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Mediated reduction of CO and CO_2 to methanol by surface-confined metal complexes in the presence of homogeneous catalysts

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The catalytic reduction of CO and CO_2 on a mediated electrode has been investigated in the presence of homogeneous catalysts. Both gases can be converted to methanol at room temperature; for the reduction of CO the maximum current efficiency was about 100% and for CO_2 was about 16%. The metal complexes used as catalyst were aquopentacyanoferrate(II), diaquobis(oxalato)chromate (III), aquopentachlorochromate(III), aquopentafluoroferrate(III), amminepentacyanoferrate(II) and 4,5-dihydroxybenzene-1,3-disulphonatoferrate(III). The general feature of a metal complex capable of operating as a catalyst in the reduction of CO and CO_2 is that it should have at least one labile ligand in its coordination shell which can be replaced by a new ligand during the course of reaction.

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1. Introduction

The fixation of CO and CO_2 is an important subject in the conversion of these very abundant resources into organic raw materials or fuel. In the methanol [1] and the Fischer–Tropsh syntheses [2], synthesis gas is converted using various heterogeneous catalysts to organic substances at 200–300° C and 20–100 atm. A method of utilizing CO_2 is proposed in which CO_2 is converted to CO at temperatures above 1000° C and from which methanol can be synthesized. These processes are possible, but only under very severe conditions and with low energy efficiency. In order to minimize the energy required for the conversion process some investigators have tried to reduce CO and CO_2 under more mild conditions. To this end, the electrochemical reduction of CO was carried out in DMF and at a CO pressure of about 200 atm [3, 4], the major product was $C_4O_4^{2-}$. The reduction of CO in liquid ammonia and at a CO pressure of 14 atm leads to the formation of the dimeric anion, $C_2O_2^{2-}$ [5]. In aqueous solution the electroreduction of CO has been attempted in the titanium (III)–molybdenum(III)–pyrocatechol system, but the amount of C_{1-4} hydrocarbons produced was very small [6].

The conversion of CO_2 into organic substances is more interesting, and the electroreduction has been studied with metal and semiconductor electrodes [7]. A shortcoming of the electrochemical method is that large overpotentials are required to reduce CO_2. To overcome this problem the photo-assisted reduction has been tried with semiconductor electrodes. However, there are still some problems to be settled including low product yield and lack of selectivity to the desired compound. The main products obtained in these processes are formic acid in aqueous solutions and oxalic acid and CO in organic solvents. The direct electrochemical reduction of CO_2 [8] as well as CO to methanol is very difficult. If these reactions are feasible with a high efficiency, however, they must be economically competitive with existing technology since methanol is probably the alternative liquid fuel in the future. For this purpose we investigated the direct conversion of CO and CO_2 to methanol at room temperature.

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In this laboratory [9–13] it has been found that CO and CO_2 can be reduced to methanol by a surface-confined Everitt's salt (ES; $K_2Fe(II)[Fe(II)(CN)_6]$). These conversions are caused by the oxidation of ES to Prussian Blue(PB; $KFe(III)[Fe(II)(CN)_6]$).

$$CO + 4ES + 4H^+ \longrightarrow CH_3OH + 4PB + 4K^+ \quad (1)$$

$$CO_2 + 6ES + 6H^+ \longrightarrow CH_3OH + 6PB + 6K^+ + H_2O \quad (2)$$

By cathodically regenerating ES using an external source of energy, the conversion reactions continue with the consumption of protons in solution. For the activation of Reactions 1 and 2, however, the existence of a homogeneous catalysis is indispensable. The homogeneous catalyst consists of a metal complex and a primary alcohol. In the present paper, ES was regenerated by electrochemical reduction and various metal complexes were used as the homogeneous catalyst.

2. Experimental details

The surface-confined metal complex used was Everitt's salt. This was prepared by the electroreduction of PB, which was deposited on a 6 cm^2 platinum plate from a mixed solution of 0.01 M $FeCl_3$ and 0.01 M $K_3Fe(CN)_6$ [14, 15]. The average amount of ES was 2.5×10^{-7} mol cm^{-2}. The metal complexes used as homogeneous catalysts were aquopentacyanoferrate(II) ($Na_3[Fe(CN)_5(H_2O)]$), diaquobis(oxalato)chromate(III) ($K[Cr(C_2O_4)_2(H_2O)_2]$), aquopentachlorochromate(III) ($(NH_4)_2[CrCl_5(H_2O)]$), aquopentafluoroferrate(III) ($K_2[FeF_5(H_2O)]$), amminepentacyanoferrate(II) ($Na_3[Fe(CN)_5(NH_3)]$), hexacyanoferrate(II) ($K_4[Fe(CN)_6]$), pentacyanonitrosylferrate(III) ($Na_2[Fe(CN)_5(NO)]$ and 4,5-dihydroxybenzene-1,3-disulphonato(=tiron) ferrate(III) ($[Fe(III)C_6H_2(OH)_2(SO_3)_2]^+$). These complexes were prepared as described in the references, expect for the Fe(III) (tiron) complex which was formed by dissolving 10^{-3} M purified ferric ammonium sulphate and 2×10^{-3} M tiron in 0.1 M KCl. The catalyst solutions were made from these metal complexes and methanol in 0.1 M KCl, and the pH was adjusted to 3.5. The solutions were kept in a reservoir of 1 dm^3 where they were saturated with CO or CO_2 by bubbling for 1 h. The CO and CO_2 used were 99.9% purity and all chemicals were reagent grade.

The electrolytic cell was made up of a cathode and an anode compartment. The cathode compartment was connected to the anode through a fine frit and to the reference saturated calomel electrode (SCE) cell through a solution-lubricated glass stopcock. The cathode was the ES-modified platinum plate and the anode was a bright platinum plate. Some of the catalyst solution (50 cm^3) was transferred to the cathode compartment and the ES-modified electrode was then immersed in this compartment. In addition, 40 cm^3 of the catalyst solution was poured into the anode compartment. The experiments were conducted under potentiostatic conditions.

Methanol was determined by a JGC-100Type gas-chromatography with a thermal conductivity detector and a Poropak Q column. The sampling procedure has been described in detail previously [9].

3. Results and discussion

3.1. *Reduction of CO*

In Fig. 1 the methanol formation is shown as a function of time for the system 5 mM $(NH_4)_2[FeCl_5(H_2O)]$ and 20 mM CH_3OH. The methanol formation is linearly related to reaction time. The turnover frequency of CO conversion to methanol, N_m, is defined as moles of methanol per mole of metal complex per hour. The values of N_m and the activation energies obtained from the Arrhenius plot of N_m are tabulated in Table 1 along with the concentration of methanol produced, the electric charge and the current efficiency. The current efficiency in the solutions containing

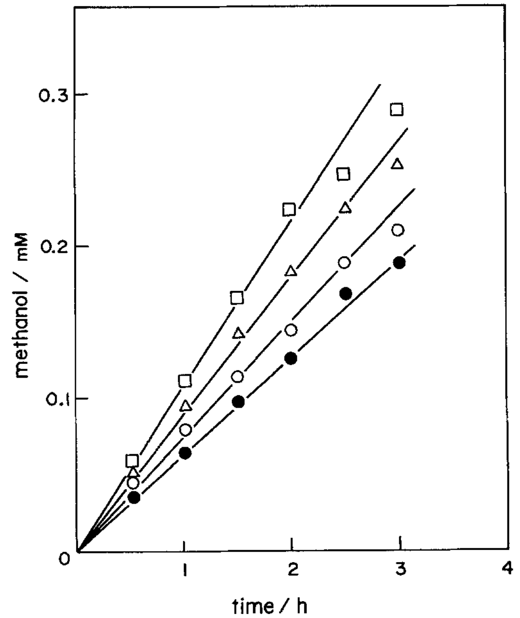


Fig. 1. Methanol formation as a function of time in the catalyst solution of pH 3.5 containing 5 mmol dm^{-3} $(NH_4)_2[CrCl_5(H_2O)]$ and 20 mmol dm^{-3} CH_3OH at 20 (●), 30 (○), 40 (△), and 50 (□) ° C. Electrolysis potential, −0.9 V versus SCE.

pentachlorochromate(III) and pentafluoroferrate(II) is much lower than those with the other four metal complexes. This is attributed to hydrogen evolution which predominates over the reduction of PB to ES. These complexes tended to decompose slightly during the electrolysis, as confirmed by deposition of the metal on the ES film after electrolysis. This presumably causes the drop of the hydrogen overpotential observed during the experiments. The activation energy is influenced by the nature of the metal complex: its value is smallest in the presence of the Fe(III) (tiron) complex, and increases in the order pentachlorochromate (III), bis(oxalato)chromate(II), pentacyanoferrate (II), pentafluoroferrate(II) and amminepentacyanoferrate(II). The activation energy ranged from 2.9 to 5.8 kcal mol^{-1}, and the reaction rate was limited by mass transfer in solution. As shown in Table 1, the formation of methanol was not observed in the presence of pentacyanonitrosylferrate(III) or hexacyanoferrate(II). Hence, in general a metal complex capable of acting as a catalyst in the

Table 1. Results obtained in the reduction of CO to methanol

Metal complex[b]	*Methanol produced (mmol dm^{-3})*	*Charge passed (C)*[c]	*Current efficiency (%)*[c]	*Turnover frequency (10^{-2} h^{-1})*[c]	*Activation energy (kcal mol^{-1})*
Fe(III) (tiron)	0.278	4.632	115.8	11.8	2.9
$(NH_4)_2[CrCl_5(H_2O)]$	0.249	8.857	52.3	2.2	3.3
$K[Cr(C_2O_4)_2(H_2O)_2]$	0.202	3.721	104.8	2.2	3.4
$Na_3[Fe(CN)_5(H_2O)]$	0.200	3.575	108.0	2.0	4.1
$K_2[FeF_5(H_2O)]$	0.198	11.58	33.0	1.8	4.2
$Na_3[Fe(CN)_5NH_3]$	0.115	2.732	81.3	1.1	5.8
$Na_2[Fe(CN)_5(NO)]$	(−0.005)	3.613	—	—	—
$Na_4[Fe(CN)_6]$	(−0.001)	2.981	—	—	—

[a] Volume of the catholyte, 50 cm^3; added methanol, 20 mmol dm^{-3}; pH, 3.5; electrolysis potential, −0.9 V versus SCE; time, 3 h.

[b] Concentration of metal complex, 5 mmol dm^{-3} except for Fe(III) + tiron, (1 + 2) mmol dm^{-3}.

[c] Temperature, 40° C.

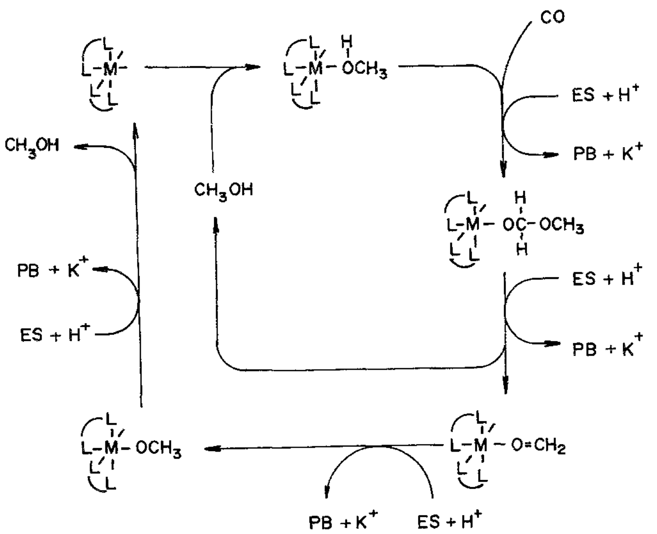


Fig. 2. Scheme of reaction for the reduction of CO.

reduction of CO should have at least one labile ligand which can be replaced by a new ligand during the course of reaction.

The presence of a metal complex and a primary alcohol which are required for the reduction of CO lead to the reaction mechanism shown in Fig. 2 [12]. The net reaction results in Reaction 1. A metal complex and a primary alcohol act as homogeneous catalysts, and an intermediate species of formate type is assumed which is reduced to methanol and the initial complex formed by the reaction with ES. This assumption is based on the IR spectra of the metal complexes isolated from the catalyst solutions after the electrolysis, i.e. two bands appeared at 1090 and 1180 cm^{-1} attributable to the stretching vibration of C–O–C as in a formate [12].

3.2. *Reduction of CO$_2$*

The conversion scheme described above has been applied to the reduction of CO$_2$. The results obtained are shown in Table 2 where methanol and ethanol were both used as homogeneous

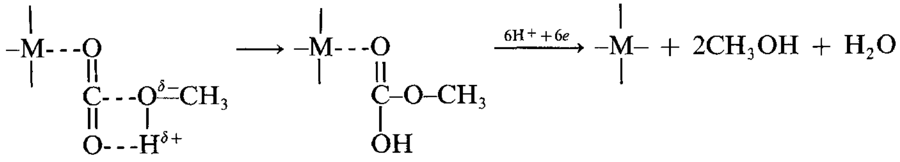
Table 2. Results obtained in the reduction of CO$_2$ to methanol

Metal complex	*Primary alcohol*	*Charge passed (C)*[b]	*Methanol produced (µmol dm^{-3})*[b]	*Current efficiency (%)*[b]	*Turnover frequency (10^{-3} h^{-1})*[b]	*Activation energy (kcal mol^{-1})*
Fe(III) (tiron)[c]	CH$_3$OH	32.2	161	14.5	89	5.8
Na$_3$[Fe(CN)$_5$(H$_2$O)][d]	CH$_3$OH	27.5	148	15.5	15	7.0
K[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$][d]	CH$_3$OH	31.8	159	14.5	16	5.8
Na$_4$[Fe(CN)$_6$][d]	CH$_3$OH	14.3	(−3)	–	–	–
Fe(III) (tiron)[e]	C$_2$H$_5$OH	51.4	1.1	0.06	0.094	8.9
(NH$_4$)$_2$[CrCl$_5$(H$_2$O)][f]	C$_2$H$_5$OH	90.7	1.4	0.05	0.045	7.9
K[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$][f]	C$_2$H$_5$OH	64.8	0.9	0.04	0.030	10.6

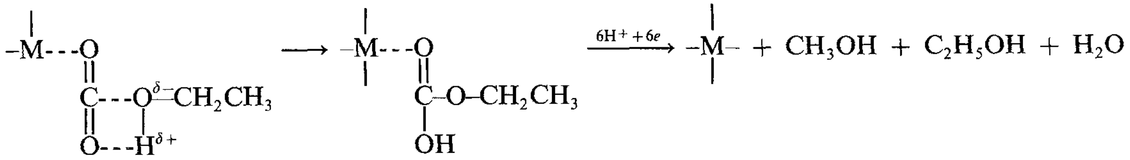
[a] Volume of the catholyte, 50 cm^3; electrolysis potential, −0.9 V versus SCE; time, 3 h.
[b] Temperature, 40° C.
[c] (1 + 1) mmol dm^{-3}.
[d] 5 mmol dm^{-3}.
[e] (4 + 8) mmol dm^{-3}.
[f] 10 mmol dm^{-3}.

catalysts along with various metal complexes. The electric charge passed in the presence of methanol is about eight times as large as that obtained for the reduction of CO, and the current efficiency is low. The activation energy is approximately twice that obtained in the case of CO. In the catalyst solution containing ethanol, the amount of methanol produced is very low, although this system gives clear evidence for the reduction of CO_2 to methanol. As shown in Table 2, CO_2 is not converted to methanol in the presence of hexacyanoferrate(II), which was also the case with pentacyanonitrosylferrate(II). Hence the metal complex acting as a homogeneous catalyst must have the same feature as described in the reduction of CO.

A catalytic process similar to the scheme described above has been proposed as the detailed mechanism [13] in which a coordination bond is first formed between a central metal and a primary alcohol. CO_2 inserts into this bond to form an intermediate of the formate type, and finally methanol and initial complex are formed by the reaction with ES. Low yield and current efficiency of the methanol formation in the presence of ethanol may be rationalized as follows. The key step in the reduction of CO_2 must be the insertion of CO_2 into the metal–alcohol bond as shown in Reactions 3 and 4.



(3)



(4)

The degree of the polarization of the $H^{\delta+}$–$O^{\delta-}$ bond is greater in $HOCH_3$ than in $HOCH_2CH_3$ because the electron density of the oxygen atom is higher and the electron-attracting effect for the H : O bond is smaller in $HOCH_2CH_3$ than in $HOCH_3$. Hence Reaction 3 could proceed more readily than Reaction 4.

It is therefore concluded that CO and CO_2 can be catalytically reduced to methanol with the ES-modified electrode at room temperature.

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