

Cu/CeO₂/AlPILC nanocomposites in preferential oxidation of CO: Effect of method of preparation on the catalytic activity

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Introduction

Pillared interlayered clays (in short, PILCs) are a class of molecular sieve-like materials that have large pores, high surface areas, strong acidity accompanied with good thermal stability [1]. Traditionally pillared clays and transition metal incorporated pillared clays have been used in a variety of reactions such as alkylation, cracking, dehydrogenation and oxidation reactions [2-3]. In recent years these solids have been used as catalytic supports for clean technology applications such as DeNO_x [4]. To our knowledge, pillared clays have not been reported as catalyst supports for preferential oxidation (PROX) of CO. It was earlier reported that CuO-CeO₂ exhibits significant activity in the oxidation of CO [5]. This paper reports the different methods of preparation of CuCeO₂ supported clay and its characterization by various techniques. The catalytic efficiency of the materials was evaluated for the preferential oxidation of CO in excess of hydrogen.

Materials and Methods

Ce(NO₃)₃·6H₂O, Cu(NO₃)₂·3H₂O and citric acid were used as received without further purification. The Al-PILC (Aluminum pillared clay) sample prepared using ultrasonication (6) was used as support for further loading of CuO-CeO₂ by different methods. A series of Cu/CeO₂/clay nanocomposites with the composition Cu_{0.01}Ce_{0.09}Clay_{0.9} to Cu_{0.05}Ce_{0.45}Clay_{0.5} were prepared by three different methods viz; the amorphous citrate route (ACR), deposition precipitation (DP) and wet impregnation method (WIM) following the literature procedure reported elsewhere.

In a typical deposition precipitation method, appropriate amounts of Ce(NO₃)₃·6H₂O and Cu(NO₃)₂ were dissolved in 10 ml of distilled water to obtain a clear solution. Calculated amounts of pillared clay was dispersed in this solution and mixed thoroughly with a magnetic stirrer. To this, 0.1M KOH was added dropwise with continuous stirring at ambient, till complete precipitation (pH 10). Subsequently, the precipitate was filtered and was washed several times with distilled water to remove the potassium ions and then dried in an air at 373 K. The dried sample was calcined at 673 K for 8 h to obtain the final catalyst.

The Cu/CeO₂/clay samples were characterized using powder X-ray diffraction, diffuse reflectance UV-visible (DRUV-vis) spectroscopy and temperature Programmed Reduction (TPR) experiments Thermal conductivity detector was employed to measure the volume of hydrogen consumed during the reduction process.

Results and Discussion

The Cu/CeO₂/clay nanocomposites prepared by three different methods were characterized for its structural, textural and redox properties. Among the various methods employed, Cu/CeO₂/clay nanocomposites prepared by deposition precipitation method showed

a high activity in the PROX of CO in hydrogen rich environment with longer durability (Figure 1). The structure-activity relationship between the samples prepared by different methods showed that the samples prepared by deposition precipitation method enables the formation of easily reducible Cu²⁺ species, with a uniform dispersion of active components (Cu/CeO₂). However, the samples prepared by other synthesis procedures showed Cu species present either as bulk oxides or as poorly reducible Cu²⁺ species. The study revealed that the method of preparation plays a vital role in the formation of different types of Cu species, which in turn alters the catalytic activity.

Significance

Pillared clays were effectively utilized as catalyst support for the preparation of Cu/CeO₂/clay nanocomposites that finds application in the preferential oxidation of CO in hydrogen rich environment.

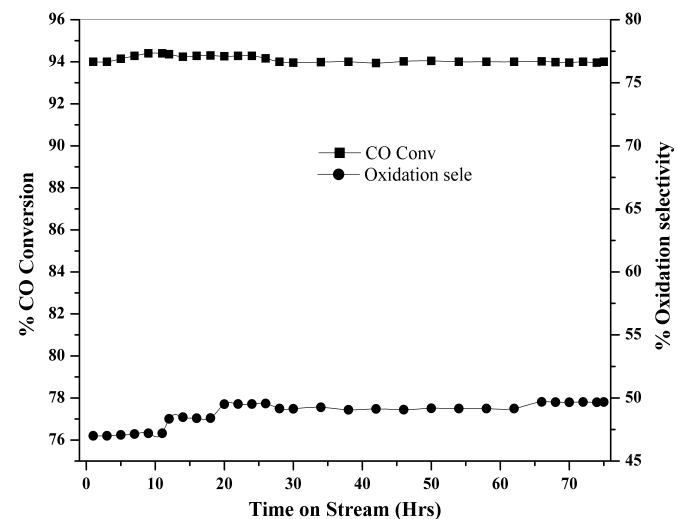


Figure 1. Effect of time on stream on the preferential oxidation of CO (PROX) over Clay supported CuO-CeO₂ nanocomposites. Reaction conditions: Catalyst: DP-50 (0.5 cc); feed: H₂ (74.05%), CO (0.5%), CH₄ (2.05) and CO₂ (23.40%); O₂/CO: 1.0; GHSV: 10,000 h⁻¹; Temperature: 423 K.

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