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Purification of CO Based on Selenium–Amine–CO Chemistry

Shinji TSUNOI, Noritaka MIYOSHI, Akiya OGAWA, Nobuaki KAMBE, and Noboru SONODA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

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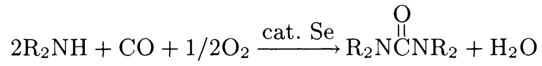
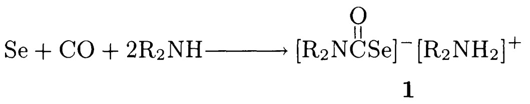
Efficient separation of carbon monoxide from a binary mixture of carbon monoxide and hydrogen with selenium and secondary amines has been developed. The process consists of (i) selective reaction of CO with selenium and a secondary amine to form the corresponding ammonium carbamoselenoate **1** and (ii) thermolysis of **1** to form pure CO (99.9%) quantitatively. A Se–alcohol system is also usable but the results are inferior to that with a Se–amine system.

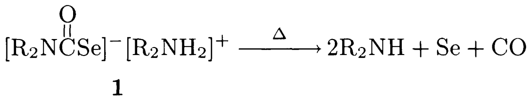
About two decades ago, we reported the first example of non-transition-metal-catalyzed carbonylation of amines to give ureas, in which elemental selenium was used as a catalyst (Eq. 1).[1)] Since then, carbonylation using a Se–CO system was extended to synthesis of a variety of carbonyl compounds, including carbamates, carbonates, and carbamothioates.[2)] The first key step of amine carbonylation may be formation of the ammonium carbamoselenoate **1**[3)] (Eq. 2), which would then undergo aminolysis to produce urea. The catalyst selenium is regenerated efficiently by the introduction of molecular oxygen into the reaction system, which allows the catalytic cycle shown in Scheme 1.[3)]



$$2R_2NH + CO + 1/2O_2 \xrightarrow{\text{cat. Se}} R_2N\overset{O}{\overset{\|}{C}}NR_2 + H_2O \qquad (1)$$



$$Se + CO + 2R_2NH \longrightarrow \underset{\mathbf{1}}{[R_2N\overset{O}{\overset{\|}{C}}Se]^-[R_2NH_2]^+} \qquad (2)$$



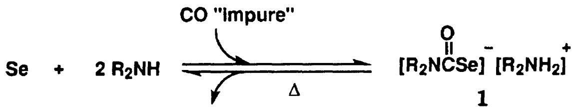
$$\underset{\mathbf{1}}{[R_2N\overset{O}{\overset{\|}{C}}Se]^-[R_2NH_2]^+} \xrightarrow{\Delta} 2R_2NH + Se + CO \qquad (3)$$

Under certain mild conditions, however, some *secondary* amines can form stable carbamoselenoates **1**, even in the presence of excess amines. We found also that carbamoselenoates **1**, when heated, decomposed to produce selenium, CO, and amines (Eq. 3). These two findings, the formation of **1** stable enough to handle under nitrogen and the thermal decomposition of **1**, are the basis of this study, which deals with a new method for purification of CO from a gas mixture of CO and H_2.[4)]

The growing importance of C1 chemistry requires efficient methods for the separation of CO from gas mixtures including synthesis gas (CO, H_2), blast furnace gas (CO, H_2, CO_2, N_2, etc.), and coke-oven gas (CO, H_2, CO_2, N_2, CH_4, etc.). The most commonly used method for the separation of CO from a gas mixture are the copper liquor method and the cryogenic separation method.[5—7)]. Recently, several processes that use Cu(I)-based solid-state adsorbents have been developed.[8—11)]. Our idea to develop a method for CO separation is based on a reversible system of ammonium carbamoselenoates **1** (Eqs. 2 and 3), in which **1** would operate as a "pure CO stock".

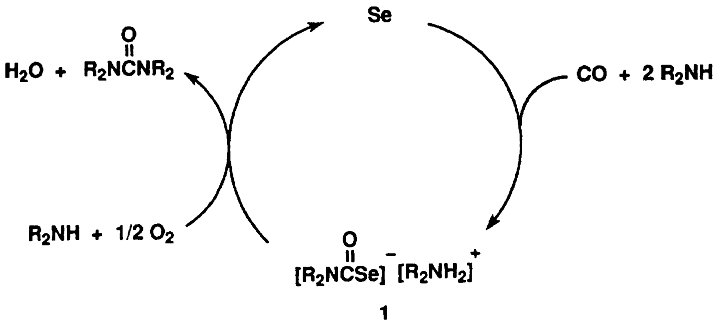
Results and Discussion

A homogeneous amine solution of **1b** (R=*n*-Pr) was prepared from selenium (2.40 g, 30 mmol) and excess dipropylamine (150 mmol, 20.6 mL) under atmospheric pressure of CO at 25 °C for 18 h. When this solution was heated, vigorous decomposition of **1b** was observed at 96—98 °C, with release of CO gas and a stoichiometric amount of elemental selenium (Eq. 4). Similarly, diethylamine, diisopropylamine, and dibutylamine were converted to **1a** (R=Et), **1c** (R=*i*-Pr), and **1d** (R=*n*-Bu), respectively. These salts were decomposed efficiently with liberation of CO at 86—89 °C, 57—59 °C, and 93—95 °C, respectively. These results, together with **1** not decomposing at room temperature, suggest that the negative value of the entropy change (ΔS) of Eq. 4 is sufficient, as expected from the stoichiometry, and that, upon heating of the reaction mixture, the equilibrium shifts to the left because $\Delta G\,(=\Delta H - T\Delta S)$ becomes positive. This is an important feature of this separation system for CO.

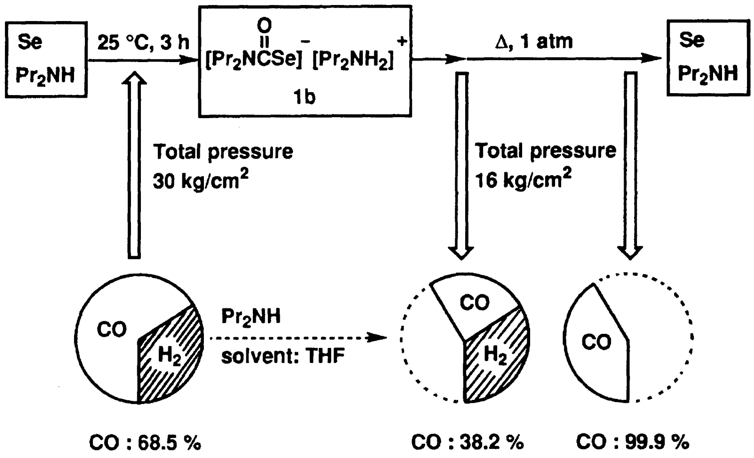


(4)

These preliminary results led us to attempt separation of CO from a binary mixture of CO and H_2, whose composition is similar to that of synthesis gas. A typical experiment was as follows. In a stainless-steel autoclave were placed selenium (30 mmol, 2.40 g) and dipropylamine (150 mml, 20.6 mL). Then the autoclave was charged with a binary mixture 20.6 kg cm^{-2} (44.8 mmol) CO and 9.4 kg cm^{-2} (20.6 mmol) H_2. After stirring of the mixture at 25 °C for 3 h, the autoclave was depressurized. After the gas remaining in the autoclave was evacuated under reduced pressure, the remaining solution was heated. At 120 °C (bath temperature), gas was evolved for about 2 h. The gas was collected into a balloon and analyzed by GC, which showed that 32.2 mmol of CO was released by thermolysis. The yield



Scheme 1.



Scheme 2.

of purified CO was quantitative (selenium basis), and the purity was 99.9% by GC analysis (Scheme 2).

The results with several amines are summarized in Table 1. With secondary amines, the purity of the CO reproduced was more than 99.9% and selenium and amines were reproduced almost quantitatively. Diisopropylamine gave inferior results compared with other secondary amines, probably because of the slow formation of **1c** due to steric effects (Run 6). When primary amines were used, **1** underwent aminolysis to give the corresponding urea (Runs 9 and 10). Aprotic solvents such as toluene, xylene, and 1,4-dioxane also could be used (Runs 2—4). The mixture of selenium and dipropylamine could be used repeatedly (yields of recovered CO: 97% (1st), 95% (2nd), 99% (3rd)). The CO purity was always >99.9%.

The results with a variety of gas mixtures are summarized in Table 2. Except for a gas mixture containing CO_2, which can react with amines, the results were always satisfactory. When selenium was used in an excess amount relative to CO, the CO in the feed gas was completely absorbed (selenium 30 mmol, dipropylamine 150 mmol, CO 10.3 $\mathrm{kg\,cm^{-2}}$ (23.5 mmol), H_2 4.7 $\mathrm{kg\,cm^{-2}}$, 25 °C, 4 d). The gas remaining consisted of >99.9% H_2, and the purity of the CO produced after thermolysis was >99.9%. Thus, synthesis gas of CO and H_2 only could be separated completely.

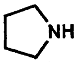
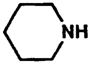
The Se-alcohol system was examined for CO separation also. Triethylamine was used to obtain the key intermediate, ammonium salt of carbonoselenoate ester **2** (Eq. 5). Thermolysis of **2** gave CO, selenium, and alcohol quantitatively (Eq. 6). The variable results of CO purification are shown in Table 3. Except for methanol (Run 1), less CO was absorbed than the amount of selenium used; this result reflects the variable efficiency of the formation of **2**. At this stage, Se–alcohol systems are inferior to Se–amine systems and improvement of reaction conditions is needed for the effective generation of **2**.

$$\mathrm{Se} + \mathrm{CO} + \mathrm{ROH} \xrightarrow{\text{base}} \underset{\mathbf{2}}{[\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{SeH}]} \tag{5}$$

$$\underset{\mathbf{2}}{[\mathrm{RO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{SeH}]} \xrightarrow{\Delta} \mathrm{Se} + \mathrm{CO} + \mathrm{ROH} \tag{6}$$

In conclusion, efficient separation of carbon monoxide was possible with selenium and secondary amine. This separation method is unusual in that it is based on the chemical reaction of CO. The process uses conventional conditions in comparison with the cryogenic process, which requires cooling to −200 °C. The yield and purity of CO are high. Gas containing CO_2 could not be treated by this method.

Table 1. Separation of CO by Se–Amine Reaction System[a)]

Run	Amine	Thermolysis temp[b)]/°C	CO Recovered[c,d)]/%	CO Purity[d)]/%	Selenium recovered/%
1	Pr_2NH	115	100	99.9	99
2[e)]			100	99.9	92
3[f)]			98	99.7	94
4[g)]			100	99.9	98
5	n-Bu_2NH	110	94	99.9	97
6	i-Pr_2NH	120	24	99.9	96
7		150	83[h)]	99.9	99
8		140	76[h)]	99.9	94
9	n-Bu_2NH_2	150	0[h)]	—	98
10	n-$C_8H_{17}NH_2$	150	0[h)]	—	91

a) Selenium (30 mmol), amine (150 mmol): (Runs 1, 5—10), selenium (10 mmol), amine (50 mmol), solvent 15 mL: (Runs 2—4), CO 20.6 kg cm^{-2}, H_2 9.4 kg cm^{-2}, 25°C, 3 h. Thermolysis was performed by heating the resulting solution gradually up to the indicated temperatures. b) Bath temp. c) Analyzed by GC (molecular sieves 5A, 2.9 m, 100 °C) d) Based on selenium used. e) Toluene was used as solvent. f) Xylene was used as solvent. g) 1,4-Dioxane was used as solvent. h) Ureas (Run 7: 5 mmol, Run 8: 6.5 mmol, Run 9: 29.4 mmol, Run 10: 15.5 mmol) were isolated.

Table 2. Separation of CO from the Various Gas Mixtures[a)]

Run	Feed gas	CO Recovered[b,c)]/%	CO Purity[c)]/%	Selenium recovered/%
1	CO–N_2	100	99.9	99
2	CO–CH_4	100	99.6[g)]	98
3	CO–CO_2[d)]	100	78.1[h)]	99
4	CO–H_2–H_2O[e)]	100	99.9	99
5	CO–H_2–H_2O[f)]	100	99.9	99

a) Selenium (30 mmol), dipropylamine (150 mmol), feed gas 30 kg cm^{-2} (N_2=14.5%, CH_4=17.4%, CO_2=16%, H_2=31.7%), 25 °C, 3 h. Thermolysis was performed by heating the resulting solution gradually up to 120 °C (bath temp). b) Analyzed by GC (molecular sieves 5A, 2.9 m, 100 °C). c) Based on selenium used. d) CO_2 was analyzed by GC (Porapak Q, 3 m, 100 °C) e) H_2O (1 mmol) was added. f) H_2O (2 mmol) was added. g) CH_4 (0.4%) was contained. h) CO_2 (21.8%) was contained.

Experimental

General Comments. Amines were purified by distillation from KOH. Alcohols were purified by distillation from CaH_2. The gas was analyzed by GC (molecular sieves 5A, 2.9 m, 100 °C: N_2, CH_4, CO, and H_2; Porapak Q, 3 m, 100 °C: CO_2).

Synthesis and Thermolysis of Ammonium Carbamoselenoates (1b). General Procedure: Metallic selenium (2.40 g, 30 mmol) and dipropylanime (150 mmol, 20.6 mL) were stirred under atmospheric pressure of CO at 25 °C. By 18 h, a homogeneous amine solution of **1b** had formed. When this solution was heated slowly, rapid gas evolution with vigorous bubbling was observed at 96—98 °C (solution temp). The gas was found to be CO by GC analysis. After the thermolysis, 2.21 g of selenium was recovered.

Separation of CO from a Mixture of CO and H_2 by the Se–Amine System. General Procedure: In a stainless-steel autoclave equipped with a glass liner were placed selenium (30 mmol, 2.40 g) and dipropylamine (150 mmol, 20.6 mL). The autoclave was charged with a binary mixture (30 kg cm^{-2}) at 25 °C of 20.6 kg cm^{-2} (44.8 mmol) CO and 9.4 kg cm^{-2} (20.6 mmol) H_2. After stirring of the reaction mixture at 25 °C for 3 h, the autoclave was depressurized and the gas inside was trapped in a balloon. GC of the gas showed that it contained 13.1 mmol of CO and 21.2 mmol of H_2. Then the gas remaining in the autoclave was evacuated under reduced pressure through a glass finger attached to the top of the autoclave to avoid contamination. The remaining solution was heated gradually and kept at 120 °C (bath temp.) for about 2 h until gas evolution ceased. The gas that evolved was collected through a cold trap into a balloon and analyzed by GC, which showed that 32.2 mmol of carbon monoxide with a purity of 99.9% was released by the thermolysis (the amount was stoichiometric for the amount of selenium used).

Separation of a Mixture of CO and H_2 by the Se–

Table 3. Separation of CO by Se–Alcohol Reaction System[a)]

Run	Alcohol	Reaction time/h	Thermolysis temp[b)]/°C	CO Recovered[c),d)]/%	CO Purity[d)]/%	Selenium recovered/%
1	MeOH	8	70	88	99.9	96
2	EtOH	5	90	35	99.9	98
3	PrOH	4	110	19	99.9	96
4	*i*-PrOH	6	90	8	99.9	99
5	*n*-BuOH	4	120	13	99.9	98
6	*t*-BuOH	4	90	3	99.9	99

a) Selenium (30 mmol), alcohol (15 mL), Et_3N (45 mmol), CO 20.2 $kg\,cm^{-2}$, H_2 9.8 $kg\,cm^{-2}$, 25 °C, 4—8 h. Thermolysis was performed by heating the resulting solution gradually up to the indicated temperatures. b) Bath temp. c) Analyzed by GC (molecular sieves 5A, 2.9 m, 100 °C). d) Based on selenium used.

Amine System. In a stainless-steel autoclave equipped with a glass liner were placed selenium (30 mmol, 2.40 g) and dipropylamine (150 mmol, 20.6 mL). The autoclave was charged with a binary mixture (15 $kg\,cm^{-2}$) at 25 °C of 10.3 $kg\,cm^{-2}$ (23.5 mmol) CO and 4.7 $kg\,cm^{-2}$ (10.3 mmol) H_2. After the solution was stirred at 25 °C for 4 d, the autoclave was depressurized and the gas inside was trapped in a balloon. GC of the gas showed that it contained 10.3 mmol of H_2 with a purity of 99.9%. Then the gas remaining in the autoclave was evacuated under reduced pressure through a glass finger attached to the top of the autoclave to avoid contamination. The remaining solution was heated gradually and kept at 120 °C (bath temp) for about 2 h until the gas evolution ceased. The gas that evolved was collected through a cold trap into a balloon and analyzed by GC, which showed that 23.2 mmol of carbon monoxide with a purity of 99.9% was released by the thermolysis.

Separation of CO from a Mixture of CO and H_2 by the Se–Alcohol System. A General Procedure: In a stainless-steel autoclave equipped with a glass liner were placed selenium (30 mmol, 2.40 g), methanol (15 mL), and triethylamine (45 mmol, 6.3 mL). The autoclave was charged with a binary mixture (30 $kg\,cm^{-2}$) at 25 °C of 20.2 $kg\,cm^{-2}$ (44.0 mmol) CO and 9.8 $kg\,cm^{-2}$ (21.4 mmol) H_2. After the solution was stirred at 25 °C for 8 h, the autoclave was depressurized and the gas inside was trapped in a balloon. GC of the gas showed that it contained 14.1 mmol of CO and 21.1 mmol of H_2. Then the gas remaining in the autoclave was evacuated under reduced pressure through a glass finger attached to the top of the autoclave to avoid contamination. The remaining solution was then heated gradually and kept at 70 °C (bath temp) for about 1 h until the gas evolution ceased. The gas that evolved was collected through a cold trap into a balloon and analyzed by GC, which showed that 26.4 mmol (88%) of carbon monoxide with a purity of 99.9% was released by the thermolysis.

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