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Electrochemical behaviour of CuO–TiO$_2$ catalysts

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In order to provide further information on the properties of CuO–TiO$_2$ catalysts, we have investigated their electrochemical behaviour in 1 M LiClO$_4$–propylene carbonate electrolyte. It appears that TiO$_2$ is electrochemically reducible at 1.8 V at room temperature, with a faradaic yield of 0.3–0.4 F per mole of TiO$_2$ with formation of a TiO$_2$Li$_x$ phase according to the reaction:

$$TiO_2 + xe + xLi^+ \leftrightharpoons TiO_2Li_x$$

The electrochemical study suggests that TiO$_2$ enhances Cu(II) electroreduction in titania-supported copper catalysts. This electroreduction of Cu(II) occurs either at 2.2 V according to the path:

$$Cu(II) + 2e \xrightarrow{TiO_2 \text{ support}} Cu(O), TiO_2$$

or at 1.8 V through an internal electron transfer between TiO$_2$Li$_x$ and Cu(II) according to the successive reactions:

$$TiO_2 + xe + xLi^+ \leftrightharpoons TiO_2Li_x$$
$$Cu(II) \xrightarrow{TiO_2Li_x} Cu(O), TiO_2$$

This study shows that electrochemistry may be a novel way of determining and controlling the redox states of metal-supported catalysts.

1. Introduction

Recent studies [1, 2] on metal–TiO$_2$ catalysts prepared by hydrogen reduction have shown that the titania support significantly enhances the reducibility of the calcined supported metal. Thus the observed hydrogen consumption stoichiometries during CuO–TiO$_2$ reduction indicate that the calcined precursor is principally reduced to zero-valent copper between 100 and 300° C [1]. High temperature (500° C) reduction of titania-supported copper results in the partial reduction of the titania support, suggesting that the copper is catalysing a deeper reduction of the support than in the case of TiO$_2$ alone. This reduction of titania was found to affect critically the ability of the titania-supported copper catalyst to hydrogenate 2-methyl butanal [1].

In order to provide further information on the properties of CuO–TiO$_2$ catalysts, we have investigated their electrochemical behaviour as redox reactions are possible. We have already shown [3] that electrochemistry is particularly suitable for providing information about the properties of catalysts, especially when they contain redox species such as copper. Moreover, TiO$_2$ (anatase and rutile forms) is electrochemically reducible in non-aqueous medium and was selected a few years ago for use in lithium batteries [4].

2. Experimental details

2.1. *Electrochemical characterization*

Electrochemical investigations were performed with electrodes of apparent surface area 1 cm^2 and thickness about 0.2 mm. For some studies the active materials were mixed with 90 wt % pure graphite which ensures a better electronic

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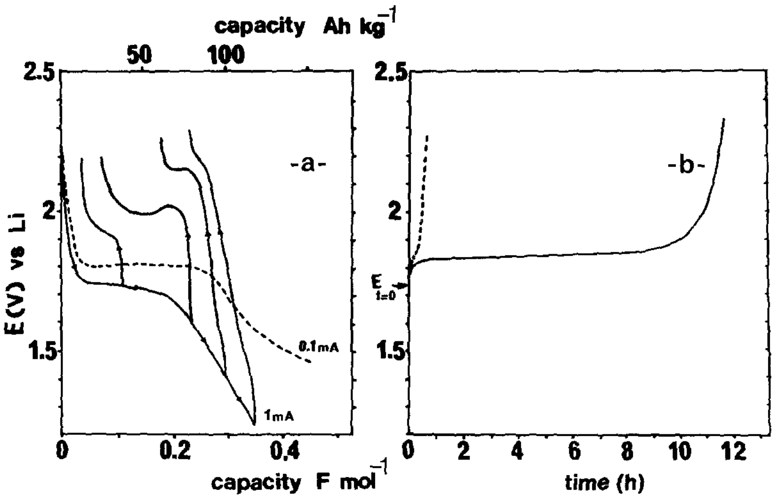

Fig. 1. (a) TiO_2 chronopotentiograms at constant current (1 M $LiClO_4$–PC at 28° C). (b) evolution of the open current voltage of Li–TiO_2 cell after a reduction of 0.1 F mol^{-1} of TiO_2. (1 M $LiClO_4$–PC at 28° C.) ——, anhydrous electrolyte (less than 50 p.p.m.); – – –, with H_2O addition (about 2000 p.p.m.).

transfer. Electrodes containing small amounts of catalyst ($\simeq$ 1 mg) were prepared by pressing the materials onto a nickel grid supplied by Sorapec. These electrodes were placed in front of a lithium auxiliary electrode and the potential was measured versus a lithium reference electrode by a capillary close to the working electrode.

Lithium perchlorate ($LiClO_4$) was vacuum dried at 90° C for 15 h. The electrolyte was prepared by dissolving this salt in propylene carbonate (PC) supplied by Janssen and vacuum bidistilled on $KMnO_4$. The electrolyte solution was then kept on dried Woelm alumina (type W200).

The voltammetric and chronopotentiometric measurements were made using an electronic apparatus supplied by Tacussel.

2.2. *Catalyst preparation*

An aqueous solution of the appropriate ratio of copper nitrate salt was added to TiO_2 Degussa P25. Impregnated samples were dried overnight at 100° C and then calcined at 350° C for 4 h to decompose the nitrate salt.

3. Results and discussion

3.1. *Electrochemical behaviour of titania support*

In order to investigate the electrochemical behaviour of titania-supported copper catalysts we first studied the redox properties of TiO_2 alone.

The Li–TiO_2 cell performances in 1 M $LiClO_4$–propylene carbonate have already been reported [4]. The proposed discharge mechanism has been shown to be a topotactic lithium insertion into the TiO_2 lattice according to:

$$TiO_2 + xe + xLi^+ \rightleftharpoons TiO_2Li_x$$

The maximum stoichiometry of TiO_2Li_x is $x = 0.7$ [5].

Such a topotactic lithium insertion also occurs during TiO_2 reduction with n-butyl lithium at room temperature [6]. The system is composed of two phases for $0 < x < 0.5$ with formation of $TiO_2Li_{0.5}$. The product of the reaction between TiO_2 and n-butyl lithium is black and TiO_2 is recovered after chemical oxidation treatment which suggests that the Ti–O framework has not undergone any major bond reorganization.

Typical chronopotentiograms of TiO_2 at 28° C under constant current are reported in Fig. 1a: TiO_2 electroreduction occurs at 1.7–1.8 V with a faradic balance depending on current density ($\cong$ 0.3 to 0.4 F mol^{-1} TiO_2). The reversibility of Li^+ ion insertion after a previous reduction is also shown in Fig. 1a. The magnitude of the reoxidation which occurs at 2–2.1 V depends on the depth of the previous reduction. As long as the final reduction potential is more positive than 1.5 V, the amount of charge recovered during the reoxidation process is 65–70% of that

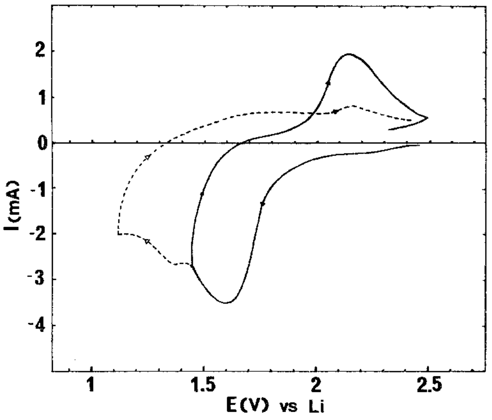

Fig. 2. TiO_2 voltammograms. (1 M $LiClO_4$–PC; 28° C; 1 mV s^{-1}.)

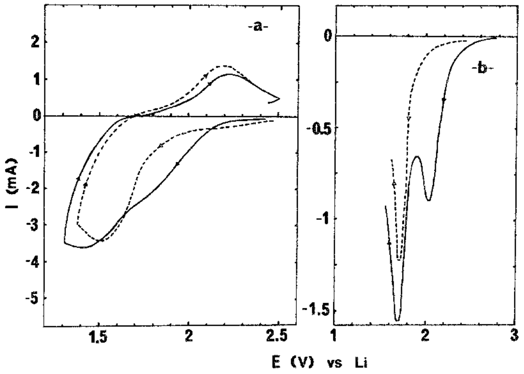

Fig. 3. Voltammograms of: a mechanical mixture of CuO and TiO_2 (10/90) (- - -); a titania-supported copper catalyst CuO–TiO_2 (10/90) (——). (a) 1 m V s^{-1}; (b) 0.1 m V s^{-1}. (1 M $LiClO_4$–PC; 28° C.)

required for the previous reduction. Beyond a reduction potential of 1.5 V, the reoxidation charge is more and more attenuated and the reaction becomes irreversible.

The evolution of the open current voltage of a Li–TiO_2 cell after a reduction of 0.1 F mol^{-1} TiO_2 is reported in Fig. 1b. It can be seen that the reversibility of the Li^+ ion insertion after partial reduction is only temporary and depends considerably on the residual H_2O content in the PC–$LiClO_4$ 1 M electrolyte: the greater the H_2O concentration, the smaller the reversibility of Li^+ ion insertion. This reaction of TiO_2Li_x with H_2O appears faster as the temperature of the cell increases. Cyclic voltammetric curves performed on TiO_2 (Fig. 2) confirm that Li^+ ion insertion is less reversible when the oxidation curves are performed after a reduction stop potential of 1.5 V.

We have taken into account these results for the study of the titania-supported copper catalysts: the electrochemical experiments have been carried out at room temperature in a small volume of electrolyte (1–2 cm^3). Under these conditions water content is less than 50 p.p.m. and no electroreduction of H_2O occurs before 1.6 V.

3.2. *Electrochemical behaviour of titania-supported copper catalysts*

3.2.1. *Characterization of CuO–TiO_2 interactions*

3.2.1.1. Voltammetry. Typical voltammetric reduction curves in 1 M $LiClO_4$–PC electrolyte of a mechanical mixture of CuO and TiO_2 (10/90) and of a titania-supported copper catalyst (CuO–TiO_2, 10/90) are reported in Fig. 3. The mechanical mixture has an electrochemical behaviour similar to that of TiO_2 showing that CuO electroreduction does not occur before 1.2 V as in the Li–CuO battery system [7]. CuO electroreduction in titania-supported copper catalyst occurs before TiO_2 and is observed at slow scan rates indicating that the reaction is slow. The potential of this reduction process (2.2–2 V) is close to the standard potential of the following reaction:

$$CuO + 2e + 2Li^+ \longrightarrow Li_2O + Cu$$

$$(E^0 = 2.25\ V)$$

This electrochemical study confirms that TiO_2 enhances the reducibility of titania-supported CuO [1]. Such an activation of the CuO electroreduction process at 2 V has already been demonstrated by electrochemical methods for CuO–ZnO catalysts [3].

In order to confirm the ascription of electroreduction processes to redox species present in CuO–TiO_2 (10/90), the titania-supported copper catalyst was reduced by H_2 at 350° C. Results of the electrochemical study performed on the reduced catalyst are reported in Fig. 4: CuO electroreduction at 2 V was not observed and the reduction of TiO_2 took place at 1.8 V as in the case of unreduced TiO_2. Such results have already been found by a temperature-programmed reduction method [1, 2]. The complete reduction of CuO by H_2 occurs before 300° C without TiO_2. Chemical reduction of TiO_2 commenced on and after 500° C.

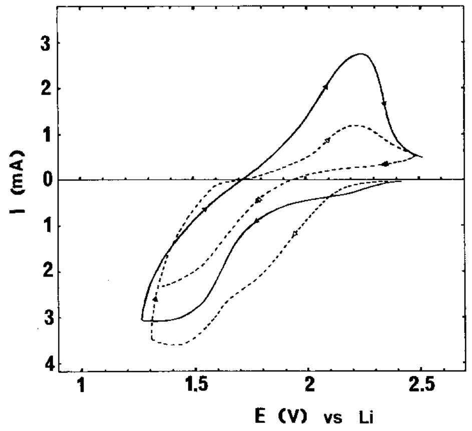

Fig. 4. Voltammograms of a titania-supported copper catalyst CuO–TiO_2 (10/90). ---, without treatment; ——, previously treated by H_2 at 350°C. (1 M $LiClO_4$–PC; 28°C; 1 mV s^{-1}.)

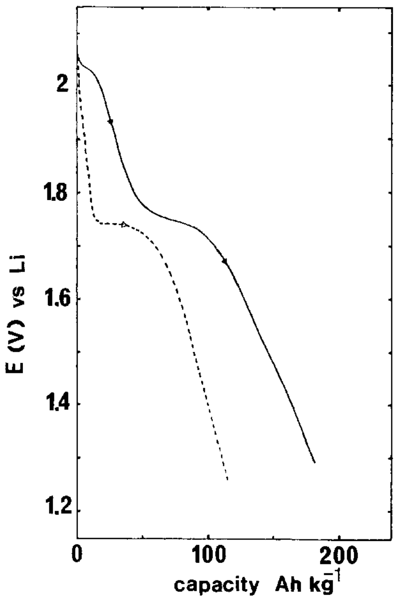

Fig. 5. Chronopotentiograms at constant current of: ---, a mechanical mixture of CuO and TiO_2 (10/90); ——, a titania-supported copper catalyst CuO–TiO_2 (10/90). (1 M $LiClO_4$–PC; 1 mA.)

3.2.1.2. Chronopotentiometry. In order to obtain quantitative information (faradic yields) on the different reduction steps observed on the voltammetric curves, electroreduction of titania-supported copper catalyst (CuO–TiO_2, 10/90) was performed at constant current (Fig. 5). The coulombic efficiency of the electroreduction process at 2.2–2 V suggests that 50–60% of CuO contained in the catalyst is reduced to copper in this potential range.

3.2.2. Composition effects of CuO–TiO_2 catalysts. Electrochemical results obtained on titania-supported copper catalysts of various compositions are reported in Fig. 6. For this study, the active materials have been mixed with pure graphite which ensures a better electronic transfer. The faradic capacity of the CuO electroreduction process at 2.2–2 V depends on CuO–TiO_2 composition: the amount of copper metal deposited on titania support in this range

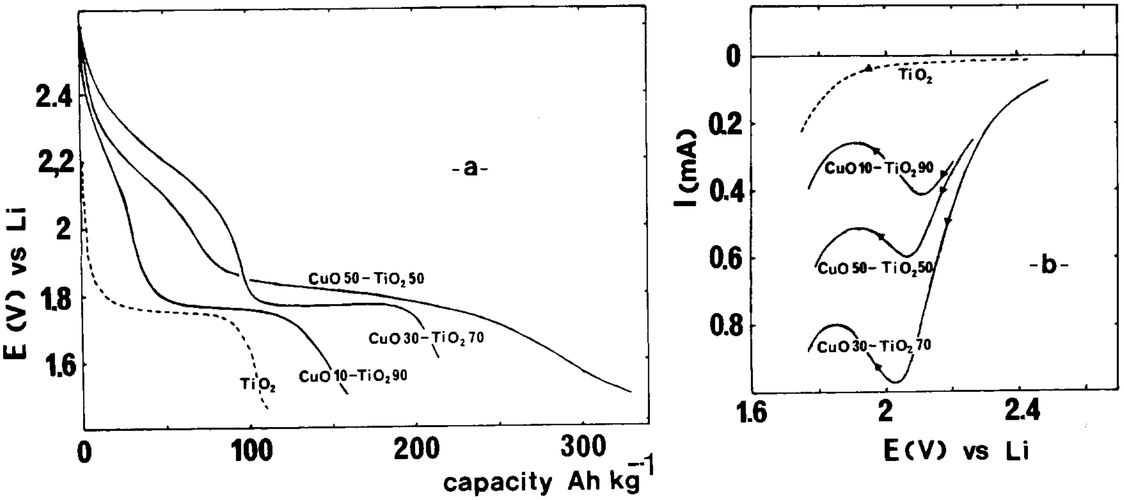

Fig. 6. Titania-supported copper catalysts of various compositions. (a) Chronopotentiometric study at constant current (1 mA); (b) voltammetric study (1 mV s^{-1}). (1 M $LiClO_4$–PC; 28°C.)

of potentials increases with CuO content. This phenomenon is limited and the amount of deposited copper is greatest (~ 15%) when the composition of the $CuO–TiO_2$ catalyst is 30/70. Furthermore, the faradic capacity of the second electroreduction process at 1.8 V increases with CuO content in the catalyst: the higher the CuO content, the deeper the reduction process at 1.8 V. Moreover, for any CuO content the faradic yield at the end of the electroreduction processes at 2 V and 1.8 V always corresponds to the theoretical yield for complete reduction of CuO and TiO_2.

In order to determine the oxidation state of titania in $CuO–TiO_2$ catalysts of various compositions during electroreduction, we have expressed the faradic yields in terms of F per mole of CuO (for potentials up to 2 V) and per mole of TiO_2 (below 2 V) (Fig. 7). As we have suggested above, it clearly appears that for any CuO content the faradic yields engaged during the electroreduction process at 1.8 V always correspond to the theoretical values required for the complete reduction of Cu(II) to Cu(O) and TiO_2 to TiO_2Li_x (with $x \cong 0.3$). Moreover, for any CuO content the quantities of electricity recovered during reoxidation processes at different stages of the electroreduction process at 1.8 V (solid curves) are always lower than the ones obtained with TiO_2 alone (dashed curves). These results suggest that the remaining titania-supported copper oxide is reducible at 1.8 V, i.e. during the TiO_2 electroreduction step. In addition, the reoxidation process of the TiO_2Li_x phase does not occur because the faradic balances engaged during the electroreduction process at 1.8 V are not close to the theoretical ones required for the complete reduction of Cu(II) to Cu(O), i.e. 0.12 F per mole of TiO_2 for $CuO–TiO_2$ (10/90) (Fig. 7a), 0.37 F for $CuO–TiO_2$ (30/70) (Fig. 7b) and 1.6 F for $CuO–TiO_2$ (50/50) (Fig. 7c). Beyond these theoretical values required for the complete reduction of Cu(II) to Cu(O), the reoxidation of the TiO_2Li_x phase occurs as for the TiO_2 support alone. This phenomenon shows that TiO_2Li_x may not be stabilized in the presence of Cu(II).

We conclude that CuO electroreduction in titania-supported copper catalysts occurs in two steps. Firstly, at a potential close to 2 V according to the path

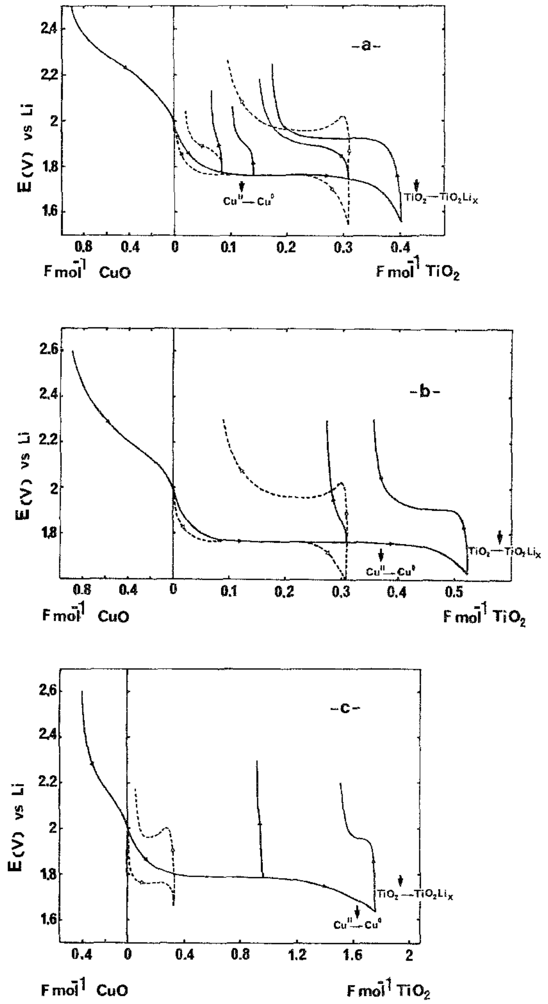

Fig. 7. Chronopotentiometric study of TiO_2 (---) and titania-supported copper catalysts of various compositions (——). (a) $CuO–TiO_2$ (10/90); (b) $CuO–TiO_2$ (30/70); (c) $CuO–TiO_2$ (50/50). (1 M $LiClO_4$–PC; 28°C; 1 mA.)

$$\mathrm{Cu(II)} + 2e \xrightarrow{\mathrm{TiO_2\ support}} \mathrm{Cu(O)},\ \mathrm{TiO_2}$$

Secondly, at a potential close to 1.8 V according to the successive reactions: electroreduction of TiO_2 according to

$$\mathrm{TiO_2} + xe + x\mathrm{Li}^+ \rightleftharpoons \mathrm{TiO_2Li}_x$$

followed by a chemical reaction of TiO_2Li_x and Cu(II) through an internal electron transfer according to

$$\mathrm{Cu(II)} \xrightarrow{\mathrm{TiO_2Li}_x} \mathrm{Cu(O)},\ \mathrm{TiO_2}$$

Such an activation of CuO electroreduction never occurs when CuO and TiO_2 are mechanically mixed.

The obvious conclusion of this electrochemical study is that copper strongly interacts with the titania support as with ZnO [3], Al_2O_3 or SiO_2 [1].

4. Conclusion

A strong interaction between CuO and the titania support is demonstrated by means of electrochemical methods. This interaction enhances the reducibility of CuO which partially occurs at room temperature at 2 V instead of 1.2 V as in the Li–CuO battery system. The remaining titania-supported copper oxide is reducible at 1.8 V, i.e. during the TiO_2 electroreduction step.

The ability of the titania support to be electrochemically reduced at room temperature, while H_2 chemical reduction only occurs on and after 500° C, may be of interest for catalysis applications. Indeed, TiO_2 electroreduction leads to lithium incorporation in the TiO_2 lattice with the formation of a Li_xTiO_2 phase which has a crystal structure close to that of TiO_2.

In conclusion, electrochemistry may be a novel way of determining and controlling the redox states of metal-supported catalysts.

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