

Synthesis and characterization of supported Sn/ γ -Al₂O₃ and Sn/ZSM5 catalysts for CO₂ reduction in electrochemical cell



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ABSTRACT

To improve CO₂ conversion efficiency at the cathode of an electroreduction cell, different loadings of Sn on high surface area supports, γ -Al₂O₃ and ZSM5, were synthesized by wet impregnation followed by hydrogen reduction. As synthesized catalysts were characterized using X-Ray diffraction (XRD), thermal gravimetric analysis (TGA), transmission electron microscope (TEM) and cyclic voltammetry studies. By comparing voltammetry results it is found that 20 wt% Sn catalyst is electrochemically more active towards CO₂ reduction than other lower and higher loadings of Sn on both the supports. The reason for such observation is explained based on physical characterization of γ -Al₂O₃ and ZSM5. In 20 wt% Sn catalyst, the Sn remains in dispersed form adhering to the porous wall of γ -Al₂O₃ and ZSM5 satisfying percolation limit. Whereas, at lower loadings, electronic connectivity between Sn particles are lost and, at higher loadings, Sn particles agglomerate blocking the pores of the support. Reduction of CO₂ using 20Sn/Al₂O₃ and 20Sn/ZSM5 catalyst is found to be selective towards methane and carbon monoxide formation from the product analysis of the electroreduction cell using gas chromatograph. In electroreduction cell, 20Sn/ZSM5 cathode produced higher current and more faradaic efficiency (20.4%) towards methane formation compared to 20Sn/Al₂O₃ cathode (12.9%).

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1. Introduction

Fossil fuel use is increasing day by day resulting in excessive release of CO₂ in the atmosphere. According to National Oceanic and Atmospheric Administration (NOAA), the atmospheric concentration of CO₂ increases each year by 2 ppm leading to an inevitable impact on global warming [1]. There is an urgent need to explore novel technique to sequester CO₂ coming out with exhaust gas and its conversion into valuable products. Several methods have been suggested for CO₂ conversions to organic compounds [2,3]. The electrochemical reduction method is one of the potential and simple alternative method that could be used for storing of renewable electrical energy in the form of CO₂ electro-reduction products [4]. Investigators have reported the use of metallic foil as cathode electrode for electrochemical reduction of CO₂ in aqueous and non-aqueous electrolyte with the proposed mechanism as described by Jitaru [5], Chaplin and Wragg [6] and Li [7]. The difficulty associated with electrochemical reduction is competing hydrogen evolution reaction (HER), which takes place along with CO₂ reductions [6,7]. However, the metal groups such as

Pb, In, Sn, Hg and Cd which have high hydrogen overvoltage [7] can minimize HER and thus can be used as cathode catalyst for CO₂ conversion to organic compounds in electrochemical cells. Different organic product obtained during CO₂ electro-reduction on different metal electrodes is discussed in detail in [5–7]. Although Cu is the most promising cathode catalyst for CO₂ reduction in terms of conversion to organic compounds [8], but it suffers from competing HER and degradation during electrochemical reduction as reported recently by Garg and Basu [9]. Sn can be a viable alternative catalyst used for CO₂ reduction due to its high selectivity towards methane formation, low cost and non-toxic in nature.

Conventionally, metallic Sn foil has been used as an electrode for CO₂ electro-reduction [5–7]. However, incorporation of supported catalysts, as used in many industrial applications, may give high surface area, which not only enables higher reaction rate but also higher heat and mass transfer. γ -Alumina (γ -Al₂O₃) and zeolite (ZSM5) are most widely used catalyst supports due to its high surface area, large porosity, favorable cost and mechanical strength [10]. In recent times, these supports have been used as an adsorbent in physical adsorption of CO₂ from flue gas [11,12], which reveals its high storing and capturing tendency of CO₂ molecules. Thus, it is expected in gas phase CO₂ electro-reduction, the

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concentration overpotential will be lower compared where γ -Al₂O₃ and ZSM5 are not used as catalyst support. It may be noted that an electrode in electro-reduction cell should provide both ionic and electronic conductivities. Since ZSM5 and γ -Al₂O₃ essentially non-conducting in nature, the electronic conductivity has to be provided by the inter connected metallic Sn catalyst particles present in the pore walls of the supports. Thus it is essential that porous supports e.g., ZSM5 and γ -Al₂O₃ is coated with catalyst particle which are interconnected and the percolation limit is reached. The ionic conductivity may be provided by electrolyte solution and Nafion[®] ionomer used during preparation of catalyst slurry to coat the electrode.

In this work, we demonstrate γ -Al₂O₃ and ZSM5 supported Sn catalysts efficiently reduce CO₂ to different organic products. As ZSM5 has more surface area compared to that for γ -Al₂O₃ therefore, the results obtained for ZSM are better compared with γ -alumina. Due to percolation limit and small pore size, it is demonstrated that there exist maxima in catalyst loading for effective CO₂ reduction. Optimum catalyst loading has been justified based on physical and electrochemical characteristics. Finally, the product obtained from electroreduction cell for CO₂ is analysed using gas chromatograph and reported in the form of faradaic efficiency.

2. Experimental

2.1. Materials

The precursors used for the preparation of cathode electro-catalyst was SnCl₂·H₂O (Merck Germany) and the supports used for preparation of catalyst were γ -Al₂O₃ (Alfa Aesar) and zeolite ZSM5 (Alfa Aesar). Carbon paper (90T, Toray, USA) was used as backing

layer for the powdered catalyst to prepare Sn/ γ -Al₂O₃ and Sn/ZSM5 coated electrodes. Nafion[®] (DE 521, DuPont, USA) dispersion and isopropanol (Merck, Germany) were used to prepare the catalyst slurry for coating. The electrolyte used for half-cell studies was KHCO₃ (99.5%, Merck, Germany). Nafion[®] 117 (DuPont, USA), proton exchange membrane (PEM), was used as electrolyte to prepare membrane electrode assembly for CO₂ reduction in electrochemical cell. H₂O₂ (30 wt%, Merck, Germany) and H₂SO₄ (Merck, Germany) were used for membrane pre-treatment. Pt/C (40%wt, Johnson Matthey) was used as anode catalyst. Tedlar bag (CEL scientific) was used to collect gases for product analyses.

2.2. Catalyst synthesis and characterization

The desired amount of tin chloride precursor and supports, γ -Al₂O₃ or ZSM5, were dissolved and dispersed in 50 mL of ultrapure water separately. The above mixture was stirred overnight using a magnetic stirrer. It was then dried at 70–80 °C, followed by calcination of the dried sample at 450 °C for 4 h in a muffle furnace. After calcination, it was reduced in a split furnace using a tubular reactor in hydrogen atmosphere at 450 °C for 5 h. Following above treatment, three different loadings of XSn/Al₂O₃ and XSn/ZSM5 (10, 20 and 40 wt% of Sn) were synthesized. The nomenclature used to name the catalysts is XSn/Support, where X is the nominal content of Sn (in wt.%) and remaining amount (100-X in wt%) is support. γ -Al₂O₃ is written as Al₂O₃ in the manuscript. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) data for Sn/ZSM5 and Sn/Al₂O₃ are given in the supplementary section. It is clearly observed in Figs A1-A3 and B1-B3 that the Sn particles are uniformly dispersed on the surface of ZSM5 and Al₂O₃. From the EDX analysis, no impurities are found in the catalyst and Sn is loaded in

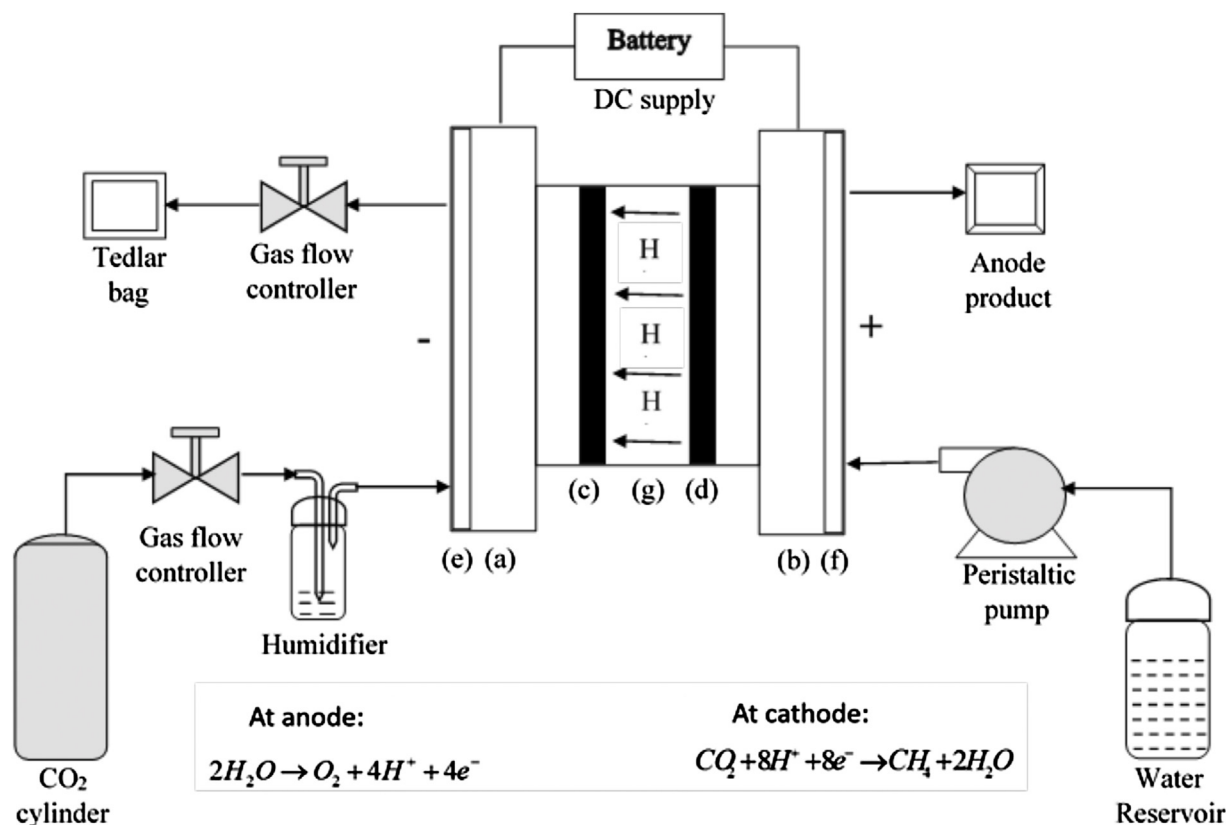


Fig. 1. Schematic diagram of electroreduction cell for continuous CO₂ reduction. (a) and (b) Teflon blocks; (c) & (d) Pt/C anode and XSn/ γ -Al₂O₃ and XSn/ZSM5 cathode (e) and (f) Current collectors; (g) Nafion[®] membrane;.

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