

# Noble metal-catalyzed homogeneous and heterogeneous processes in treating simulated nuclear waste media with formic acid

R.B. King<sup>a,\*</sup>, N.K. Bhattacharyya<sup>a</sup>, H.D. Smith<sup>b</sup>, K.D. Wiemers<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Georgia, Athens, GA 30602, USA

<sup>b</sup> Pacific Northwest Laboratory, Richland, WA 99352, USA

## Abstract

Simulants for the Hanford Waste Vitrification Plant feed containing the major non-radioactive components Al, Cd, Fe, Mn, Nd, Ni, Si, Zr, Na,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  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  $\text{CO}_2$ ,  $\text{H}_2$ , NO, and  $\text{N}_2\text{O}$  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  $\text{H}_2$ . 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  $\text{H}_2$  generation from formic acid above  $\sim 80^\circ\text{C}$  in the presence of nitrite ion. The  $\text{H}_2$  production rate has an approximate pseudo first-order dependence on the Rh concentration. (2) Generation of  $\text{NH}_3$  from the formic acid reduction of nitrate and/or nitrite is undesirable because of a possible explosion hazard from  $\text{NH}_4\text{NO}_3$  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  $\text{NH}_3$ . (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

## 1. 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  $\text{RuO}_4$ . [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 for-

\* Corresponding author.

mic acid into the melter feed. Formic acid is also found to decrease the melter feed viscosity thereby facilitating pumping.

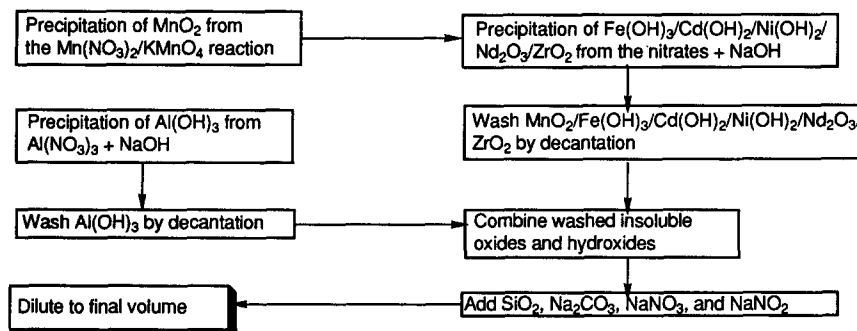
The use of formic acid to process nuclear wastes for vitrification plants can lead to two detrimental side reactions:

1. *Decomposition of formic acid into  $CO_2 + H_2$ :* The production of  $H_2$  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  $NH_3$  in nuclear waste vitrification plants is of concern because of the generation of a possible explosion hazard from  $NH_4NO_3$  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,  $CO_3^{2-}$ ,  $NO_3^-$ , and  $NO_2^-$ .

## 2. Experimental approach

Feed simulants were prepared on a 1-l scale from reagent grade chemicals using the protocol summarized in Fig. 1. The feed simulant contain-



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

Component	Molarity	Source	g/liter	Water solubility
Al	0.226	$Al(NO_3)_3 \cdot 9H_2O$	84.8 g	63.7 g/100 g @ 25°C
Cd	0.03	$Cd(NO_3)_2 \cdot 4H_2O$	9.2 g	215 g/100 g @ 25°C
Fe	0.45	$Fe(NO_3)_3 \cdot 9H_2O$	181.8 g	"soluble"
Mn	0.0314	$\begin{cases} KMnO_4 \\ Mn(NO_3)_2 \cdot 6H_2O \end{cases}$	$\begin{cases} 2.0 g \\ 5.4 g \end{cases}$	$\begin{cases} 6.38 g/100 g @ 20^\circ C \\ 426.4 g/100 g @ 0^\circ C \end{cases}$
Nd	0.0264	$Nd(NO_3)_3 \cdot 6H_2O$	11.6 g	152.9 g/100 g @ 25°C
Ni	0.0392	$Ni(NO_3)_2 \cdot 6H_2O$	11.6 g	238.5 g/100 g @ 0°C
Si	0.0854	$SiO_2$	5.1 g	insoluble
Zr	0.156	$ZrO(NO_3)_2 \cdot 6H_2O$	52.9 g	soluble
Na <sup>+</sup>	0.801	$Na_2CO_3 + NaNO_3 + NaNO_2$	see below	see below
$CO_3^{2-}$	0.125	$Na_2CO_3$	13.2 g	7.1 g/100 g @ 0°C
$NO_3^-$	0.116	$NaNO_3$	9.9 g	92.1 g/100 g @ 25°C
$NO_2^-$	0.435	$NaNO_2$	30.0 g	81.5 g/100 g @ 15°C

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

ing all 12 components listed in Fig. 1 is designated as UGA-12M1. Samples of these feed simulants (generally 40 to 50 ml) were treated with 88 wt.% 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  $0.0194 \pm 0.0002$  ml/min (1.164 ml/h) corresponding to 0.448 mmol HCO<sub>2</sub>H/min or 26.9 mmol HCO<sub>2</sub>H/h. The composition of the gas phase was analyzed periodically for H<sub>2</sub>, CO<sub>2</sub>, NO, and N<sub>2</sub>O using gas chromatography. The H<sub>2</sub> analyses were performed using a Varian 90P gas chromatograph with a 20 cm × 6 mm column packed with a 40/60 mesh 13 × molecular sieve material and argon as the carrier gas. The column temperature was maintained at 80°C. The CO, CO<sub>2</sub>, N<sub>2</sub>O, 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 × 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 NO<sub>2</sub> ⇌ N<sub>2</sub>O<sub>4</sub> equilibrium.

After the feed simulants had been treated with the formic acid, the resulting reaction mixture was analyzed for NH<sub>4</sub><sup>+</sup> produced by NO<sub>3</sub><sup>-</sup> or NO<sub>2</sub><sup>-</sup> 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<sub>4</sub><sup>+</sup> to NH<sub>3</sub>. The NH<sub>3</sub> concentration was then determined using a MI-740 microammonia electrode obtained from Microelectrodes, Inc., Londonderry, New Hampshire. This electrode is designed to measure NH<sub>3</sub> gas and to record the NH<sub>3</sub> concentration as millivolts on a standard pH meter; an Orion 290A port-

able 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<sub>4</sub>Cl solutions made basic with 10 N NaOH.

### 3. Results and discussion

#### 3.1. Decomposition of formic acid to CO<sub>2</sub> + H<sub>2</sub>

There is a strong precedent in the literature for the noble metal catalyzed decomposition of formic acid to H<sub>2</sub>. The earliest studies by Müller and Loerpabel [8] 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 Upadhye [9] on the catalytic decomposition of aqueous formic acid over Pd black, work by Aguilò [10] on the Pd(II)-catalyzed oxidation of formic acid in acetic acid solution, and work by Hill and Winterbottom [11] on the Pd-catalyzed decomposition of formic acid/sodium formate solutions. Soluble derivatives of other noble metals including Ru carbonyls [12] and the Rh phosphine complex Rh(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> (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 of nuclear waste simulants containing Ru, Rh, Pd, and Ag produced H<sub>2</sub> 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 studies [16] 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  $\text{NO}_2^-$ , were found to modify profoundly the catalytic activity of the noble metals of interest for formic acid decomposition. The most active catalyst precursor for  $\text{H}_2$  evolution from the sludge simulant was found to be  $\text{RhCl}_3$ , even though it was inactive as a catalyst precursor for  $\text{H}_2$  evolution from pure formic acid at the same temperature. Effects of changing the Rh source, Rh concentration,  $\text{NO}_2^-$  concentration, and temperature on the nitrite-promoted Rh-catalyzed formic acid decomposition in nuclear waste feed simulant media (Fig. 1) have been examined.

Fig. 2 illustrates a titration of 50 ml of the UGA-12M1 feed simulant with 88 wt.% formic acid at  $90^\circ\text{C}$  in the presence of 14 mg of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  as a soluble Rh catalyst precursor. Production of  $\text{H}_2$  began only after all of the  $\text{CO}_3^{2-}$  had been converted to  $\text{CO}_2$  and the  $\text{NO}_2^-$  to  $\text{NO}$  and  $\text{N}_2\text{O}$ . This immediately suggests that one method of limiting  $\text{H}_2$  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  $\text{CO}_3^{2-}$  to  $\text{CO}_2$  and the  $\text{NO}_2^-$  to  $\text{NO}$  and  $\text{N}_2\text{O}$ . A total of 1.3 mmol of  $\text{H}_2$  was produced in this experiment.

Insoluble Rh sources rather than soluble  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  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  $\text{Rh}_2\text{O}_3$  by coprecipitation in the iron fraction (Fig. 1) 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 mmol of formic acid at  $88 \pm 2^\circ\text{C}$  led to the production of a total of 1.4 mmol of  $\text{H}_2$  as compared with 1.3 mmol of  $\text{H}_2$  in a comparable experiment in which Rh was introduced as the soluble ' $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ '. 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

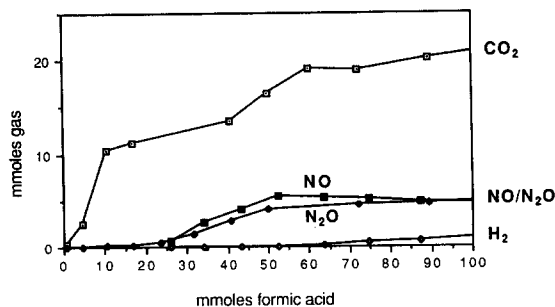
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  is added to the slurry immediately before the start of the experiment.

In the second method, Rh was introduced as a 5% dispersion of the metal supported on carbon or alumina using 0.1175 g of 5% Rh/C or 0.115 g of 5% Rh/ $\text{Al}_2\text{O}_3$ , 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 85 mmol of 88 wt.% formic acid at  $90^\circ\text{C}$  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  $\text{H}_2$  was produced (0.16 mmol and 0.28 mmol at the end of the experiments with 5% Rh/C and 5% Rh/ $\text{Al}_2\text{O}_3$ , respectively).
2. The initially produced  $\text{NO}$  but not the  $\text{N}_2\text{O}$  was almost entirely consumed during the course of the experiment. For example, a maximum of 9.29 mmol of  $\text{NO}$  was measured after 216 min but only 1.25 mmol of  $\text{NO}$  remained at the end of the experiment with 5% Rh/C.

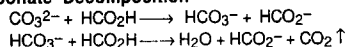
The drastically reduced production of  $\text{H}_2$  and the consumption of  $\text{NO}$  as the reaction proceeds suggests that Rh dispersed on carbon might be an active catalyst for the hydrogenation of  $\text{NO}$ . This is supported by the production of a relatively large amount of  $\text{CO}_2$  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  $91^\circ\text{C}$  with a total of 86 mmol of formic acid in the presence of amounts of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  ranging from 1.4 mg (0.0056 mmol) to 14 mg (0.056 mmol) in a detailed attempt to assess the minimum amount of Rh needed to catalyze  $\text{H}_2$  evolution from formic acid. Generation of  $\text{H}_2$  began to occur after sufficient formic acid has been added to deplete the  $\text{NO}_2^-$  and  $\text{CO}_3^{2-}$ . The maximum rate of  $\text{H}_2$  production was found to be pseudo first order in Rh concentration (moles per liter) according to the following equation:

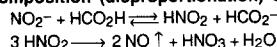


### Reactions Involved

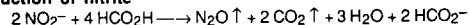
#### Carbonate Decomposition



#### Decomposition (disproportionation) of nitrous acid



#### Reduction of nitrite



#### Formic acid decomposition

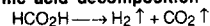


Fig. 2. Gas generation upon titration of 50 ml of the UGA-12M1 feed simulant with 88% formic acid at a rate of 0.0196 ml/min = 0.42 mmol/min in the presence of 14 mg of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and equations for the reactions involved.

### H<sub>2</sub> production (mmol/min)

$$= -0.92 + 8030[\text{Rh}] \quad R^2 = 0.952 \quad (1)$$

Since  $\text{NO}_2^-$  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  $\text{NO}_2^-$  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  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , 10 ml of water, and amounts of  $\text{NaNO}_2$  ranging from 0.6 g to 1.5 g in 0.3-g increments with 85 mmol of formic acid indicated that the rate of  $\text{H}_2$  production is relatively insensitive to  $\text{NO}_2^-$  concentration at relatively high  $\text{NO}_2^-$  concentrations. The expected production of NO and  $\text{N}_2\text{O}$  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  $\text{NaNO}_2$  used.

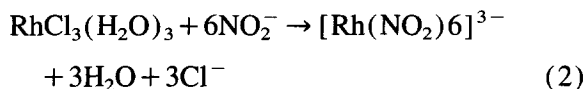
Another question of interest: what is the minimum amount of  $\text{NO}_2^-$  needed to promote this reaction? Accordingly, 50 ml of the nitrite-free and nitrate-free feed simulant UGA-10XNN/1 mixed with 10 ml of water and 0.5 g. (5.88 mmol) of  $\text{NaNO}_3$  was titrated at 90°C with 85 mmol of 88 wt.% formic acid in the presence of 14 mg of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (0.054 mmol) and varying amounts of  $\text{NaNO}_2$  ranging from 11.6 mg (0.17 mmol) to 0.5 g. (7.24 mmol). Considerable amounts of  $\text{H}_2$  were produced in all of these experiments, even in the experiment using only 11.6 mg  $\text{NaNO}_2$  (corresponding to a  $\text{NO}_2^-/\text{Rh}$  ratio of  $\sim 3$ ) in which  $\sim 4$  mmol of  $\text{H}_2$  was produced at the end of the experiment. This contrasts with the production of only 0.4 mmol of  $\text{H}_2$  at the end of an otherwise similar experiment in which no  $\text{NO}_2^-$  was added. This confirms that  $\text{NO}_2^-$  promotes the Rh-catalyzed decomposition of formic acid but that stoichiometric amounts of  $\text{NO}_2^-$  corresponding to formation of a trinitrorhodium derivative suffice for catalyst promotion.

The effect of temperature on the Rh-catalyzed  $\text{H}_2$  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  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (1.4 mg  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{ml}$ ) was titrated with a total of 85 mmol of formic acid. As expected, the rate of  $\text{H}_2$  production increases with increasing temperature with a  $\text{H}_2$  production rate of 0.29 mmol  $\text{H}_2/\text{min}/\text{l}$  feed simulant at 94°C. Hydrogen production at temperatures below  $\sim 85^\circ\text{C}$  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  $\text{H}_2$  production can be shut off at temperatures below  $\sim 75^\circ$ .

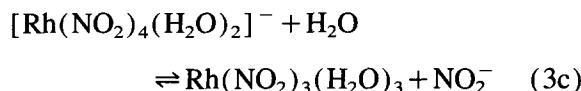
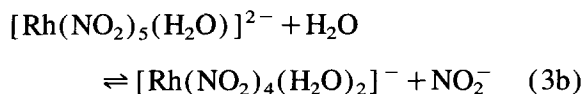
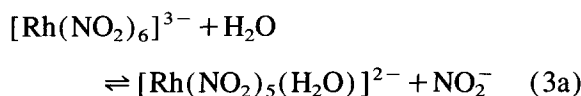
The role of  $\text{NO}_2^-$  ion as a promoter suggests the role of soluble nitrorhodium complexes as intermediates in the Rh-catalyzed decomposition of formic acid. In this connection,  $\text{RhCl}_3$  was reported more than a century ago [17] to react with excess  $\text{NO}_2^-$  in boiling water 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 oxidants [18] or sulfamic acid [19] 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.

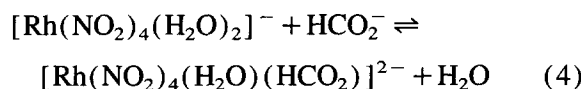
The reaction of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with  $\text{NO}_2^-$  to give  $[\text{Rh}(\text{NO}_2)_6]^{3-}$  can be summarized by the following equation:



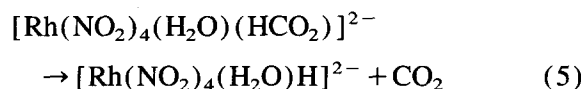
The lability of three of the six nitro groups in  $[\text{Rh}(\text{NO}_2)_6]^{3-}$  can be summarized by the following equations in which nitro groups are successively replaced by more labile aquo ligands:



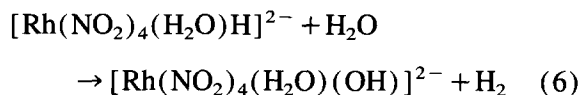
Formate can then displace the aquo ligands by reactions such as the following:



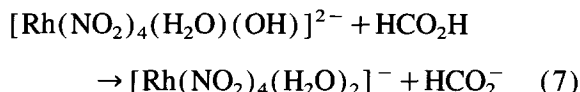
Coordinated formate can undergo a hydrogen shift from carbon to a vacant rhodium site with carbon dioxide evolution to generate a rhodium hydride according to the following equation:



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 Eqs. 4–7 is the observed formic acid decomposition



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

### 3.2. Generation of ammonia from the formic acid reduction of nitrate and/or nitrite

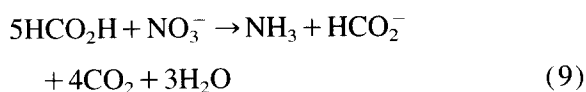
The  $\text{NH}_4^+$  concentrations produced by selected titrations of various nitrite and/or nitrate-containing feed simulants with 88 wt.% formic acid in the presence of various noble metals were determined by  $\text{NH}_3$  analyses as outlined above. The  $\text{NH}_3$  analyses were performed 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  $\text{NH}_3$  ( $> 1$  mmol) 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  $\text{CO}_2$  to arise solely from reactions of formic acid leading to  $\text{CO}_3^{2-}$  decomposition,  $\text{MnO}_2$  reduction to  $\text{Mn}^{2+}$ ,

Table 1  
Ammonia analyses on samples from selected titrations of feed simulants with formic acid

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

NO<sub>2</sub><sup>-</sup> reduction to N<sub>2</sub>O, and formic acid decomposition to H<sub>2</sub>. 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<sub>3</sub> by NO<sub>3</sub><sup>-</sup> reduction can convert four moles of formic acid to CO<sub>2</sub> 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 HCO<sub>2</sub>H=3.7) but in the range of the carbonic acid/bicarbonate buffer (pK<sub>1</sub> of H<sub>2</sub>CO<sub>3</sub>=6.4). Thus some of the CO<sub>2</sub> liberated by the formic acid forms HCO<sub>3</sub><sup>-</sup> and thus cannot be measured in the gas phase.

These preliminary observations suggest that NH<sub>3</sub> production by the Rh-catalyzed reduction of NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> 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<sub>3</sub>

and NO<sub>2</sub><sup>-</sup>) are much less active catalysts. Furthermore, Rh coprecipitated with the iron fraction in the feed simulant UGA-13+Rh1 as the hydrous oxide Rh<sub>2</sub>O<sub>3</sub> is not an active catalyst for NH<sub>3</sub> production even though the Rh<sub>2</sub>O<sub>3</sub> is presumably dispersed in the other insoluble metal hydrous oxides. Since NH<sub>3</sub> production appears to occur at the expense of H<sub>2</sub> production, we suspect that the supported Rh metal catalysts are functioning as hydrogenation catalysts for NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, 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<sub>3</sub>.

A question of considerable interest is whether NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> is the source of the NH<sub>3</sub> nitrogen. A feed simulant prepared according to the standard protocol but leaving out both NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> (UGA-10XNN'1) was titrated with formic acid in the presence of NaNO<sub>3</sub> as well as 5% Rh on charcoal. The amount of NH<sub>3</sub> produced in this experiment (1.6 mmol) was essentially identical to the amount of NH<sub>3</sub> produced in an experiment using the full feed simulant UGA-12M1 containing NO<sub>2</sub><sup>-</sup>. 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 wt.% formic acid at 90°C in the presence of  $NaNO_3$  gave negligible amounts of  $NH_3$  and 0.4 mmol 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 wt.% 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.

## Acknowledgements

We are indebted to the US Department of Energy for support of this work at the University of Georgia through the Westinghouse Hanford Corporation and the Pacific Northwest Laboratory. Pacific Northwest Laboratory is operated by the Battelle Memorial Institute for the Department of Energy under contract DE-AC06-76RLO1830.

## References

- [1] D.F. Bickford, C.J. Coleman, C.-L. W. Hsu, and R.E. Eibling, *Ceram. Trans., Nucl. Waste Management IV*, 23 (1991) 283.
- [2] D.F. Bickford, R.B. Diemre, Jr., and D.C. Iverson, *J. Non-Cryst. Solids*, 84 (1986) 285.
- [3] D.S. Goldman, *J. Non-Cryst. Solids*, 84 (1986) 276.
- [4] D.S. Goldman, D.W. Brite, and W.C. Richey, *J. Am. Ceram. Soc.*, 69 (1986) 413.
- [5] D.F. Bickford, P. Hrma, and B.W. Bowen, II, *J. Am. Ceram. Soc.*, 73 (1990) 2903.
- [6] D.S. Goldman and D.W. Brice, *J. Am. Ceram. Soc.*, 69 (1986) 411.
- [7] C. Lucktong and P. Hrma, *J. Am. Ceram. Soc.*, 71 (1988) 23.
- [8] E. Müller and W. Loerpabel, *Monatshefte*, 53/54 (1929) 825.
- [9] D.M. Ruthven and R.S. Upadhye, *J. Catal.*, 21 (1971) 39.
- [10] A. Aguilò, *J. Catal.*, 13 (1969) 283.
- [11] S.P. Hill and J.M. Winterbottom, *J. Chem. Tech. Biotechnol.*, 41 (1988) 121.
- [12] R.M. Laine, R.G. Rinker, and P.C. Ford, *J. Am. Chem. Soc.*, 99 (1977) 252.
- [13] S.H. Strauss, K.H. Whitmire, and D.F. Shriver, *J. Organomet. Chem.*, 174 (1979) C59.
- [14] K.D. Wiemers, results presented at the American Institute of Chemical Engineers National Meeting, Denver, CO, August, 1993.
- [15] R.B. King, A.D. King, Jr. and N.H. Bhattacharyya, results presented to the Division of Inorganic Chemistry at the Fall 1992 National Meeting of the American Chemical Society, Washington, D.C., August, 1992, abstract INOR 124.
- [16] R.B. King, A.D. King, Jr., N.K. Bhattacharyya, C.M. King and L.F. Landon, in *Chemical Pretreatment of Nuclear Waste for Disposal*, W.W. Schulz, E.P. Horwitz, Eds., Plenum, New York, 1994, p. 101–113.
- [17] E. Leidié, *Compt. Rend.*, 111 (1890) 106.
- [18] Yu. N. Kukushkin and O.V. Stefanova, *Russ. J. Inorg. Chem.*, 22 (1977) 1844.
- [19] N.V. Mel'chakova, G.P. Ozerova and V.M. Peshkova, *Russ. J. Inorg. Chem.*, 12 (1967) 577.
- [20] H.D. Smith, K.D. Wiemers, M.H. Langowski, J.D. Matheson, M.D. Merz, M. R. Powell and D.E. Larson, Report PNL-10369 from the Pacific Northwest Laboratory, November, 1994.