presence of Pd.

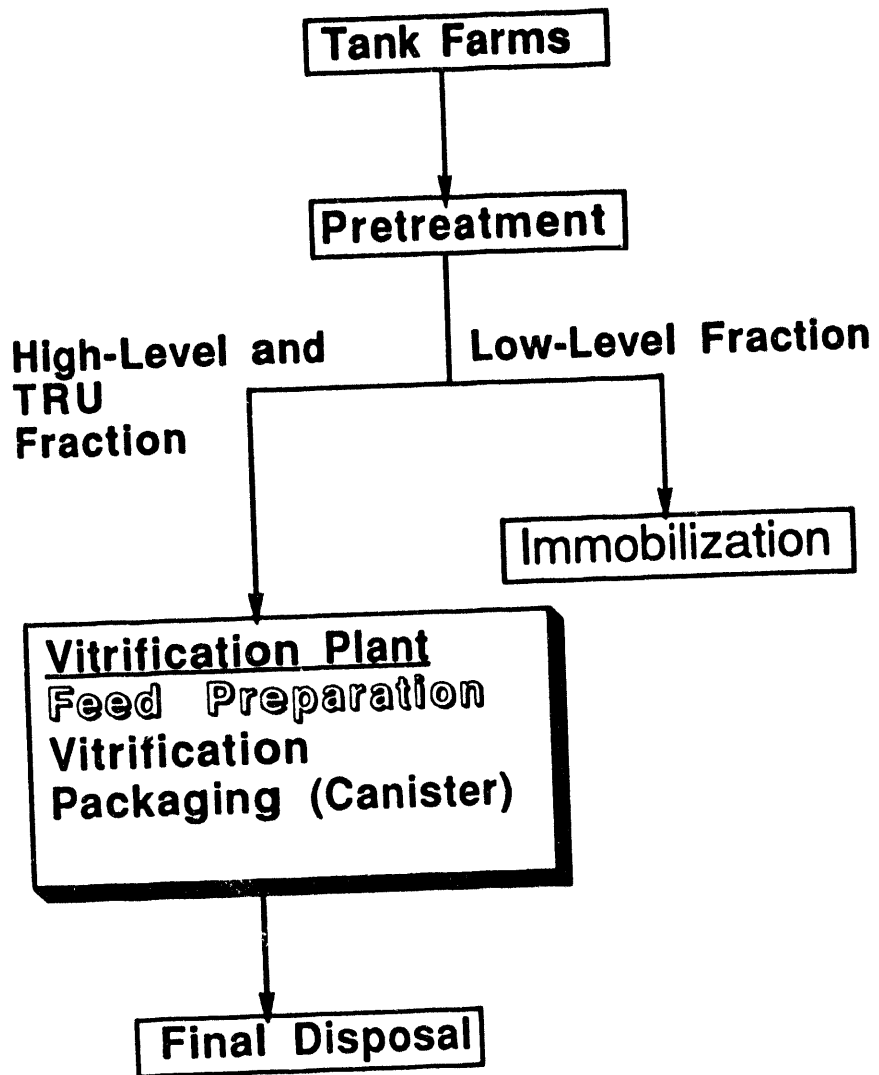
Titration of the feed simulants with formic acid in the presence of Rh is also informative with regard to the pH dependence of the NO_2^- -promoted Rh-catalyzed H_2 evolution from formic acid. Addition of formic acid first decomposes the CO_3^{2-} according to equations 2a and 2b to give CO_2 . When all of the CO_3^{2-} is decomposed, further addition of formic acid decomposes the NO_2^- to give NO and N_2O according to equations 4 and 5. Hydrogen evolution from formic acid only occurs after essentially all of the CO_3^{2-} is decomposed to CO_2 and all of the nitrite to NO and N_2O and thus requires lower pH's than these other processes. From the practical point of view these observations suggest that one method of limiting hydrogen production during the treatment of nuclear wastes with formic acid is to limit the amount of formic acid to that required for conversion of all of the carbonate to CO_2 and the nitrite to NO and N_2O .

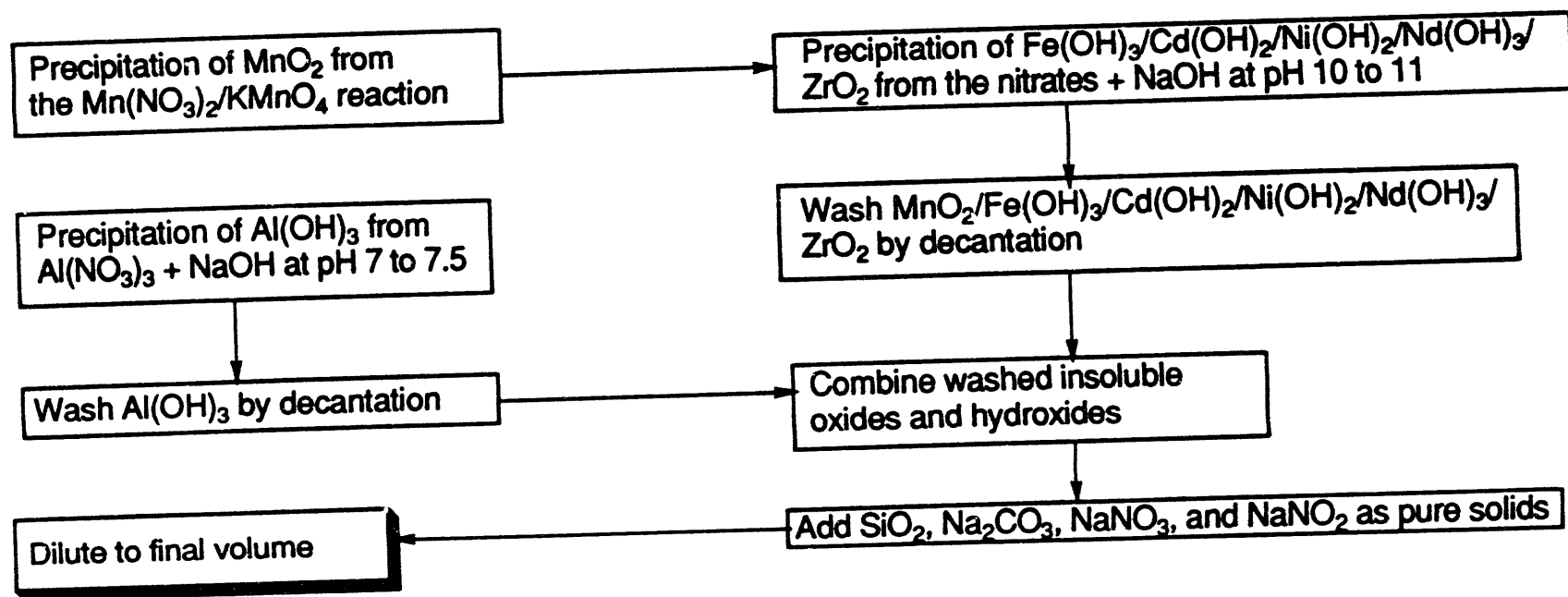
Acknowledgement: We are indebted to the U. S. Department of Energy for support of this work at the University of Georgia through the Westinghouse Hanford Corporation and the Battelle Pacific Northwest Laboratories. We are also indebted to Ms. J. L. Walters and Ms. N. B. Turner for experimental assistance.

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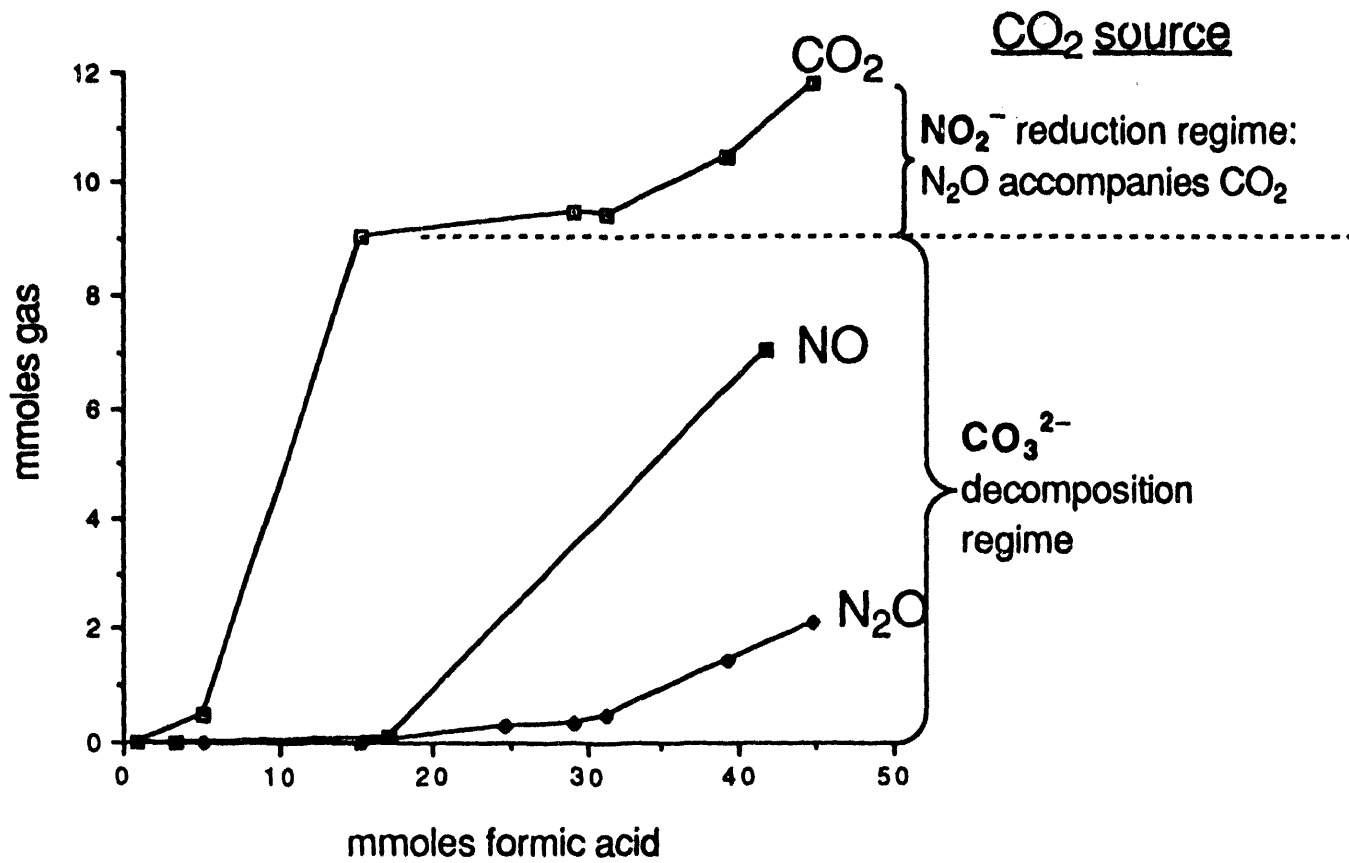
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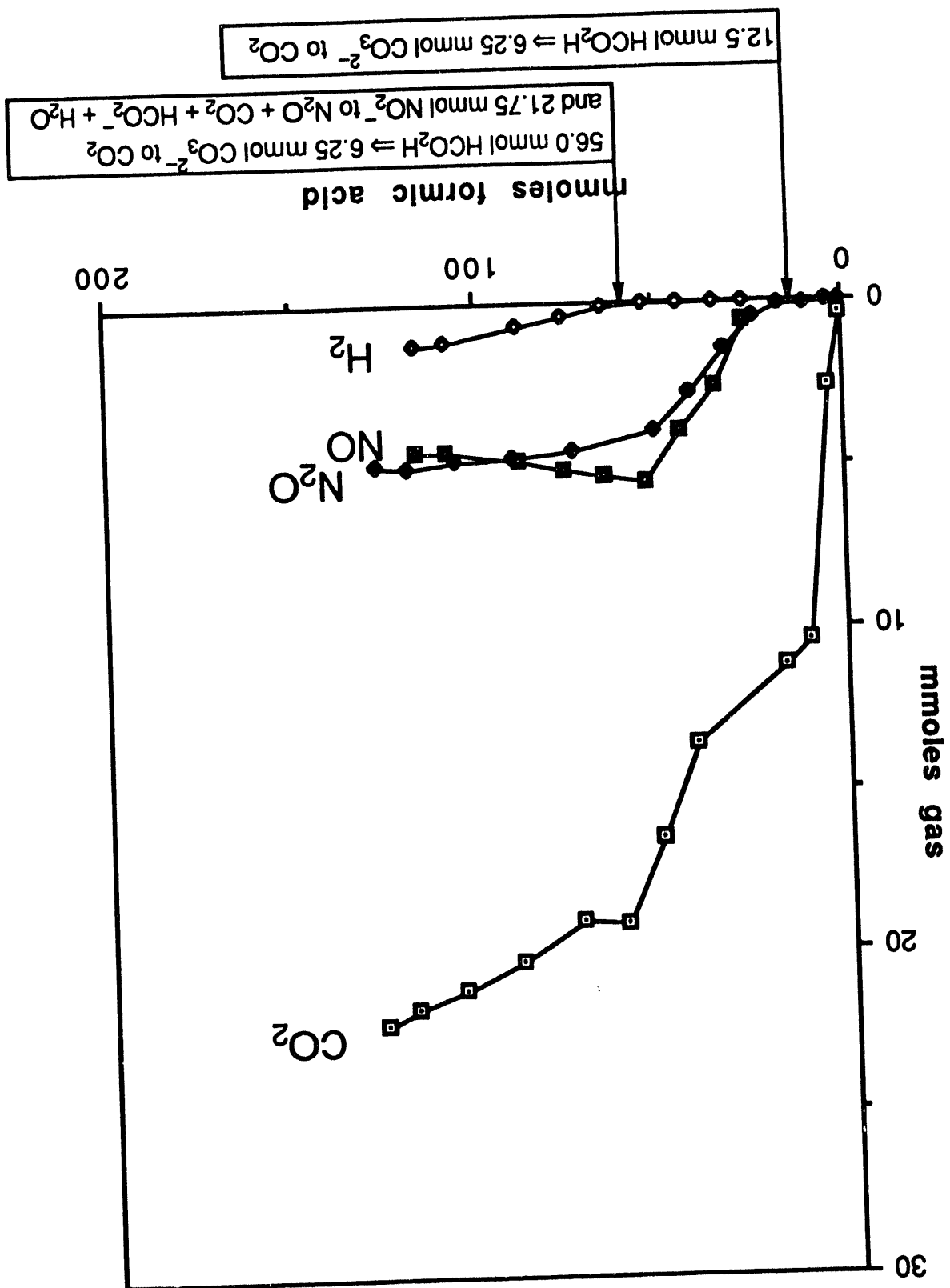
- Figure 1:** Flow chart for the vitrification of nuclear wastes.
- Figure 2:** Outline of the scheme for the preparation of the UGA-12M1 feed simulant.
- Figure 3:** Titration of 50 mL of the UGA-12M1 feed simulant with 88% formic acid at a rate of 0.0196 mL/min = 0.42 mmol/min in the absence of noble metals using the syringe pump.
- Figure 4:** The CO_3^{2-} decomposition and NO_2^- reduction regimes for the CO_2 produced in the 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 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.
- Figure 5:** Titration of 50 mL of the UGA-12M1 feed simulant, 10 mL of water, and 14 mg. of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with 88% formic acid at $91 \pm 1^\circ\text{C}$.
- Figure 6:** Production of H_2 and other gases by titration of 50 mL of the feed simulant UGA-12M1 with 88% formic acid in the presence of 0.1175 g of 5% rhodium on carbon at $90 \pm 1^\circ\text{C}$.
- Figure 7:** Effect of Rh concentration on H_2 production upon titration of 50 mL of the UGA-12M1 feed simulant and 10 mL of water with formic acid at $91 \pm 1^\circ\text{C}$.
- Figure 8:** Maximum H_2 production rate (mmole/minute) versus rhodium concentration ($\text{M} \times 10^{-3}$) in the regime of catalyst activity at $90 \pm 1^\circ\text{C}$.
- Figure 9:** Effect of NaNO_2 concentration on the production of H_2 upon titration of 50 mL of UGA-11XN1 and 10 mL of water with formic acid at $90 \pm 1^\circ\text{C}$ in the presence of 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.
- Figure 10:** Hydrogen production versus time from the formic acid titration of 50 mL of UGA-11XN1, 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 0.5 g of NaNO_3 , and 10 mL of water at $90 \pm 1^\circ\text{C}$ in the presence of small amounts of added NaNO_2 .
- Figure 11:** Hydrogen evolution at different temperatures upon formic acid titration of 50 mL UGA-12M1C feed simulant, 14 mg. of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 10 mL of water.
- Figure 12:** Generation of hydrogen at $90 \pm 1^\circ\text{C}$ after pretreatment of 50 mL of UGA-12M1C, 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 10 mL of water at 70°C with 85.3 mmoles of 88% formic acid for the indicated period of time.
- Figure 13:** Ruthenium-catalyzed formic acid decomposition in feed simulants: (a) Reaction of 40 mL UGA-12M1 feed simulant, 10 mL of water, 48 mg of hydrated RuCl_3 , and 2.1 mL of 88% formic acid at $98 \pm 2^\circ\text{C}$; (b) Reaction of 40 mL UGA-11XN1 feed simulant, 10 mL of water, 14 mg of hydrated RuCl_3 , and 2.1 mL of 88% formic acid at $98 \pm 1^\circ\text{C}$.

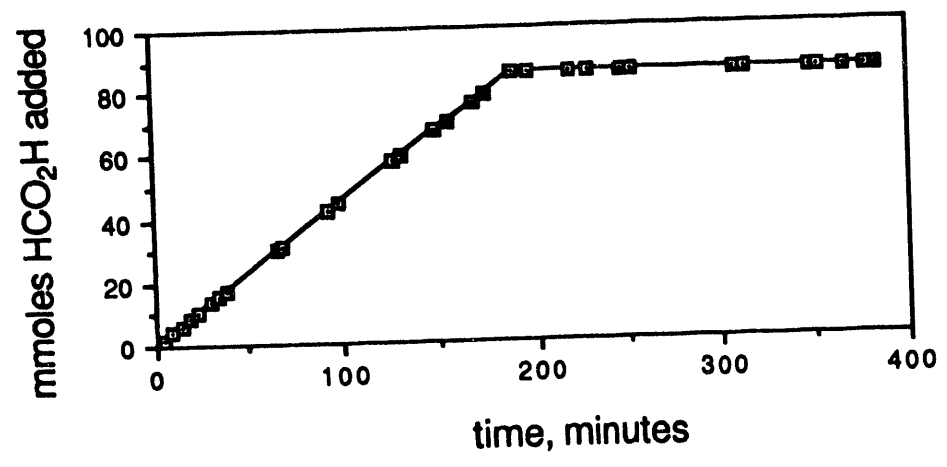
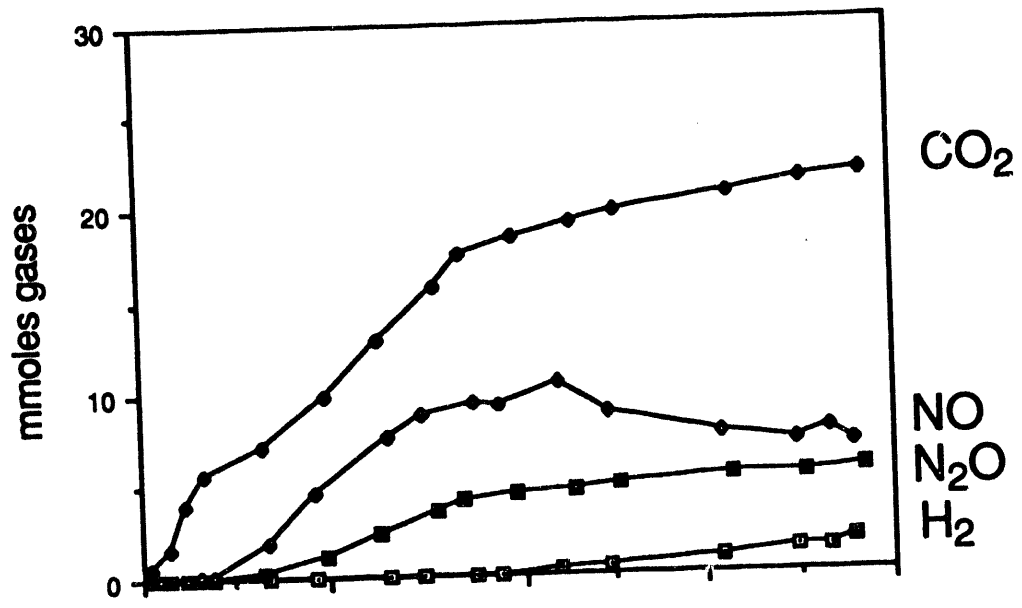


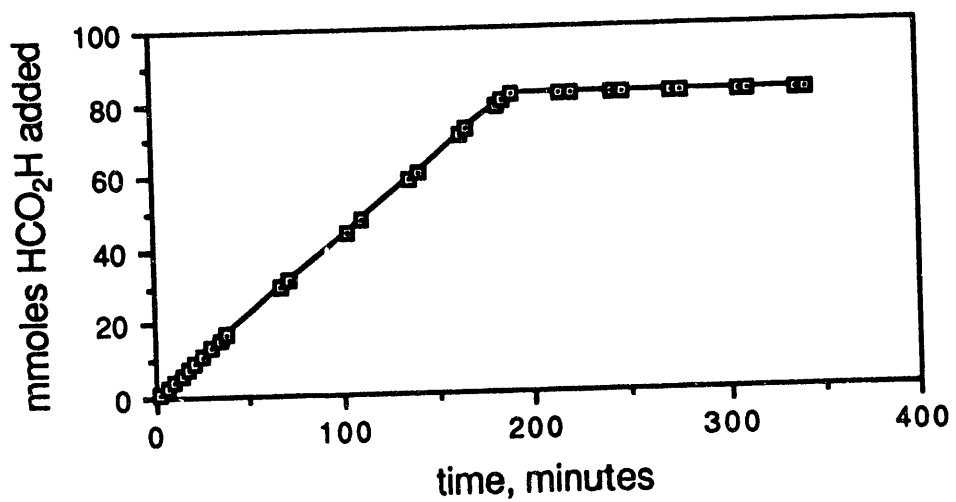
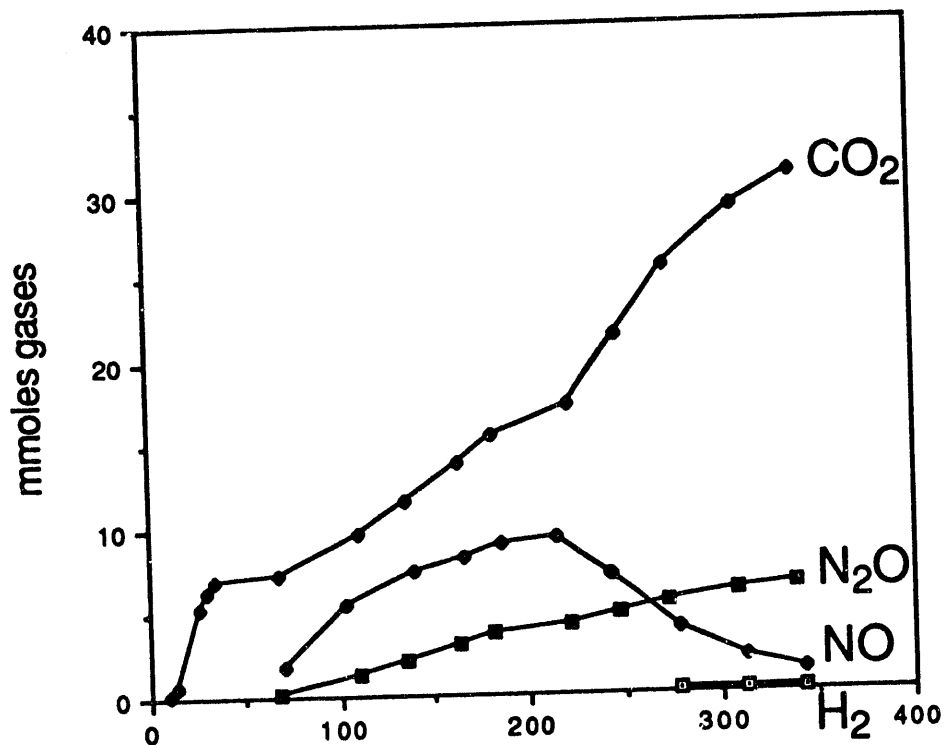


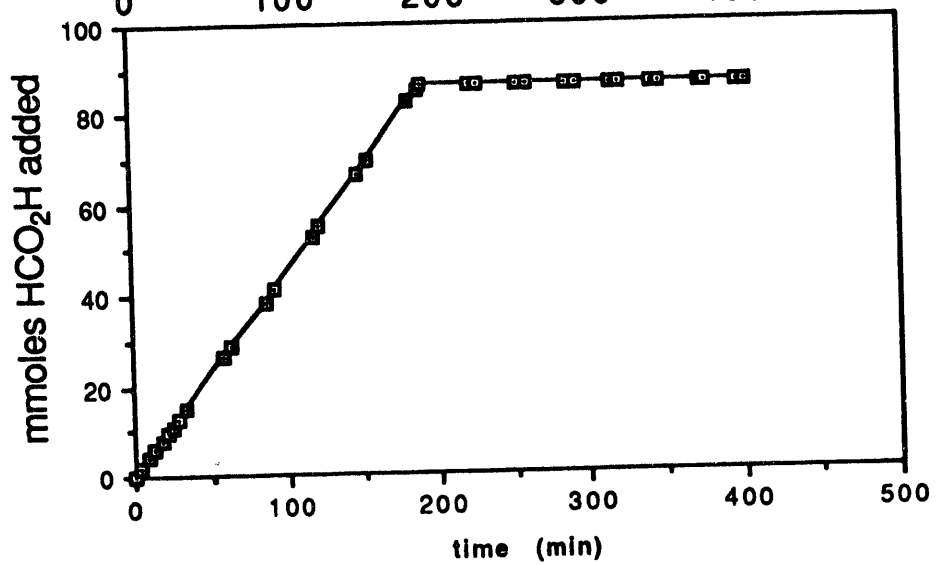
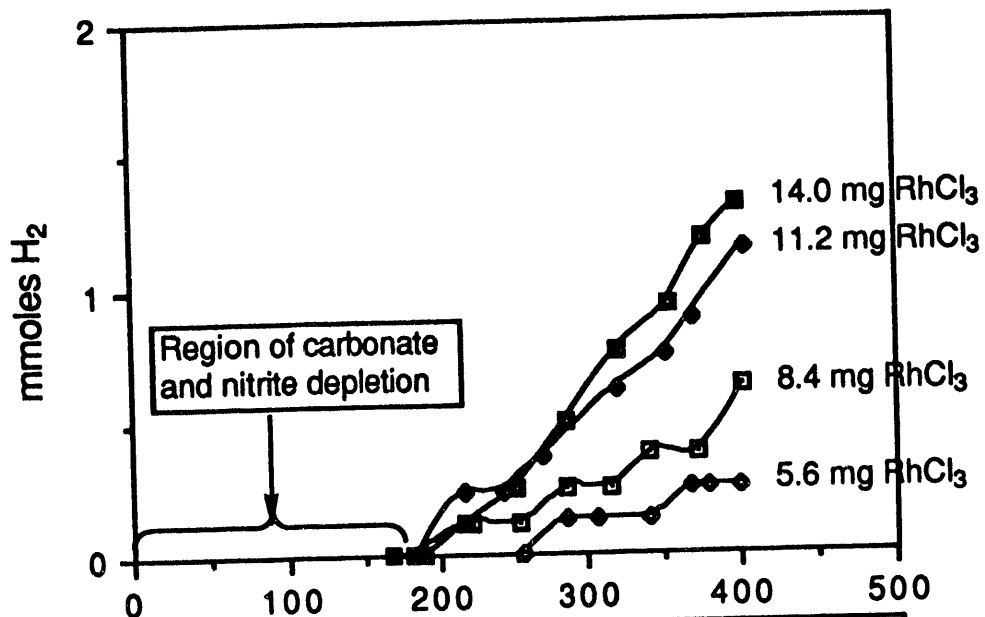
Noble metals were added as their chlorides immediately before formic acid treatment.

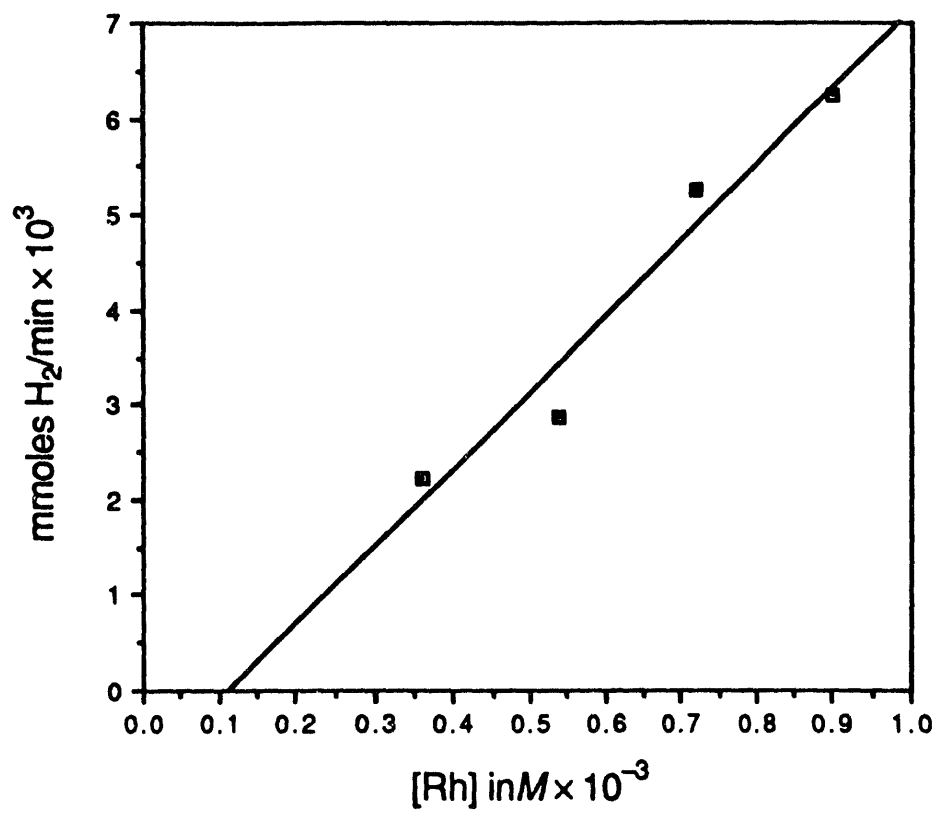


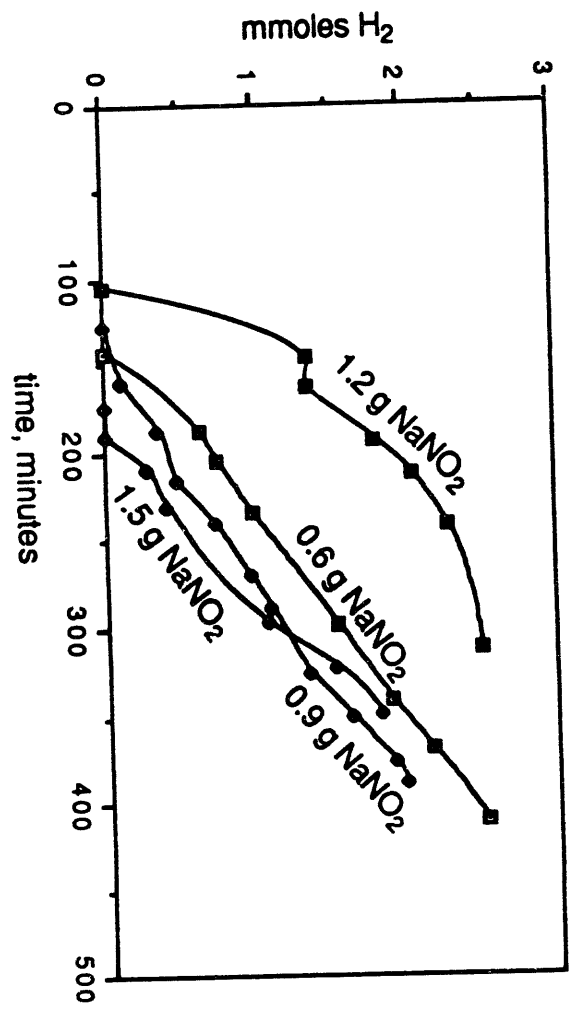


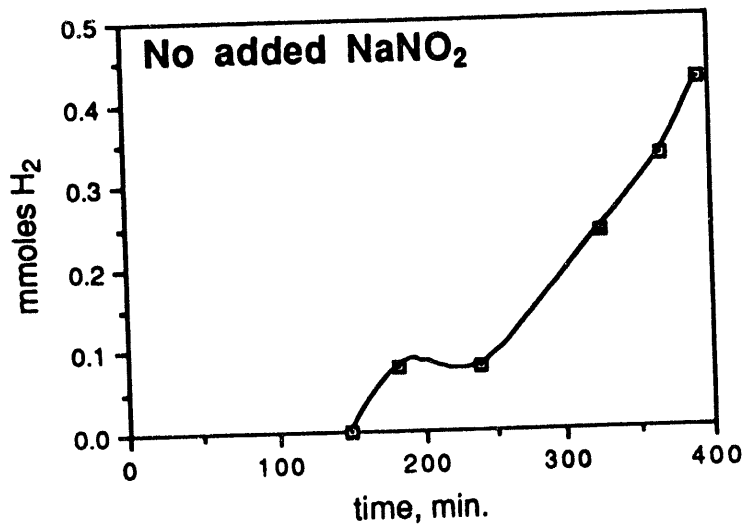
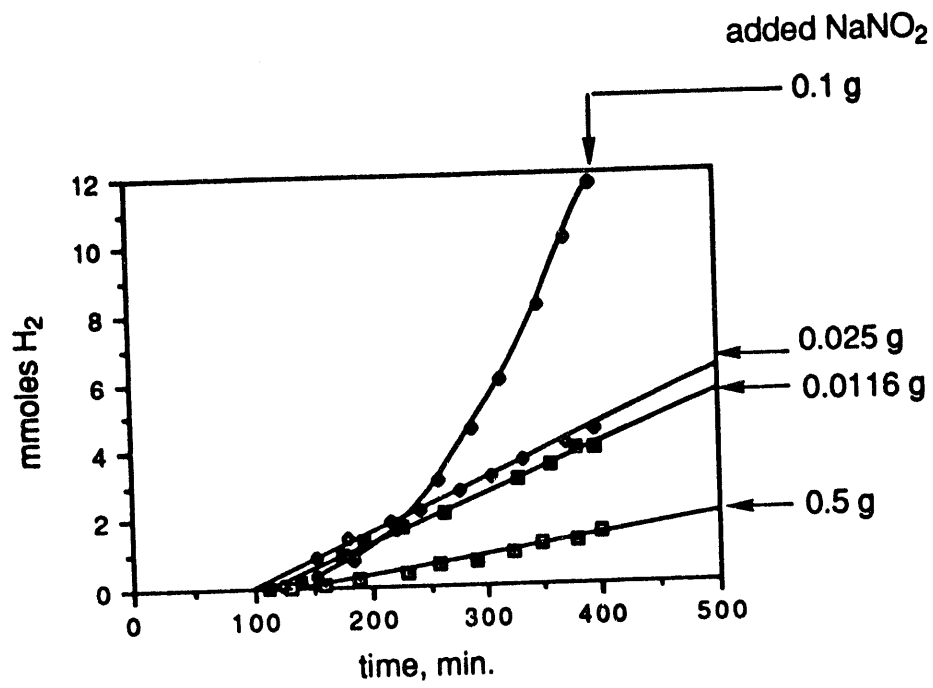


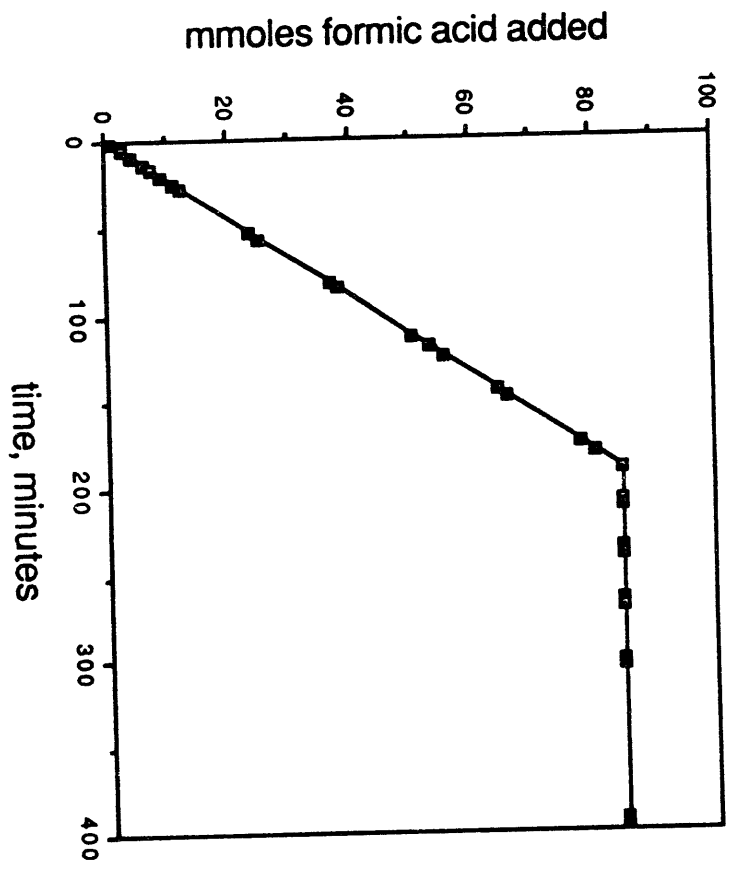
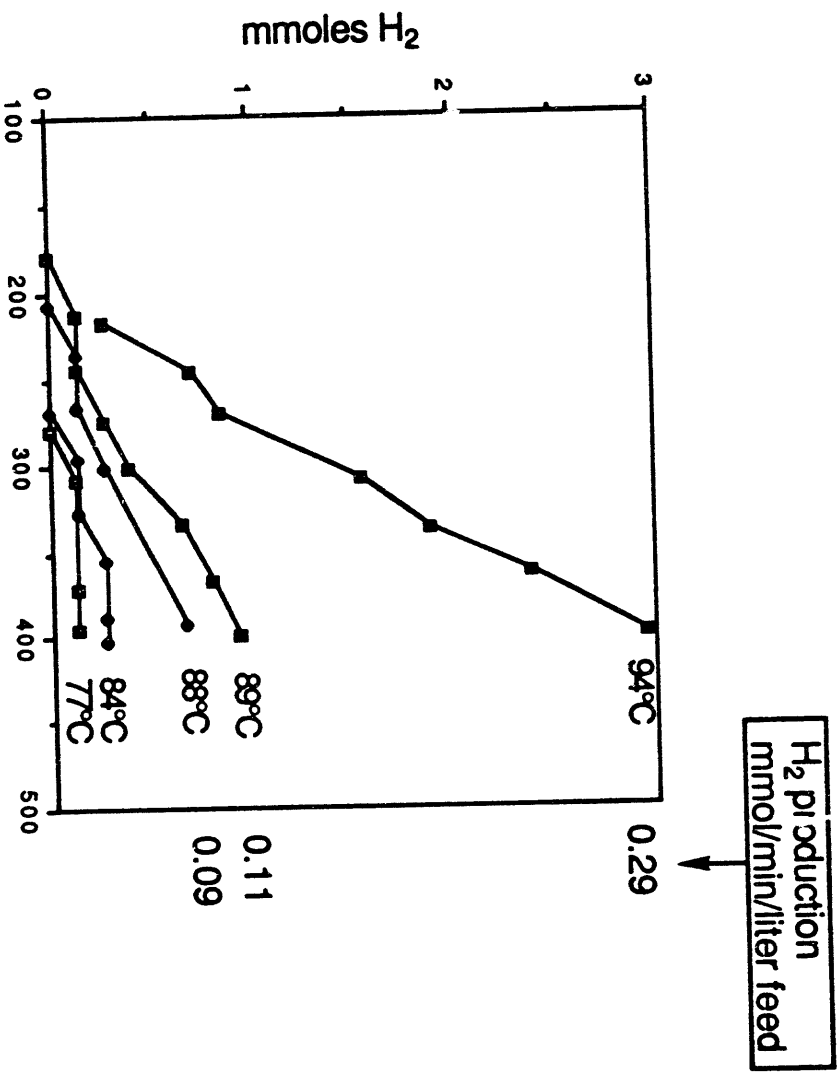


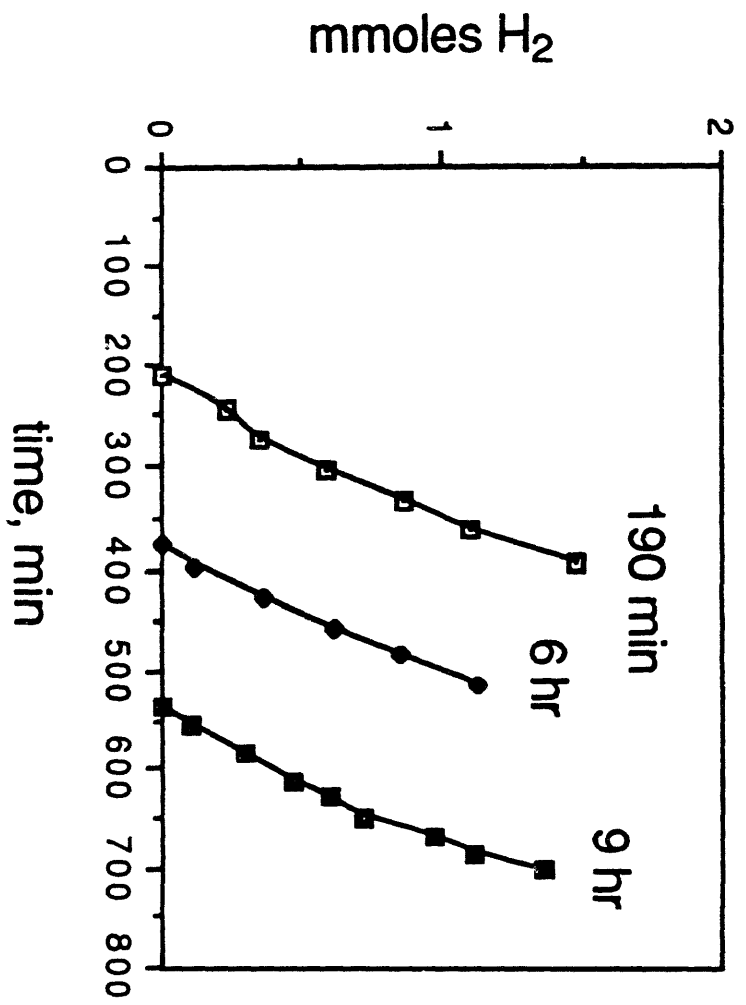












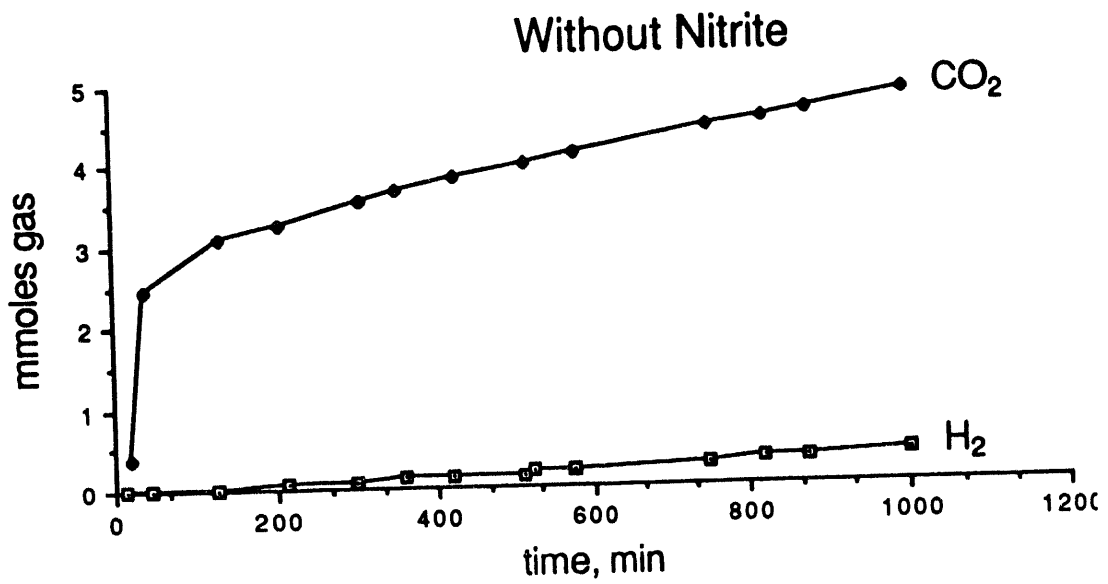
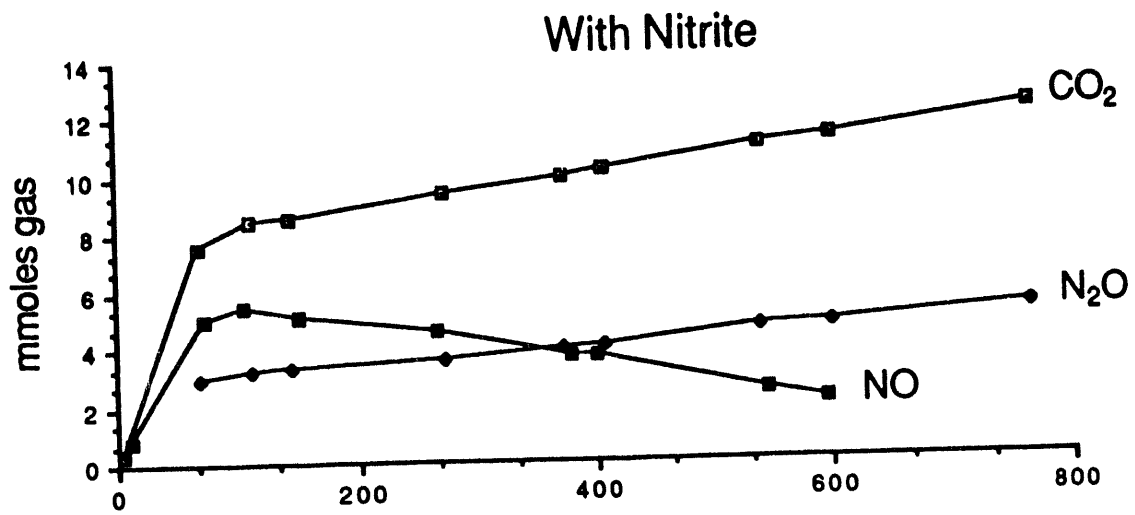
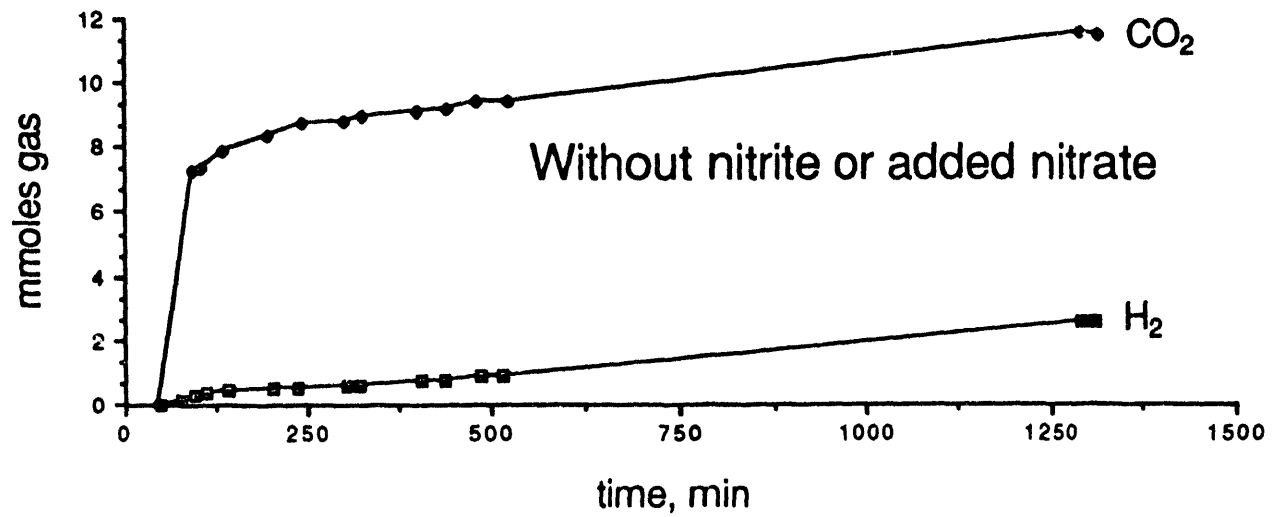
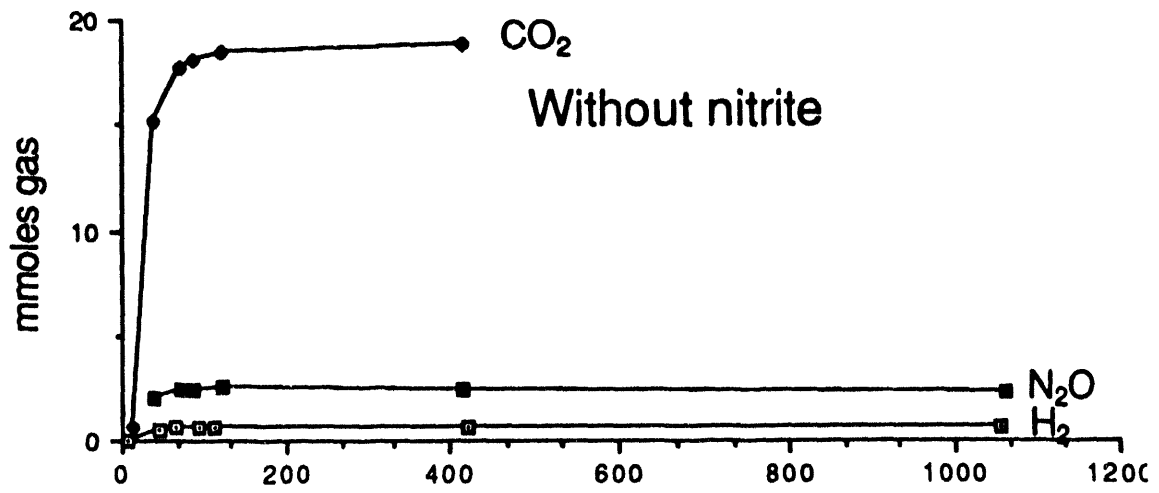
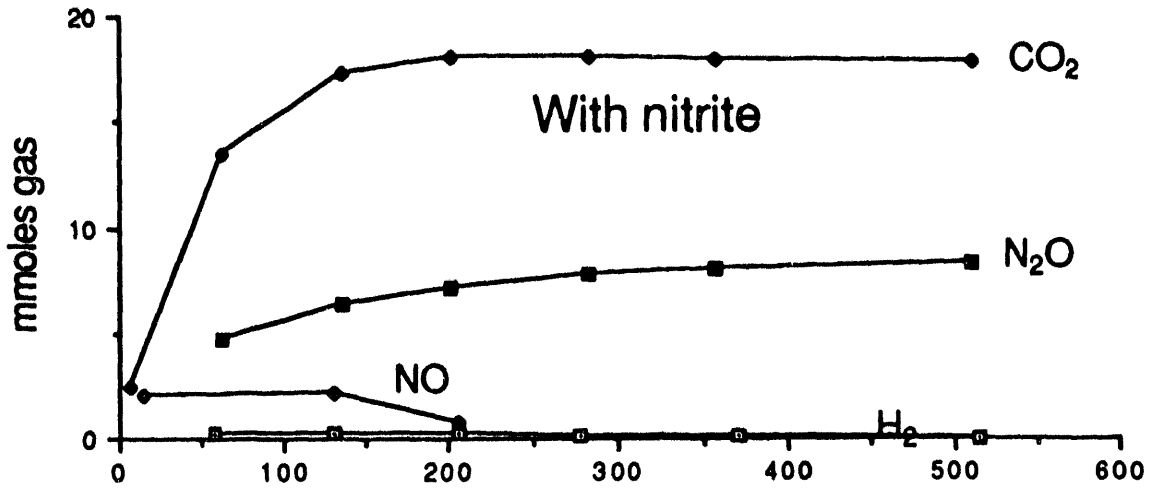
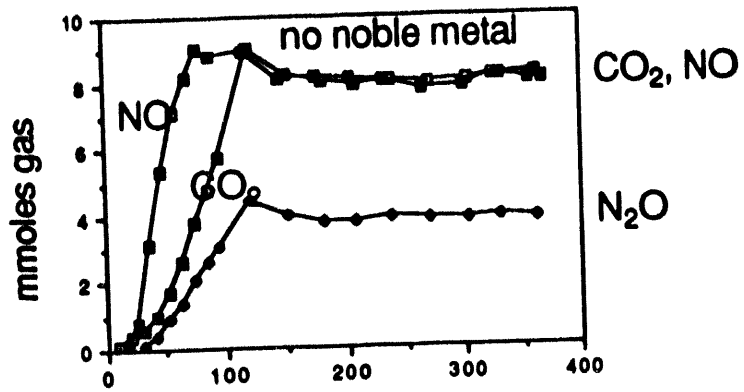


Figure 14: Palladium-catalyzed formic acid decomposition in feed simulants: (a) Reaction of 40 mL UGA-12M1, 10 mL of water, 12 mg of PdCl₂, and 2.1 mL of 88% formic acid at 98±2°C; (b) Reaction of 40 mL UGA-11XN1, 10 mL of water, 13 mg of PdCl₂, and 2.1 mL of 88% formic acid at 96±1°C; (c) Reaction of 40 mL UGA-10XNN'1, 10 mL of water, 13 mg of PdCl₂, and 2.1 mL of 88% formic acid at 96±3°C.

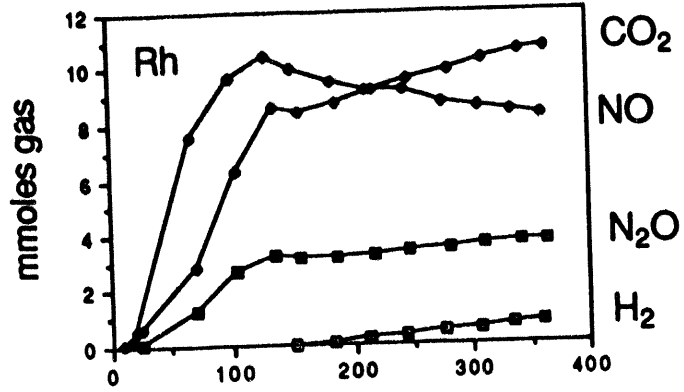
Figure 15: Titration of the carbonate-free feed simulant UGA-11M1DXC with 88% formic acid: (a) No noble metals; (b) Rh only added; (c) Ru only added; (d) Pd only added.

Figure 16: Titration of the carbonate-free feed simulant UGA-11M1DXC with 88% formic acid: (a) Rh + Ru only added; (b) Rh + Pd only added; (c) Ru + Pd only added; (d) All three noble metals (Rh + Ru + Pd) added.

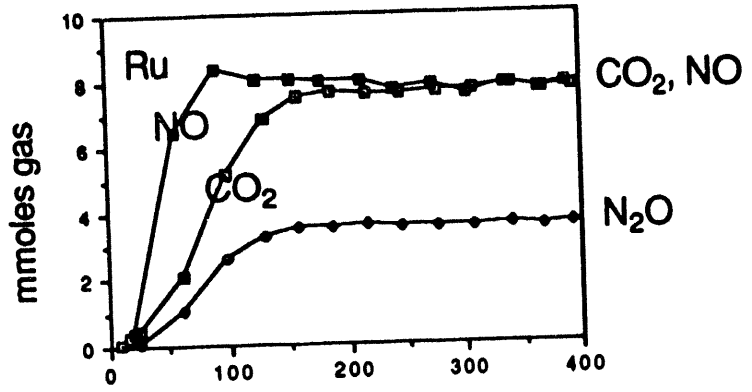




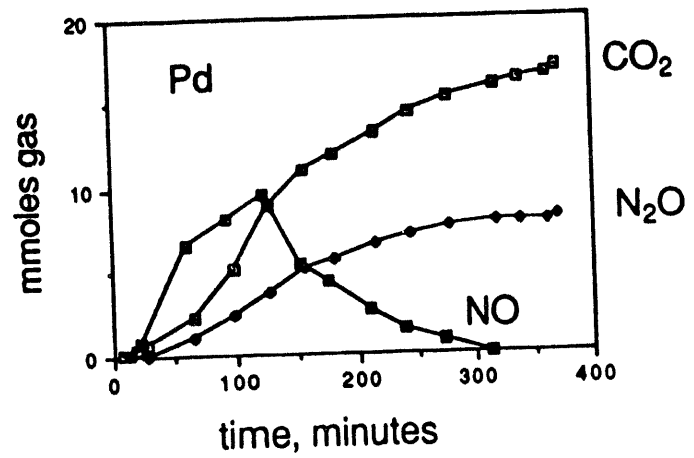
50 mL UGA-11M1DXC
 10 mL water
 72.4 mmoles HCO₂H
 added over first 162 min
 89 ± 1°C



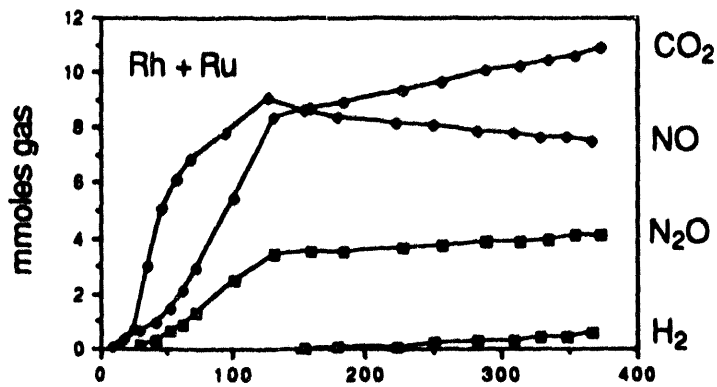
50 mL UGA-11M1DXC
 10 mL water
 14 mg RhCl₃·3H₂O
 72.7 mmoles HCO₂H
 added over first 162 min
 90 ± 2°C



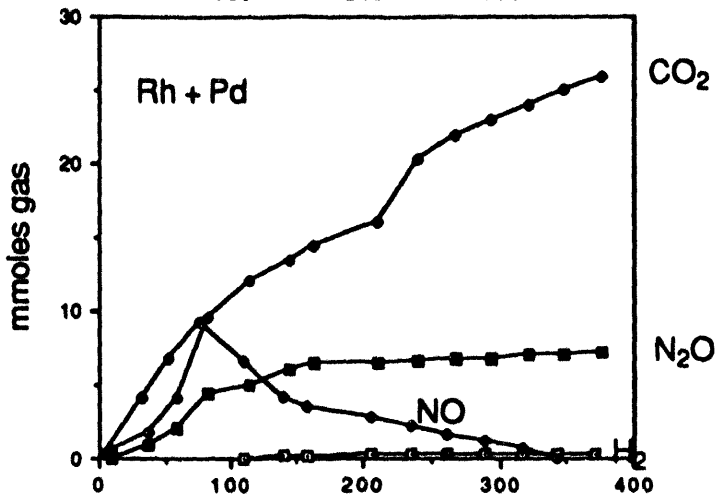
50 mL UGA-11M1DXC
 10 mL water
 15.5 mg hydrated RuCl₃
 81.6 mmoles HCO₂H
 added over first 182 min
 89 ± 1°C



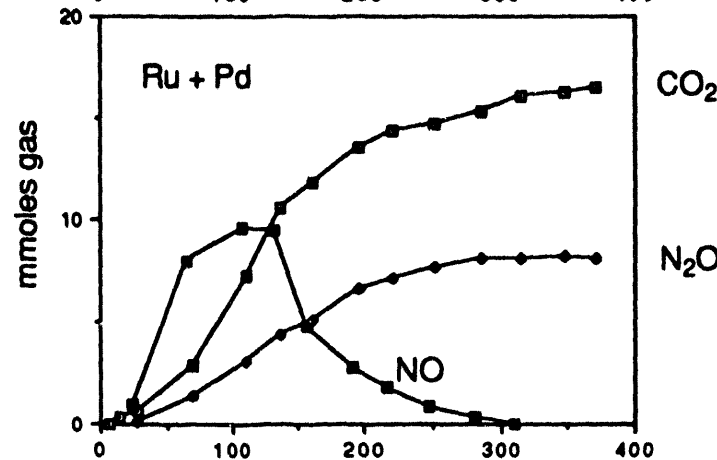
50 mL UGA-11M1DXC
 10 mL water
 13.5 mg PdCl₂
 72.7 mmoles HCO₂H
 added over first 162 min
 89 ± 1°C



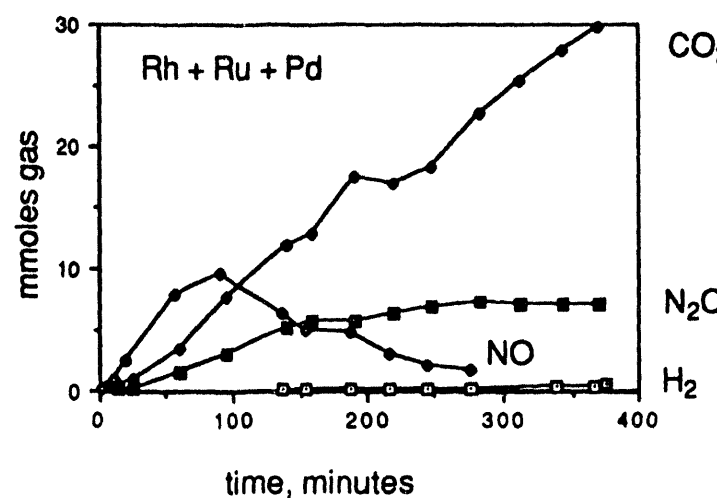
50 mL UGA-11M1DXC
 10 mL water
 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$
 15 mg hydrated RuCl_3
 72.4 mmoles of formic acid
 added over first 162 min
 $90 \pm 1^\circ\text{C}$



50 mL UGA-11M1DXC
 10 mL water
 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$
 14 mg PdCl_2
 72.4 mmoles of formic acid
 added over first 162 min
 $89 \pm 2^\circ\text{C}$



50 mL UGA-11M1DXC
 10 mL water
 13.8 mg hydrated RuCl_3
 14 mg PdCl_2
 72.4 mmoles of formic acid
 added over first 162 min
 $90 \pm 1^\circ\text{C}$



50 mL UGA-11M1DXC
 10 mL water
 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$
 14 mg hydrated RuCl_3
 13 mg PdCl_2
 72.7 mmoles of formic acid
 added over first 162 min
 $90 \pm 1^\circ\text{C}$

DATE

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