Exclusion of CO and CO$_2$ from ammonia synthesis gas by an electrocatalytic process

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A new exclusion process for CO and CO$_2$ from ammonia synthesis gas has been proposed: this takes place at room temperature and atmospheric pressure. The process is based on the electrochemical reduction of CO and CO$_2$ to methanol proceeding at a mediated electrode via homogeneous catalysis. The maximum percentages of CO and CO$_2$ excluded from the initial gas were about 1.5 and 4.1%, respectively, with a mediated electrode of 82.8 cm^2 area in a reaction time of 5 h. The amount of excluded CO and CO$_2$ was equivalent to the sum of moles of methanol formed and gases dissolved into the solution alone. The electroreduction of CO and CO$_2$ was more efficient at three-phase (electrode/solution/gas) and at two-phase (electrode/solution) interfaces, respectively.

1. Introduction

Ammonia is one of the most important inorganic chemicals, and the process used most widely for its manufacture is the Haber process. The theoretical conversion of this reaction is high, but the yield is very low at room temperature. Hence, the reaction is generally assisted by heterogeneous catalysis in which the typical catalyst is an iron-based oxide. The production of ammonia requires hydrogen and nitrogen in the ratio of 3:1. In practice, the hydrogen is supplied from synthesis gas, which is produced by steam reforming and partial oxidation of the materials containing carbon and hydrogen such as methane or coal [1]. These processes are attended by the inevitable mixing of CO and CO$_2$ in the ammonia synthesis gas, and these gases need removing from the reaction system. The exclusion of CO and CO$_2$ involves the following processes in practice: (i) CO is converted to CO$_2$ by the shift reaction at typical temperatures of 400 to 500° C over a chromium-doped iron oxide; (ii) CO$_2$ is absorbed into an absorbant such as monoethanolamine (15 to 30%) and ammonia (4 to 7%) solutions under pressure; (iii) the remaining CO and CO$_2$ are further eliminated by the methanation reaction at 300 to 400° C over a Ni-based catalyst. Simplification of these processes and mitigation of the severe reaction conditions are required for the supply of cheaper ammonia.

In the present paper, the exclusion of CO and CO$_2$ from ammonia synthesis gas was investigated, based on a new principle. The proposed exclusion process is based on the electrochemical conversion of CO and CO$_2$ which takes place at a mediated electrode via homogeneous catalysis [2–4]. The scheme of this process is shown in Fig. 1, where M represents the homogeneous catalyst, and X and Y are the reduced and oxidized forms, respectively, of the mediator immobilized on the electrode. CO$_2$ (or CO) is first captured by the homogeneous catalyst to form the electroactive intermediate, M–CO$_2$ (M–CO), and this species is reduced by reaction with the reduced form (Y) of the mediator. The generation of the active mediator (X) is electrochemically activated. CO and CO$_2$ were simultaneously excluded from ammonia synthesis gas by such an electrocatalytic process.

2. Experimental

The ammonia synthesis gas was supplied by Mitsui Toatsu Chemicals, and the gas composition is given in Table 1. The apparatus used in this experiment is shown schematically in Fig. 2. The electrolytic cell used was a conventional H-type, and cathode and anode compartments were separated by a cation exchange membrane (Asahi Garasu Semion CMG 10). In some experiments, CO$_2$ was eliminated from the ammonia synthesis gas using a CO$_2$-absorbant before entry to the reaction cell. The CO$_2$-absorbant used was 4.5 mol dm^{-3} KOH solution, and the content of CO$_2$ in the pretreated ammonia synthesis gas was reduced to less than 0.01%. The effluent gas from the cathode compartment was circulated by means of a pump. The total pressure of the reaction system was kept at atmospheric pressure by controlling the level of the NaCl saturated solution in the pressure adjusting tank.

The mediator immobilized on the electrode was Everitt's salt (ES) which is in the reduced form of Prussian Blue. The ES film was prepared by the electroreduction of the PB film deposited on the electrode of 82.8 cm^2 area from an aqueous ferric ferricyanide solution [5]. The average amount of the ES film was about 2.8 × 10^{-7} mol cm^{-2} as measured by coulometry. The mediator–solution interface was built up in two different ways: the mediated electrode was completely submerged (two-phase) and partially immersed (three-phase) in the catholyte, since the
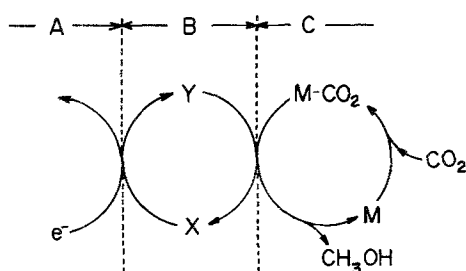
Fig. 1. Schematic representation of the electrode/mediator/ homogeneous catalysis system for the reduction of CO_2 (or CO). A: electrode; B: surface-confined mediator; C: homogeneous catalysts.

Table 1. Ammonia synthesis gases (*vol%*)

H_2	59.9
N_2	23.5
CO	11.4
CO_2	10.6
CH_4	0.4
Air	0.3

reduction of CO at the three-phase interface is considerably enhanced [6]. In the two-phase and three-phase experiments, the reaction gas was bubbled in and admitted only above the electrode, respectively. The catholyte was a catalyst solution prepared by dissolving a metal complex and methanol in 0.1 M KCl solution, the pH being adjusted to 2.0 by addition of H_2SO_4. The metal complex used was 1-nitroso-2-naphthol-3,6-disulphonatocobalt(II), [Co^{II} {$C_{10}H_4$ (NO) (OH) $(SO_3)_2$}$_2$]. The catalyst solution (0.2 dm³) was transferred to the cathode compartment. The anode (0.22 dm³) was N_2-saturated 0.1 M K_2SO_4 solution of pH 2. A bright platinum plate was used as the counter electrode, and the reference was a saturated calomel electrode. The electrochemical experiments were performed with a potentiostat (Nichia, NP-G 1000) and a coulometer (Nichia, N-CR 564).
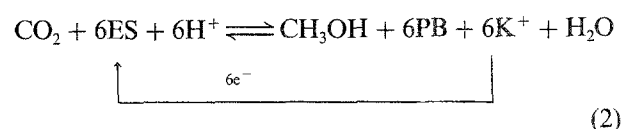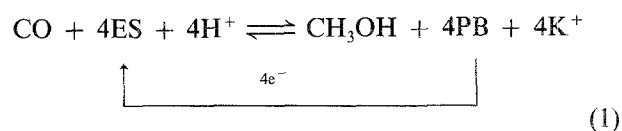
The amount of methanol produced was determined using a JGC-1100 gas chromatograph with a thermal-conductivity detector and a Porapak Q column. The sampling for the gas chromatograph was conducted as follows: 2.5 cm³ of the sample solution was transferred to a cell connected to vacuum through a stopcock. A side-port of the cell was fitted with a rubber septum in order to withdraw samples, and the solution was evaporated under 1 torr pressure at 70° C. After nitrogen gas was admitted to the cell, gas samples (2 cm³) were taken with a syringe. The amount of methanol which moved through the cation exchange membrane to the anode compartment was determined using an Ohkura model SSC-1 steam chromatograph with steam as the carried gas, a flame ionization detector and a Porapak R column.

3. Results and discussion

The electrocatalytic reduction of CO and CO_2 developed in our laboratory are given by the following reactions [7]

$$CO + 4ES + 4H^+ \rightleftharpoons CH_3OH + 4PB + 4K^+$$

$$\qquad \underset{4e^-}{\overline{\underline{\qquad\qquad\qquad\qquad\qquad}}} \tag{1}$$

$$CO_2 + 6ES + 6H^+ \rightleftharpoons CH_3OH + 6PB + 6K^+ + H_2O$$

$$\qquad \underset{6e^-}{\overline{\underline{\qquad\qquad\qquad\qquad\qquad}}} \tag{2}$$

The reduction of CO and CO_2 naturally terminates when the oxidation of ES to PB reaches an equilibrium, and hence the re-reduction of PB to ES with an external energy source is required to achieve continuous reduction of CO and CO_2. Furthermore, it is essential to achieve Reactions 1 and 2 with a homogeneous catalyst consisting of a metal complex and methanol. In the process, product methanol is used as one of the homogeneous catalysts and, to demonstrate the reduction of CO and CO_2 to methanol, various experiments were performed [4, 7], for example: the electrocatalytic reduction of $^{13}CO_2$ and ^{13}CO in the presence of a metal complex and $^{12}CH_3OH$ led to the formation of $^{13}CH_3OH$; the reduction of $^{12}CO_2$ and ^{12}CO in D_2O solution (pH adjusted by DCl) containing the same catalyst gave CD_3OD; ^{13}C-NMR spectra of the $^{13}CO_2$- and ^{13}CO-saturated solutions electrolysed at a given potential indicated the formation of $^{13}CH_3OH$ and methylformate as an intermediate. The entire mechanism proposed is given for the reduction of CO in Scheme I:
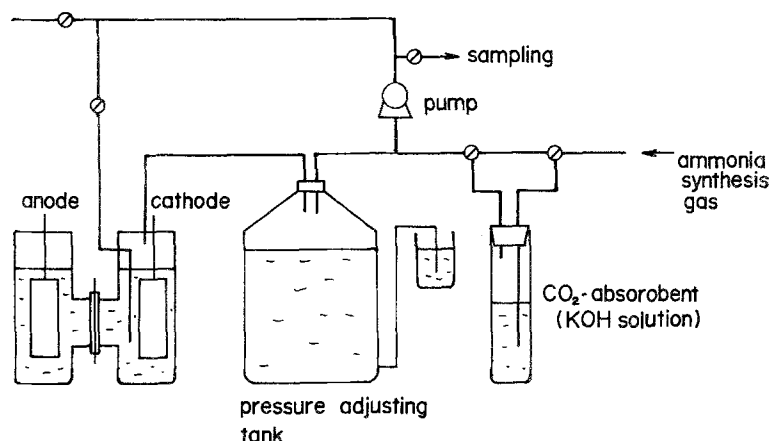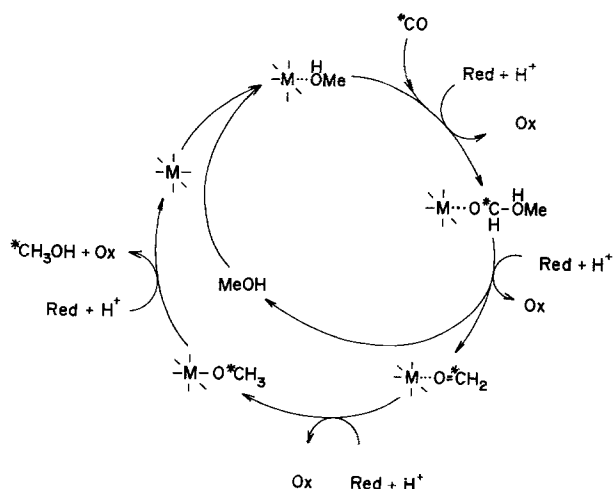

Fig. 2. Schematic diagram of the exclusion system of CO and CO_2 from ammonia synthesis gas.

Scheme 1.

CO_2 is also converted to methanol following a similar mechanism [7].

The conversion process was here applied to exclude CO and CO_2 from ammonia synthesis gas, and these gases were converted to methanol. It is known that CO and CO_2 dissolve into aqueous solution to some extent, the Bunsen absorption coefficient (25° C) being: CO_2, 7.59×10^{-1}; CO, 2.14×10^{-2}. In addition to the conversion of CO and CO_2 to methanol, a part of these gases may merely dissolve into solution. Hence, the amount of the excluded CO and CO_2 is equivalent to the sum of the moles of methanol and gases dissolved. In Fig. 3, the concentration of methanol obtained at two-phase and three-phase interfaces in the electrocatalytic reduction of the ammonia synthesis gas is plotted as a function of the cathodic potential. The methanol formation was slightly higher in the
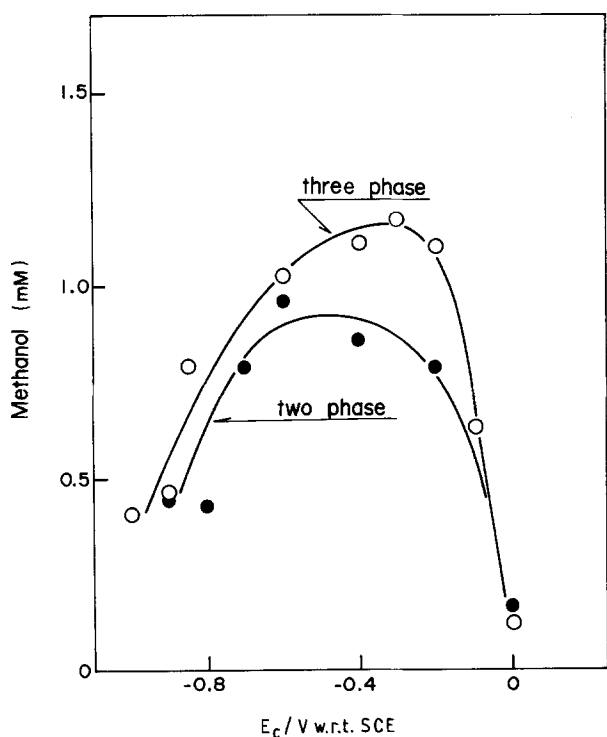

Fig. 3. Methanol formation as a function of cathodizing potential for the ammonia synthesis gas at two-phase (●) and three-phase (○) interfaces.

three-phase condition than in the two-phase. In the CO_2-removed ammonia synthesis gas, however, the conditions of the electrode–solution interface affected the methanol formation strongly, as described later. The formation of methanol was observed at potentials more negative than 0 V w.r.t. SCE, and the build-up of methanol concentration passed through a maximum at about -0.3 or -0.5 V. At potentials more positive than 0 V, the electrode mediator could not be regenerated, and reduction of CO and CO_2 was not achieved. At very negative potentials, the decline in methanol formation is due to the preferential reduction of protons.

The total percentage of CO and CO_2 excluded from the initial ammonia synthesis gas was estimated by gas chromatography. The results are shown, along with the concentration of methanol formed, electric charge passed, and the current efficiency for the formation of methanol in Tables 2 and 3, where the ammonia synthesis gas was provided under two- and three-phase conditions, respectively. In this experiment, no distinction was made between methanol originated from CO and CO_2, and the apparent current efficiency (η) for methanol formation was calculated taking the number of electrons involved in the reduction to be four

$$\eta(\%) = \frac{4FC_m}{Q} \times 100 \qquad (3)$$

where C_m is the amount of methanol formed, Q the electric charge, and F the Faraday number.

Comparison of the data in Tables 1 and 2 shows that the elimination of CO and CO_2 form the ammonia synthesis gas and the formation of methanol were consistently better in the three-phase condition. This is due to the rapid transport of gases to the active zone of the mediated electrode in the three-phase condition as pointed out previously [6]. In the two-phase condition, the reaction gas first dissolves into the electrolyte, and then the gas captured by the homogeneous catalysts must diffuse toward the electrode surface to accept electrons. In three-phase conditions, however,

Table 2. Results of the total percentages of CO and CO_2 excluded from the ammonia synthesis gas, concentration of methanol produced, electric charge passed, and the current efficiency (η) for the formation of methanol in the two-phase condition*

E (w.r.t. SCE)	Q (C)	ΔCO (%)	ΔCO_2 (%)	$[CH_3OH]$ ($mmol\,dm^{-3}$)	η (%)
0	13.3	1.1	3.4	0.16	102
-0.2	128.3	1.5	2.7	0.79	52
-0.4	407.8	1.0	2.7	0.86	18
-0.6	610.4	1.1	2.9	0.96	13
-0.7	540.5	0.8	3.3	0.78	12
-0.8	848.9	0.8	3.0	0.43	4
-0.9	2151	0.8	3.9	0.47	2

* Reaction time, 5 h; catalyst solution, $0.1\,mol\,dm^{-3}$ KCl (pH 2.0) containing Co(II)-nitroso-R-salt ($15\,mmol\,dm^{-3}$: $30\,mmol\,dm^{-3}$) + $20\,mmol\,dm^{-3}$ methanol; the volume of catholyte was $220\,cm^3$.

Table 3. Results of the total percentages of CO and CO_2 excluded from the ammonia synthesis gas, concentration of methanol produced, electric charge passed, and the current efficiency (η) for the formation of methanol in the three-phase condition*

E (w.r.t. SCE)	Q (C)	ΔCO (%)	ΔCO_2 (%)	$[CH_3OH]$ ($mmol\,dm^{-3}$)	η (%)
−0.1	46.4	0.8	3.4	0.63	104
−0.2	174.1	1.3	3.7	1.10	49
−0.3	260.0	1.4	4.1	1.23	37
−0.4	332.3	1.5	3.7	1.16	27
−0.6	419.2	1.6	3.8	1.02	19
−0.8	921.3	1.3	3.6	1.06	9
−0.9	2074	1.1	3.8	0.4	2
−1.0	1438	1.1	4.0	0.4	2

* Reaction time, 5 h; catalyst solution, 0.1 mol dm⁻³ KCl (pH 2.0) containing Co(II)-nitroso-R-salt (15 mmol dm⁻³: 30 mmol dm⁻³) + 20 mmol dm⁻³ methanol; the volume of catholyte was 200 cm³.

the reaction gas from the gas phase first adsorbs onto the electrode surface, and then the gas diffuses along the surface from the point of adsorption to the intersection of the three phases. In general, the diffusion coefficient of a neutral molecule is much larger on a solid surface than in a liquid, and hence the reduction of CO and CO_2 is favoured at the three-phase interface.

CO and CO_2 are both reducible to methanol, and in the following experiments CO_2 was removed from the ammonia synthesis gas by using CO_2-absorbant. The content of CO_2 in the pre-treated gas was less than 0.01%, and the methanol formation originated almost entirely from CO. The results obtained are shown in Fig. 4. As seen by comparison of Figs 3 and 4, there is no large difference between the amounts of meth-
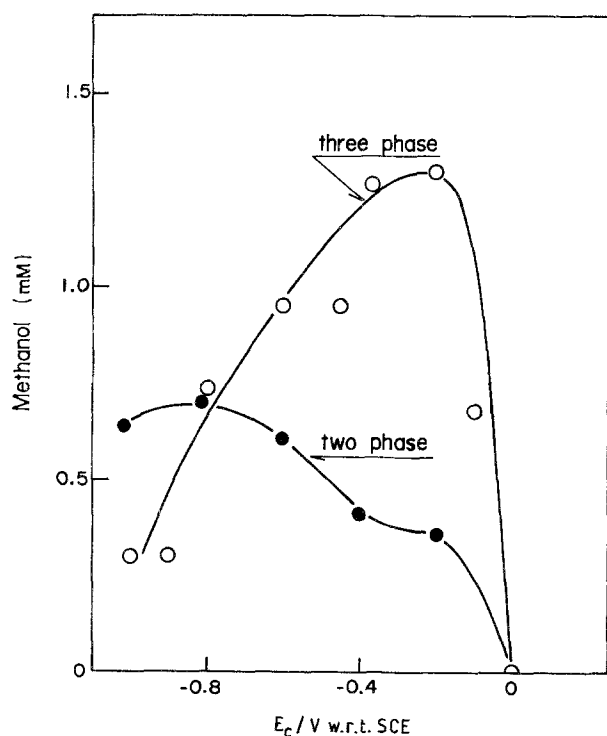

Fig. 4. Methanol formation as a function of cathodizing potential for the CO_2-removed gas at two-phase (●) and three-phase (○) interfaces.

anol obtained with the pre-treated and untreated ammonia synthesis gases. In the two-phase condition, however, the yield of methanol was considerably changed by the pre-treatment of ammonia synthesis gas. This is attributed to the different values of the solubilities of CO and CO_2 in aqueous solution. As noted above, the Bunsen absorption coefficient of CO_2 is 35 times larger than that of CO. In the two-phase condition in Fig. 4, the reaction gas must dissolve into solution, and the reduction of CO to methanol is less effective. In the three-phase condition, however, the reaction gas is transported to the three-phase interface along the electrode surface, and the reduction of CO is not directly related to the solubility. It is concluded from these results that the reduction of CO_2 to methanol is more effective in two-phase conditions, but that of CO is more effective in the three-phase condition.

Thus, CO and CO_2 can be excluded from ammonia synthesis gas by the present method at room temperature and atmospheric pressure. The existing process consists of the shift reaction of CO to CO_2, the absorption of CO_2 into an absorbant under pressure, and the release of CO_2 from the absorbant under decompression. Compared with such a process, the proposed new process may be much simpler. However, the current efficiency for the CO and CO_2 reduction is presently low at higher current density. This is due to the reaction condition of atmospheric pressure, since the concentration of CO and CO_2 dissolved in solution is so low that the transport of the electroactive species to electrode is inefficient. Hence, the electrocatalytic reaction, in practice, may be recommended to be performed under slightly higher pressure. In the present method, the reduction product of CO and CO_2 is methanol, and the re-use of methanol is possible if it is isolated from the catalyst solution by distillation. In either event, the commercial feasibility of the process will require a current efficiency of at least 20%, and further improvement is required involving cell design and homogeneous catalysis.

4. Conclusions

(1) CO and CO_2 can be excluded from ammonia synthesis gas by the proposed electrocatalytic reaction. The maximum percentages of CO and CO_2 excluded from the initial gas were about 1.5 and 4.1%, respectively, with a mediated electrode of 82.8 cm² area in a reaction time of 5 h.

(2) CO and CO_2 were both reduced to methanol, and the amount of the excluded CO and CO_2 was equivalent to the sum of moles of methanol formed and gases dissolved into the solution alone. The electroreduction of CO and CO_2 was more efficient in three-phase and two-phase conditions, respectively.

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