Electrochemical carboxylation of olefins to form monocarboxylic products by using $12CaO•7Al_2O_3$ electride cathode

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The conversion and utilization of CO_2 have attracted extensively attention in the whole world. Electrochemical fixation of CO_2 into unsaturated hydrocarbons to form useful compounds is attractive [1,2]. Conventionally, electrocarboxylation with CO_2 is performed in undivided cell using Al or Mg as sacrificial anodes, and both mono- and dicarboxylic or only dicarboxylic products are produced. Enhancement in the yield of the monocarboxylic product is desired.

Recently, we found that $12CaO•7Al_2O_3$ (C12A7) electride [3] could be used as a cathode for generation of superoxide ions and hydroxylation of arylboronic acid [4]. C12A7 electride is an oxide with unique structures, which contains positive framework and extraframework electrons are located in the cages as anions. It exhibits metallic conduction with the work function of 2.4 eV. On the other hand, CO_2 molecules are easily adsorbed on C12A7 electride surface. However, similar to glassy carbon, the CO_2 reduction is not observed at C12A7 electride cathode in Bu_4NClO_4-MeCN solution. These properties may lead to the reduction of substrate, and further combination of CO_2 to form monocarboxylic products.

In this presentation, we show the carboxylation of cinnamate esters and styrene derivatives with CO_2 by using C12A7 electride cathode in a divided cell without sacrificial anode to form the monocarboxylic products. For instance, the carboxylation of methyl cinnamate followed by EtI treatment gives the corresponding product, ethyl methyl 2-benzylmalonate, with a yield of 91% at a charge apply of 3 $F \cdot mol^{-1}$ at C12A7 electride cathode, while that at Pt and GC cathode is 82% and 67%, respectively. However, Pt is not active for the carboxylation of styrene derivatives. As an example, at a charge apply of 3 $F \cdot mol^{-1}$, the monocarboxylic product, 2,3-diphenylpropionic ester, from *trans*-stilbene is 82%, 60% and 20% at C12A7 electride, GC and Pt cathode, respectively. We suggest that C12A7 electride could be a new cathode for potential applications in electrochemistry.

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References

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