Effect of method of preparation of $CuCeO_2$ mixed oxides supported on Al-PILC on 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 DeNOx [4]. To our knowledge, pillared clays have not been reported as catalyst supports for preferential oxidation (PROX) of CO.

Cerium oxide is used as a promoter in the three-way catalyst (TWC) for automotive emission control. $CuO–CeO_2$ exhibits significant activity in the oxidation of CO [5]. The well-known enhancement of oxidation activity of CuO, when supported on reducible oxides like CeO_2, was attributed to "synergistic" effect [6]. It is proposed that well dispersed CuO on CeO_2, which is reducible at a lower temperature with respect to bulk CuO, could easily adsorb CO. As a result, this catalyst exhibited high activity/selectivity for low temperature CO oxidation [7]. It was postulated that the presence of copper enhances the redox behavior, the oxygen storage capacity and thermal stability of ceria [8]. This paper reports the preparation of $CuCeO_2$ on clay by three different methods and their characterization by various techniques. The catalytic activity was investigated for PROX of CO in excess of hydrogen on the physico-chemical properties of the catalyst samples.

Materials and Methods

$Ce(NO_3)_3.6H_2O$ (Loba Chemie, 99.9%), $Cu(NO_3)_2.3H_2O$ (Merck, 99%) and citric acid (S.D. Fine Chem., 99.7%) were used as received without further purification. A series of $CuCeO_2$-Clay nanocomposites with the composition $Cu_{0.01}Ce_{0.09}Clay0_{.9}$ 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). The Al-PILC (Aluminum pillared clay) sample prepared using ultrasonication [9] was used as support for further loading of $CuO-CeO_2$ by different methods. The $CuCeO_2$-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

Fig. 1 shows powder XRD patterns of CuCeClay composites prepared following three different routes with varying $CuCeO_2$ loadings. The (001) reflection of the Al-PILC ($2\theta=5.6°$) in all the samples was intact indicating the preservation of pillared clay structure. Peaks due to cubic fluorite CeO_2 (PDF-ICDD 34-0394) were seen in all samples and no characteristic peaks due to crystalline CuO phase (typically at $2\theta= 35.5, 38.7, 48.7$ and 61.5)

were observed indicating the absence of bulk CuO phase (with crystallite size ≥ 3 nm). This suggests that the copper oxide was highly dispersed on the CeO_2 surface in all the samples prepared in this study. The crystallite size calculated by the Scherrer analysis of $CeO_2(111)$ peak was found to depend on the method of preparation and it increased in the order; amorphous citrate route < deposition precipitation < wet impregnation method. Crystallite size of ceria was found to be larger in the samples prepared by wet impregnation method (5-6 nm) than that in the samples prepared by amorphous citrate or deposition precipitation methods (< 3nm).

Fig.2 shows the typical UV-Vis spectrum of the sample (50 wt% $CuCeO_2$) prepared by three different methods. A wide band in the region at 215 to 350 nm was attributed to the $Ce^{4+}-O^{2-}$ charge transfer and a broad band in the 400-500 nm range assigned to the spinel like $CuAl_2O_4$ species. The samples ACR-10 to ACR-30 did not show absorption in this region, indicating the absence of $CuAl_2O_4$ species. This suggests that CuO, which is present on the surface of the clay matrix easily interacts with the Al-PILC support to form $CuAl_2O_4$ species in the WIM samples. A broad band in the region 600-900 nm is attributed to the *d-d* transition of Cu^{2+} situated in octahedral environment with O_h symmetry. This band is most prominent in the samples prepared by WIM even with low Cu content which signifies that majority of the Cu^{2+} is present in the octahedral position in the WIM sample.

TPR profiles (Fig. 3) shows that the method of preparation clearly affects the nature of the CuO species formed and no peak due to Al-PILC is seen, as alumina is known to be passive to H_2 reduction. Pure CuO exhibits a single reduction peak, T_{max} at 588 K. Pure CeO_2 shows reduction maximum at 703 (normally not, unless solid solutions are prepared involving other cations) and 1100 K attributable to the reduction of ceria surface oxygen and bulk oxygen, respectively.

The TPR profile of the sample ACR-30 shows three reduction maxima at 648, 734 and 795 K (not matching with Fig) (Fig.3a, nomenclature in the Fig is not correct). The T_{max} at 648 K may be assigned to the reduction of well-dispersed CuO in close contact with ceria. The higher temperature required for reduction than pure CuO suggests that Cu^{2+} ions are present in a highly isolated state, which strongly interacts with the support, thereby requiring higher reduction temperature. The peak at 734 K is attributed to the reduction surface oxygen of ceria. In the ACR technique, the citric acid used as a complexing agent as well as a fuel, on calcination, generates heat that helps in the fine dispersion of copper and ceria on the surface of the Al-PILC, resulting in the strong interaction of the metal ions with Al-PILC matrix.

The TPR profile of the sample prepared by deposition precipitation route (DP-30) gave two reduction peaks at 423 and 494 K assigned to the reduction of cationic copper, signifying the presence of two types of copper oxide species. The peak at lower temperature may be attributed to a very finely dispersed CuO interacting with ceria whereas the high temperature peak was due to clustered CuO interacting with ceria. The sample prepared by wet impregnation method (WIM-30) showed peaks similar to those of DP-30 indicating that the nature of Cu species formed were similar in these two methods. However, the temperature of reduction of Cu species was higher in the WIM-30 as compared to the DP-30 sample.

In order to study the effect of concentration of copper on the nature of Cu species formed, the TPR of the samples obtained through deposition precipitation method containing different amounts of $CuCeO_2$ in Al-PILC was carried out and the profiles are shown in Fig. 3 b. At lower concentration of CuO (DP-10), the TPR profile shows three peaks viz., a shoulder

at 474 K and two peaks at 561 and 802 K. The shoulder at 474 K is due to the reduction of highly dispersed CuO on the CeO_2 surface and the peak at 561 K is due to the reduction of clustered CuO present in the $CuCeO_2$clay nanocomposites. Increasing the concentration of CuO in the CuCeClay nanocomposite resulted in the shifting of the lower temperature peak towards the low temperature regime. In contrast the higher temperature peak shifted to the higher temperature regime with the peak becoming relatively broad. The broadening of the peak with increase in the concentration of CuO in the CuCeClay nanocomposites can be attributed to the formation of larger CuO crystallites accompanied by poor dispersion of CuO on the surface of ceria-Al-PILC. As can be seen, in all the samples under study, the ceria surface oxygen reduction takes place at higher temperature as compared to pure ceria (Fig.3). This is because the dispersion of ceria on alumina is known to stabilize the surface ceria and facilitate bulk ceria reduction. However with increase in the CeO_2 and CuO content in the nanocomposites, the temperature of surface ceria reduction shifts towards lower temperature (Fig. 3 b). This observation implies that with high ceria loading the surface ceria is less stabilized and interaction of copper oxide with ceria surface improves ceria reducibility.

Significance

The information gained may aid in the development of these catalysts, which may help to find an alternative to precious metal based catalysts for the Preferential Oxidation (PROX) of CO.
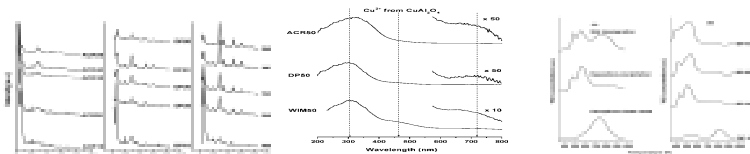

Fig.1. PXRD patterns of the samples prepared by different methods

Fig.2 DRUV-Vis spectra of the $CuCeO_2$ clay nanocomposites

Fig. 3a TPR of 30 wt % Cu CeO_2 by three methods, 3b. Deposition Precipitation method with different $CuCeO_2$ content

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