Efficient Catalytic Reduction of Concentrated Nitric Acid on the Adsorption Sites of Activated Carbon

Akane Miyazaki,* Kazumasa Shibazaki, Yoshio Nakano, Mitsuteru Ogawa, and Ioan Balint[†]
Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Technology,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8502
[†]*Institute of Physical Chemistry, Romanian Academy, Spl. Independentei 202, 77208 Bucharest, Romania*

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The adsorption sites of active carbon were found to promote efficiently the catalytic reduction of concentrated HNO_3 by HCOOH at low temperature.

Concentrated nitric acid is used intensively as a strong oxidizing medium in the nuclear fuel reprocessing technology. The nitric acid should be removed from radioactive wastes during the chemical separation, conversion steps as well as in waste disposal procedures.[1] The neutralization of HNO_3 with alkali is inconvenient because of the increase in the salt content in the waste water. One practical way is the chemical denitration by formic acid. This reaction is governed by a complex mechanism[2] and gives (excepting water) only gaseous products (CO_x and NO_x), which can be further removed from the system. One technical problem encountered is that the process of homogeneous denitration exhibits a relatively long induction period. The induction period is related to the formation of nitrous acid, which is one of the reaction intermediates. This period can be shortened by increasing the temperature of the reacting solution to the boiling point or, in a more efficient way, by using a catalyst. Platinum supported on SiO_2 was reported to promote the formation of HNO_2 and thus to decrease significantly the induction period.[3] The main disadvantage of using supported metal catalysts is the extensive metal leaching (and eventually support dissolution) in time due to the concentrated acid medium. Therefore, new catalytic materials that can minimize the induction period and at the same time withstand very acid medium should be developed.

The catalytic behavior of SiO_2 (Wako), active carbon (AC, Kureha), Pt/SiO_2 and Pt/AC for HNO_3/HCOOH reaction was investigated. The supported platinum materials were prepared by polyol method.[4] Firstly, SiO_2 or AC was added under stirring to a 1 mM ethylene glycol solution of K_2PtCl_4 (Wako). Then the homogeneous suspension was heated to 453 K for 1 h in order to allow the reduction of platinum precursor on the surface of SiO_2 or AC. The materials obtained were collected by filtration, dried, and finally treated with H_2 at 773 K for 1 h. The typical platinum loading was 0.5 wt %. The average diameter, determined by TEM and H_2 chemisorption, was ca. 50 nm, regardless the support (AC or SiO_2).

Denitration was conducted at 323 K in a glass reactor. Prior to the addition of formic acid, the solid materials were suspended in the HNO_3 solution. The initial concentration of the reactants was 3 N HNO_3 and 1 N HCOOH. The total volume of the reacting solution was 207.91 mL and the amount of the solid added was 2.0 g. The reactor was purged with Ar gas (10.0 mL/min). The gaseous reaction products (NO, NO_2, N_2O, N_2, CO, CO_2) were analyzed by a gas chromatograph equipped with TCD detectors. The composition of liquid phase was also monitored periodically by sampling aliquots of 1 mL. The concentration of HNO_2 was measured spectrophotometrically by using Griess reagent. The concentrations of HNO_3 and HCOOH were obtained by titration with a 0.4 N NaOH solution.

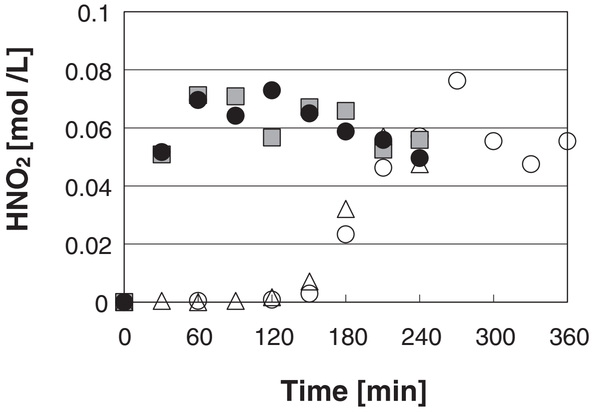

Figure 1. The time course of HNO_2 concentration in the absence of solid (○) and in the presence of 2 g of Pt/AC(●), AC(■) or Pt/SiO_2(△).

Figure 1 shows the effect of different solid materials, i.e., Pt/AC, Pt/SiO_2, and AC, on the formation of HNO_2. The monitoring of HNO_2 formation is important because the reductant (HCOOH) does not react directly with HNO_3 but with HNO_2.[3] Interestingly, Pt/SiO_2 did not show any significant catalytic activity for HNO_2 formation. The induction period was insensitive to the presence of Pt/SiO_2 in the reacting system. Apparently, the denitration catalytic activity reported by Guenais–Langlois et al.[3] for 0.6 wt % Pt/SiO_2 can be attributed to the smaller Pt particle size of their catalyst (1–2 nm) as compared with ours (50 nm). On the other hand, both of Pt/AC and AC showed similar catalytic activity for HNO_2 generation. The induction period was practically suppressed and the HNO_2 profiles were almost identical. The question arising from here is if really the supported Pt particles have catalytic activity for HNO_2 formation. The similar behavior of AC and Pt/AC as well as the absence of any catalytic activity for Pt/SiO_2 strongly suggests that the catalytic role of the supported large Pt nanoparticles (around 50 nm) for HNO_2 formation is minor. Since the surface area of AC and SiO_2 were close to each other (943 and 842 m^2/g, respectively) it comes out that what plays a key factor is not the physical surface itself but the nature of adsorption sites.

The effect of the concentration of the AC adsorption sites on

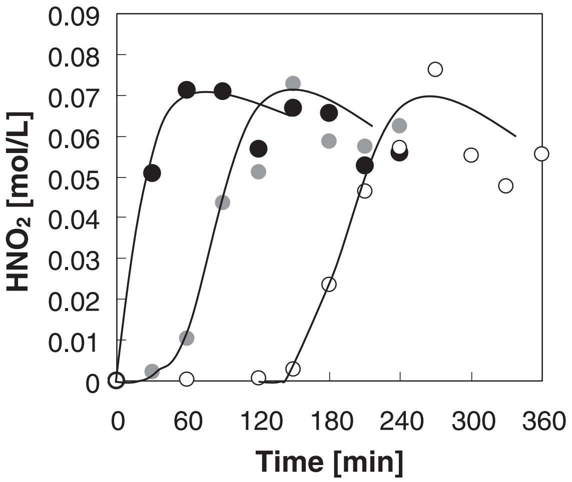

Figure 2. The time course of HNO_2 formation as a function of AC amount suspended in 200 mL of reacting solution. 2.0 g (●), 0.020 g (◍), and 0.0 g (blank experiment) (○).

the formation of HNO_2 is presented in Figure 2. It can be observed that the induction period for HNO_2 formation decreased gradually with increasing the amount of AC in reacting suspension. After the induction period, which was related to the AC amount, the rate of HNO_2 formation and the maximum concentration of HNO_2 (ca. $7.2 \cdot 10^{-2}$ mol/L) were independent of the AC concentration. The HNO_2 formation rate measured for 2.0, 0.020, and 0.0 g of AC were $1.3 \cdot 10^{-3}$, $0.7 \cdot 10^{-3}$, and $0.7 \cdot 10^{-3}$ [mol/L/s], respectively. The experimental data show that the adsorption sites of AC promote the rapid formation of HNO_2, up 0.005 mol/L. Once the reaction is triggered by the fast formation of HNO_2, the reaction develops autocatalytically and AC does not behave as catalyst any more. Thus, the function of the AC is to enhance the formation of HNO_2 up to a threshold value. The effect of AC observed here is exactly same to what has been reported for precious metals.[2,3]

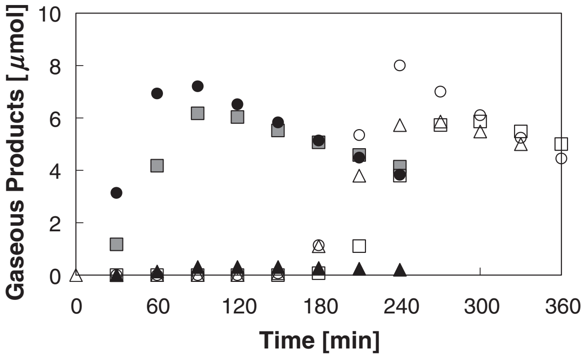

Figure 3. The time course of the reaction products formation during denitration process. CO_2 (●, ○), NO + NO_2 (■, □), and N_2O (▲, △) were measured. The closed symbols represent the experiments with AC whereas the open symbols represent the blank experiments.

The formation of gaseous reaction products (NO, N_2O, NO_2, and CO_2) in the presence or absence (blank experiment) of AC is comparatively presented in Figure 3. The formation of N_2 and CO during denitration reaction was not evidenced. From Figure 3 it comes out that the reaction mechanism is independent on the presence or absence of AC, because the profile of reaction products is similar in both cases. From analysis of the experimental data depicted in Figures 2 and 3, three stages of the chemical denitration by formic acid can be identified. In the first stage, called induction period, the concentration of HNO_2 increase up to ca. 0.005 mol/L. In the second stage the concentration of HNO_2 increases fast as a result of an autocatalytic generation of HNO_2, with a rate of around $0.9 \cdot 10^{-3}$ mol/L/s, until a threshold value of ca. 0.07 mol/L is reached. Then, in the third stage, the effective denitration starts by the formation of gaseous reaction products (NO, N_2O, NO_2, and CO_2). The surface of AC has a catalytic effect only in the first stage of denitration process by increasing the initial rate of HNO_2 formation. In the absence of AC, the low temperature denitration (i.e. 325 K) requires an induction period as long as 240 min. On the other hand, the addition of AC (i.e. 10 g/L) suppresses practically the induction period.

The relationship between the decrease of the HCOOH concentration in the reacting solution and CO_2 formation is not affected by the presence of AC. The amount of formed CO_2 is significantly smaller than HCOOH consumption. It can be also observed that the amounts of reacted HCOOH and corresponding CO_2 are not related to the presence of AC. In other words, the carbon balance is not affected by the presence of AC. From here it is clear that the AC itself is not involved as a reactant in the formation of CO_2. At present, it is not clear the reason for the difference observed between carbon consumption and release.

As a conclusion, AC was found to be an effective catalyst for denitration of concentrated HNO_3 by HCOOH at low temperature (325 K). This catalytic effect was attributed to rapid formation of HNO_2 on the adsorption site of AC. The delay in HNO_2 formation was found to be dependent on the concentration of the AC adsorption sites. AC promotes the fast formation of HNO_2. The catalytic reduction on the adsorption sites on the surface of AC is significantly different from the redox-type mechanism proposed for the surface of Pt.[3] However, our experimental results cannot rule out completely the possibility that the redox-type mechanism becomes a predominant reaction route for long reacting time (i.e. >240 min). It is obvious that using AC has several advantages as a catalyst when compared to supported precious metal catalysts. It is inexpensive and the problem of metal dissolution is solved. The denitration system based on AC should be further improved to decrease the maximum concentration level of HNO_2, and thus to completely exclude the hazard of explosions.

References

1 E. R. Merz, "Denitration of Radioactive Liquid Waste," Graham & Helaszovich, London (1986), p 1.
2 J. C. Fanning, *Coord. Chem. Rev.*, **199**, 159 (2000).
3 S. Guenais-Langlois, C. Bouyer, J. C. Boudie, and B. Coq, *Appl. Catal., B*, **27**, 199 (2000).
4 A. Miyazaki, I. Balint, K. Aika, and Y. Nakno, *J. Catal.*, **204**, 364 (2001).

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