JOURNAL OF APPLIED ELECTROCHEMISTRY **17** (1987) 760–764

Electrochemical behaviour of Cu–Zn–Al oxide catalysts in $DMSO_2$ at 150° C

A. TRANCHANT, R. MESSINA, J. PERICHON

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique CNRS, 2 rue Henri-Dunant, 94320 Thiais, France

Received 17 September 1986; revised 10 November 1986

The electrochemical behaviour of Cu–Zn–Al oxide catalysts in a high-temperature solvent, dimethylsulphone ($DMSO_2$), at 150° C has been investigated. It has been shown that CuO electroreduction becomes easier and/or deeper in the Cu–Zn–Al oxide catalysts than in CuO alone. This electroreduction occurs at higher potentials, and the overall faradic yield decreases when CO_2 is dissolved in $DMSO_2$ on account of a strong interaction between the reduced species formed during the electronic transfer and CO_2. These results are consistent with the characterizations of the physical and chemical properties of these catalysts. They confirm that electrochemistry is a suitable method to determine the redox states of some copper industrial catalysts used in methanol synthesis.

1. Introduction

Industrial catalysts for low pressure methanol synthesis are generally composed of Cu–Zn–Al mixed oxides. The catalytic activity of these compounds is markedly higher than that of the isolated components [1, 2]. We have previously investigated the electrochemical behaviour of these catalysts [3] in 1 M $LiClO_4$–propylene carbonate at room temperature and have shown that electrochemistry may be a convenient method to study the redox properties of some metallic oxide catalysts.

The aim of this work is to define the electrochemical properties of Cu–Zn–Al oxide catalysts at high temperature (150° C) in order to provide information about the redox state of catalysts in a temperature range consistent with methanol synthesis. Catalyst characterization is usually performed at room temperature with ultra-high vacuum techniques in conditions very different from those needed for methanol synthesis.

In this work, interactions of the catalysts with CO_2 have also been studied electrochemically. If the role of CO_2 is to maintain the redox state of copper during methanol synthesis, as has been suggested [4], the electrochemical behaviour of copper in catalysts may be dependent on the presence of CO_2.

2. Experimental details

2.1. *Electrochemical characterization*

Electrochemical investigations were performed with electrodes of apparent area 1 cm^2 and thickness 0.2 mm. The active materials were mixed with 90 wt % pure graphite which ensured a better electronic transfer. Electrodes containing small amounts of catalysts ($\cong 2$ mg) were prepared by pressing the mixture of active compound and graphite on an aluminium grid. Electron transfer was achieved by an aluminium electrode and the potential of the catalyst electrode was measured versus a lithium electrode. All the potentials mentioned are expressed versus the reference system Li/Li^+. Control of the current during the determination of chronopotentiograms was achieved by means of a three-electrode galvanostatic device (Tacussel). The electrochemical cell was thermostated with silicon oil whose temperature and circulation were controlled by a Polystat 8N.

Experiments were performed using 12.4 g dimethylsulphone ($DMSO_2$) as solvent and 1.6 g $LiClO_4$ (1 mol kg^{-1}) as electrolyte salt. Lithium perchlorate ($LiClO_4$) was vacuum-dried at 190° C for 12 h. $DMSO_2$, supplied by Janssen, was first recrystallized in water and then twice

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from absolute methanol, air dried at 90° C for 48 h and dried again *in vacuo* at 30° C for 12 h. $DMSO_2$ and $LiClO_4$ were kept moisture-free in an argon-filled glove box.

In some experiments, propylene carbonate (PC) was used as solvent. PC, supplied by Janssen, was vacuum bidistilled on $KMnO_4$. The electrolyte solution (PC and $LiClO_4$, 1 M) was kept on dried Woelm alumina (type W200).

2.2. *X-ray diffraction*

Diffraction patterns were obtained using a Inel X-ray diffractometer using $CuK\alpha$ radiation. Diffraction patterns at various stages of CuO electroreduction were made on a mechanical mixture of CuO and ZnO. ZnO may be used as internal reference for X-ray measurements since its electroreduction does not interfere with that of CuO (ZnO is not electroreducible until a 2 V cut-off voltage, i.e. after CuO electroreduction).

The electrochemically reduced samples were washed with freshly distilled tetrahydrofuran under argon in order to remove $LiClO_4$ before X-ray diffraction measurements.

2.3. *Catalyst preparation*

All Cu–Zn–Al oxide catalysts contained 10 wt % Al_2O_3. Precursors with various ratios of Cu–Zn were prepared by co-precipitation from copper(II), zinc(II) and aluminium(III) nitrate solutions by sodium carbonate addition. The co-precipitation was carried out at 90° C until the pH had risen from approximately 3 to 7 [1, 2]. After filtration, the precipitates were washed with distilled water and dried overnight at 60° C. The temperature of the calcination step under O_2 was raised to 350° C by increments of 50° C every 30 min. CuO was prepared from copper(II) nitrate solution in the same way as for the Cu–Zn–Al catalysts.

3. Results and discussion

3.1. *CuO*

3.1.1. Electrochemical behaviour. In order to investigate the electrochemical behaviour of Cu–Zn–Al oxide catalysts, the redox properties of CuO alone in $DMSO_2$ at 150° C were first studied.

The Li–CuO cell performances in various solvents have already been reported [5, 6]. In PC, CuO electroreduction occurs only at 1.3 V instead of 2.27 V which is the standard potential of the reaction

$$CuO + 2Li^+ + 2e \longrightarrow Li_2O + Cu \quad (1)$$

At temperatures higher than 70° C and in solvents where ions are poorly solvated, CuO electroreduction occurs in two steps.

(i) Insertion of lithium (at 1.8 V) into the CuO lattice [5] according to the reaction

$$CuO + xe + xLi^+ \longrightarrow CuOLi_x \quad (2)$$

where $0 < x < 1$. This reaction may occur in so far as internuclear spacings in the structure of CuO are similar to that of TiO_2 which is known to form intercalates with lithium.

(ii) Electrochemical reduction of $CuOLi_x$ (at 1.5 V) with the formation of copper.

The relative length of these two reduction steps depends on the temperature and the nature of the solvent.

$DMSO_2$ may be a suitable solvent to enhance such reactions since it has been previously reported [7] that sulphone-based electrolytes, and especially molten $DMSO_2$, may be of interest as electrolytes for lithium intercalation batteries.

Chronopotentiograms of CuO in $DMSO_2$ (150° C) and PC (60° C) are reported in Fig. 1. In $DMSO_2$ (curve b) CuO electroreduction occurs in two steps: firstly at 2.5 V with a faradic yield of 0.5 F per mol of CuO, and secondly at 2.25 V with an overall faradic balance of about 1.3 F per mol of CuO (at a 2.1 V cut-off voltage). (Electroreduction of residual water occurs after CuO reduction, i.e. at about 1.8–2 V in $DMSO_2$ [7] and at about 1.3 V in PC [3].)

Differences in the CuO electrochemical behaviour are observed when $DMSO_2$ (150° C) is replaced by PC (60° C); in particular, the CuO electroreduction step at 2.5 V is not significantly detected in PC (Fig. 1, curve c).

In $DMSO_2$ the potential of the first electrochemical step (2.5 V) shows that CuO electroreduction does not lead to Cu_2O or Cu formation since the standard potentials of the following

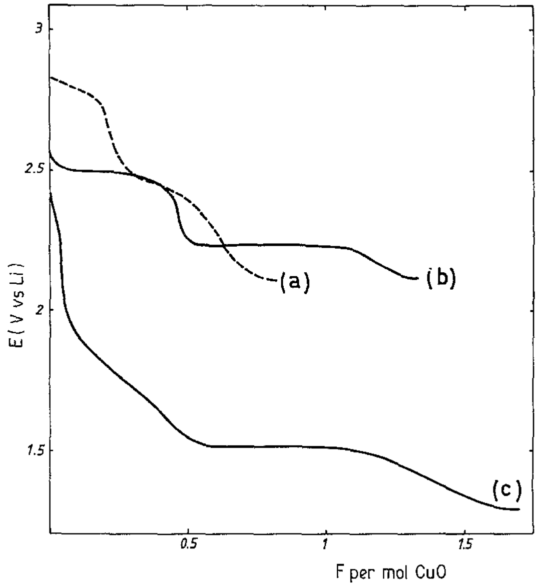

Fig. 1. CuO chronopotentiograms at constant current (100 μA). (a) 1 M $LiClO_4$–$DMSO_2$ (150° C) with CO_2; (b) 1 M $LiClO_4$–$DMSO_2$ (150° C) with argon; (c) 1 M $LiClO_4$–PC (60° C) with argon.

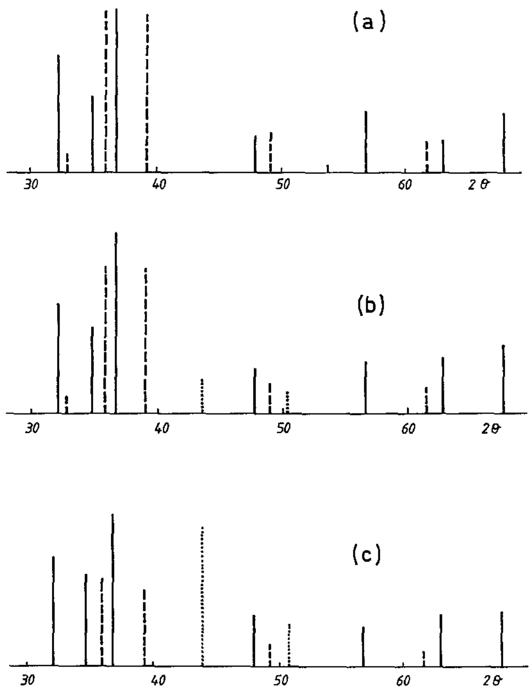

Fig. 2. X-ray diffraction patterns of a mechanical mixture of CuO and ZnO, (a) before electroreduction, (b) after electroreduction on the first step at 2.5 V and (c) after electroreduction until a cut-off voltage of 2.1 V. (——) ZnO; (---) CuO; (···) Cu.

reactions

$$2CuO + 2Li^+ + 2e \rightleftharpoons Cu_2O + Li_2O \quad (3)$$

or

$$CuO + 2Li^+ + 2e \rightleftharpoons Cu + Li_2O \quad (4)$$

are 2.31 V and 2.21 V at 150° C respectively.

In the same way, the second CuO electroreduction process does not correspond to the reaction

$$Cu_2O + 2e + 2Li^+ \rightleftharpoons 2Cu + Li_2O \quad (5)$$

since its thermodynamic potential is 2.11 V at 150° C.

We can conclude that during the first electoreduction step (at 2.5 V), $DMSO_2$ stabilizes a reduced copper species with an overall oxidation state between 2 and 1. This intermediate species may correspond to an intercalation compound such as $CuOLi_x$ as has been suggested by Gabano [5]. The second electroreduction step (at 2.25 V) may correspond to the reduction of $CuOLi_x$ with the formation of copper.

X-ray diffraction analyses, performed at various stages of electroreduction of a mixture containing CuO and ZnO (10 wt %) used as internal reference, are shown in Figure 2. Analyses, performed on the reduced sample (to a 2.1 V cut-off voltage) shows that ZnO is not affected by this treatment (Fig. 2c). This result agrees with electrochemical data relative to ZnO, indicating that ZnO reduction occurs below 1.5 V [3]. The intensity of the CuO diffraction peaks weakens during the first and second electroreduction processes at 2.5 V (Fig. 2, curve b) and 2.25 V (Fig. 2, curve c) which confirms that CuO electroreduction occurs in this potential range.

A diffraction pattern for Cu_2O is never observed, either during the first or the second process, and copper is only significantly detected during the second step.

3.1.2. Interaction with CO_2. No modification of the CuO electrochemical behaviour was observed in PC (at 60° C) when argon was replaced by CO_2.

In $DMSO_2$ at 150° C (Fig. 1, curve a) CuO electroreduction occurs in two steps: the first at 2.8 V and the second at 2.4 V, i.e. at potentials higher than those observed under argon. This result suggests that CO_2 interacts strongly with reduced species produced during CuO electroreduction, especially with $CuOLi_x$.

The potential of the first electroreduction step changes with the composition of the gaseous mixture (CO_2–argon): the higher the CO_2 partial pressure, the higher the potential of the first reduction step. Such an influence of CO_2 partial pressure shows that $CuOLi_x$ interacts with CO_2 dissolved in $DMSO_2$.

The first electroreduction step at 2.8 V corresponds to the formation of a compound $CuOLi_x$, CO_2 according to the path

$$CuO + xe + xLi^+ \longrightarrow CuOLi_x$$

$$E_1 = 2.5\,V \qquad (6a)$$

$$CuOLi_x \xrightarrow{CO_2} CuOLi_x,\ CO_2 \qquad (6b)$$

$$CuO + xe + xLi^+ \xrightarrow{CO_2} CuOLi_x,\ CO_2$$

$$E_2 = 2.8\,V \qquad (6c)$$

The chemical interaction between CO_2 and $CuOLi_x$ (Reaction 6b) induces an increase in the CuO electroreduction potential (2.8 V instead of 2.5 V). The second electroreduction step at 2.5 V could correspond to $CuOLi_x$ formation, without interaction with CO_2, if Reaction 6c is limited by the diffusion of CO_2 in solution; the same electrochemical process which occurs under argon at 2.5 V is then observed.

The overall faradic yield obtained for a 2.1 V cut-off voltage, being lower when reduction is performed under CO_2 (0.7 F per mol CuO instead of 1.2 F under argon), suggests that no significant copper formation occurs under CO_2 in this potential range since CO_2 strongly interacts with $CuOLi_x$. Such a result is consistent with the assumption that the role of CO_2 is to prevent the reduction of copper during methanol synthesis and maintain a highly active catalyst.

3.2. *Cu–Zn–Al oxide catalysts*

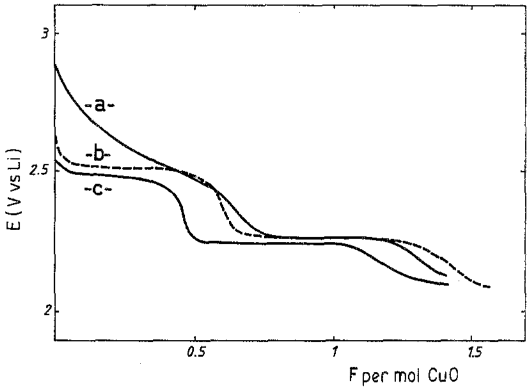

Fig. 3. Chronopotentiograms of Cu–Zn–Al oxide catalysts at constant current (100 μA) under argon. (a) 10 wt % CuO, 90 wt % ZnO, 10 wt % Al_2O_3; (b) 50 wt % CuO, 50 wt % ZnO, 10 wt % Al_2O_3; (c) 100 wt % CuO, 10 wt % Al_2O_3. 1 M $LiClO_4$–$DMSO_2$; 150° C.

3.2.1. Electrochemical behaviour. Chronopotentiograms of Cu–Zn–Al oxide catalysts with various compositions of Cu–Zn are reported in Fig. 3. The addition of alumina during CuO synthesis modifies neither the potentials nor the faradic balances of the reduction processes observed with CuO alone (Fig. 1, curve b).

When zinc is added to Cu–Al samples (Fig. 3, curves a and b) the faradic yield involved during the first step at 2.5 V becomes 20% greater. This result suggests that some structural modifications of CuO exist in Cu–Zn–Al catalysts which enhance the capacity of lithium insertion in the host lattice of CuO. When the zinc content is greater than 70% (Fig. 3, curve a) these modifications allow an easier lithium insertion (the CuO electroreduction potential increases), but the faradic yield remains unchanged.

These results are consistent with the conclusions of other workers [8–10] who proposed that the catalytically active species in Cu–Zn–Al oxide catalysts in the synthesis of methanol was Cu^+ dispersed in ZnO lattice. These interactions between the reduced species of CuO and ZnO may explain the modification of the electrochemical behaviour of CuO in Cu–Zn–Al oxide catalysts.

3.2.2. Interaction with CO_2. Chronopotentiograms of Cu–Zn–Al oxide catalysts with various ratios of Cu–Zn in $DMSO_2$ (150° C) and under CO_2 are reported in Fig. 4. For any CuO content, the reduction potentials are higher when

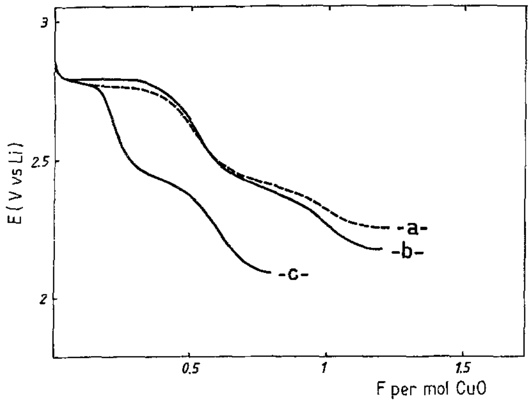

Fig. 4. Chronopotentiograms of Cu–Zn–Al oxide catalysts at constant current (100 μA) under CO_2. (a) 50 wt % CuO, 50 wt % ZnO, 10 wt % Al_2O_3; (b) 100 wt % CuO, 10 wt % Al_2O_3; (c) 100 wt % CuO. 1 M $LiClO_4$–$DMSO_2$; 150° C.

argon is replaced by CO_2, particularly for the first step (2.8 V under CO_2 as against 2.5 V under argon). This result shows the ability of the electrochemically reduced catalysts to interact with CO_2.

Alumina contributes to CuO elecroreduction in Cu–Zn–Al oxide catalysts under CO_2. The presence of alumina (Cu–Al sample, Fig. 4, curve b) induces an increase in the faradic yield involved during the first electroreduction step (i.e. during $CuOLi_x$, CO_2 formation), i.e. 0.55 F with Cu–Al compound instead of 0.25 F with pure CuO. Such an increase (induced by alumina) is not observed when electroreduction of Cu–Al sample is performed under argon (curve c). This enhancement of $CuOLi_x$, CO_2 formation may be related to the ability of CO_2 to be adsorbed on alumina. This compound may be a ready provider of CO_2 to the $CuOLi_x$ compound as it is electrochemically formed. Nevertheless, the overall faradic balance (close to 1 F) under CO_2 is always weaker than that observed under argon (1.2 F, Fig. 3, curve c) which suggests that copper formation occurs less readily under CO_2 than argon. Addition of zinc to Cu–Al samples (Fig. 4, curve c) modifies neither the reduction potentials nor the faradic yield observed under argon.

These electrochemical results confirm that the main role of the zinc component only consists in stabilizing the catalytically active species.

4. Conclusion

It has been shown that the electroreduction of CuO in $DMSO_2$ at 150° C is enhanced in Cu–Zn–Al oxide catalysts. This result is consistent with the role attributed to zinc in methanol synthesis [8–10]. Indeed, zinc is reported to stabilize and disperse a reduced species of copper (may be Cu^+) which is the active component of the catalysts.

Moreover, CuO electroreduction is easier when CO_2 is dissolved in $DMSO_2$ due to a strong interaction between the reduced species of CuO and CO_2. We have also shown that CuO electroreduction under CO_2 is promoted by alumina, which probably adsorbs CO_2 and provides it to the reduced species of CuO as they are electrochemically formed.

This work confirms the usefulness of electrochemical methods in the characterization of some solid catalysts. The ability of these compounds to be electrochemically reduced in a temperature range consistent with methanol synthesis may be of interest for catalysis applications.

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