DIRECT PROPYLENE OXIDATION USING MOLECULAR OXYGEN USING MESOPOROUS SILICA AS THE SUPPORT

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ABSTRACT

We synthesized and investigated CuO\textsubscript{x}/SiO\textsubscript{2} catalysts in the propylene partial oxidation. Ordered mesoporous silica (KIT-6, \textit{Ia\overline{3}d} morphology) was used to load 1-10 wt. \% Cu and subsequently modified with Na, K and Ca. The synthesized materials were characterized by N\textsubscript{2} physisorption, XRD, TEM-EDS, CO\textsubscript{2}-TPD, \textit{operando} UV/Vis DRS, \textit{operando} XANES and pyridine DRIFT spectroscopy. Regardless of the CuO\textsubscript{x} loading, catalyst deactivation was observed during propylene oxidation in the presence of non-modified catalysts. The resulting bulk CuO\textsubscript{x} promotes acrolein selectivity. Alkali (K and Na) modification produces finely dispersed alkali metal cations, associated with the CuO\textsubscript{x} phase, resulting in a greatly stabilized morphology and catalytic activity. The effect of Ca on decreasing the nucleophilic character of oxygen species in CuO\textsubscript{x} is negated by charge compensation by strongly adsorbed hydroxyl groups and Ca modification for PO selectivity is inefficient.

Keywords: nucleophilicity modulation, epoxidation, mesoporous silica.

INTRODUCTION

Propylene can be catalytically converted into several useful C\textsubscript{3} oxygenates, such as propylene oxide (PO), propanal and acrolein [1]. PO is a highly desired chemical as it is used in the production of propylene glycol ethers, propylene glycol and polyether polyols [2]. Most PO is produced by the mature and industrially established chlorohydrin process (CHPO), PO/styrene and PO/tert-butyl processes through a peroxidized intermediate and lately the hydrogen peroxide to propylene oxide (HPPO) process over single-site TS-1 or Ti-MWW catalysts using H\textsubscript{2}O\textsubscript{2} as an oxidant. HPPO process uses H\textsubscript{2}O\textsubscript{2} as an oxidant and produces PO with a selectivity of 99 \% [3]. There are several drawbacks for each of these processes, such as high cost of the reactants (H\textsubscript{2}O\textsubscript{2}), large quantity and a low price of the co-products (stylene monomer or tert-butyl alcohol) and environmental pollution (chlorinated lime as side product)[2,4]. The above mentioned drawbacks have driven research into direct gas-phase epoxidation of propylene using molecular oxygen. In our work [5], we investigated the underlying reasons which determine PO selectivity in propylene epoxidation.

EXPERIMENTAL

The KIT-6 silica support material was synthesized according to a procedure from Kim et al.[6] CuO\textsubscript{x}/SiO\textsubscript{2} catalysts were prepared by precipitation of the copper-ammonia complex ([Cu(NH\textsubscript{3})\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2+}) via dilution hydrolysis method (inspired by Menget et al.[7]). For the alkali and earth alkali modification, 30 mL of aqueous solutions of nitrate salts (0.1 M NaNO\textsubscript{3}, 0.05 M Ca(NO\textsubscript{3})\textsubscript{2} and 0.1 M KNO\textsubscript{3}) was used. The samples were marked as xCu\textsubscript{y}, where x is the mass loading of copper and y is the modifying adatom. The BET surface area, total pore volume and average pore size distribution were determined from N\textsubscript{2} adsorption/desorption isotherms obtained at -196 °C (Micromeritics, model TriStar II 3020).
Mesoporous ordering of the prepared CuO$_x$/SiO$_2$ catalysts was analyzed using powder X-ray diffraction (XRD) analysis. The PANalytical Empyrean diffractometer with Bragg-Brentano geometry and Cu Kα radiation was used. The core morphology of the samples was studied by Schottky field-emission transmission electron microscope (JEM-2200FS, JEOL Ltd.), operating at 200 kV. The chemistry of the samples was analysed in scanning-TEM mode using windowless ultrafast large angle 100 nm$^2$ SDD-EDS spectrometer (EX-24200M1G2T, JEOL), allowing efficient collection of X-rays. High-angle annular dark field (HAADF) detector (EM-24630UHADF, JEOL) was used for collecting of only incoherently scattered electrons, highly sensitive to variations in the atomic number (Z contrast). Structural and electronic properties of CuO$_x$ phase with and without alkali modification were analyzed with UV/Vis spectrophotometry (Perkin Elmer, model Lambda 35) at room temperature in the range between 200-1100 nm. In-situ experiments were performed in the HVC-VUV Praying Mantis Reaction Chamber (Harrick) using the Perkin Elmer Lambda 650 UV/Vis spectrophotometer. Lewis and Bronsted acidity of the prepared catalysts was investigated using pyridine as a probe molecule. Experiments were performed in a DiffusIR cell (PIKE Technologies) attached to a Perkin Elmer Frontier spectrometer. Basicity of the prepared catalysts was analyzed using CO$_2$ as a probe molecule. Experiments were performed in a Micromeritics AutoChem II 2920 apparatus. The Cu K-edge X-ray absorption spectra (XAS) of 5Cu, 5CuNa and 5CuCa catalysts were recorded in-situ during the propylene oxidation reaction at 350 °C in transmission detection mode at the XAFS beamline of the ELETTRA synchrotron radiation facility in Trieste, Italy. Catalytic performance of the synthesized catalysts was tested in a tubular fixed-bed quartz reactor (I.D.=10 mm) at atmospheric pressure. In a typical experiment, 50 mg of the catalyst was diluted with 200 mg of SiC and fixed between two quartz wool flocks. The reaction products were monitored by gas chromatography (Agilent, model 7890A); the GC device was equipped with the DB-WAXETR (Agilent) and the HP-PlotQ columns and a TCD detector.

**RESULTS AND DISCUSSION**

Figure 1. BF-STEM image of the 5CuNa catalyst showing ordered mesoporous SiO$_2$ support, and aggregates of highly-dispersed CuO$_x$ in the 5CuNa catalyst on the surface of SiO$_2$ substrate.
oxidation of the catalyst where the structural changes induced by the reduction are, to a greater extent, reversible in the 5CuNa catalyst, when compared to the unmodified catalyst.

Abundance and strength of basic sites in the synthesized catalysts was analyzed using CO$_2$-TPD analysis, which revealed two separate clusters of peaks for all the catalysts: a low-temperature cluster related to weak basic sites (between 0 and 300 °C), and a high-temperature cluster (comprised of two peaks centered at 450 and 600 °C) connected to strongly basic sites. Deconvolution of CO$_2$-TPD profiles showed that only in case of Na and K modification, the low-temperature cluster consists of three distinct peaks, centered at 60, 94 and 155 °C.

Abundance and binding strength of hydroxyl groups to the catalyst surface was analyzed using H$_2$O-TPD-MS technique. It can be seen that Cu addition to KIT-6 causes an increase in the amount of water and hydroxyls. Their number is decreased after Na and K modification. The largest abundance and strength of hydroxyl binding to the catalyst surface (based on the position of the high-temperature desorption peak) is observed after modification with Ca.

Operando XANES analysis revealed that a substantial fraction of Cu$^{2+}$ is reduced to Cu$^+$ during propylene oxidation. The kinetics of oxygen abstraction and replenishment are substantially different, indicative of modified chemistry of the nucleophilic oxygen species, present in 5CuNa catalyst in contrast to others (5Cu and 5CuCa). LCF (linear combination fit) analysis of the 5Cu, 5CuNa and 5CuCa catalysts (at 350 °C in O$_2$/He atmosphere) shows that all Cuis present as Cu$^{2+}$ and the majority (~90 %) is subnanometer Cu$^{2+}$ clusters. Only ~10 % is present as nanocrystalline CuO.

Over the non-promoted catalysts, the catalytic reaction products are CO$_2$, CO, water, acrolein and trace amounts of other oxygenates (acetone, propanal, propanol), however, the latter present less than 5 % of the C-containing products. Regardless of the Cu content, strong deactivation is observed over all unmodified catalysts: they lost more than 60 % of initial activity during the 17 h of propylene oxidation, which is likely related to sintering of oligomeric [Cu-O-Cu]$_n$ species. Modification of 5Cu catalysts with Na and K greatly minimized catalyst deactivation: minimal deactivation is observed during 17 h TOS for the 5CuNa catalyst, whereas catalytic activity of 5CuK and 2.5CuNa stabilizes after 10 h following the initial decrease of about 25 %. After Na and K addition, a notable (~10 %) PO selectivity was also observed, which increased with prolonging TOS. With Ca modification of

Figure 2. Temporal evolution of propylene conversion (left panel) and the selectivity (mid panels) and Cu$^+$ fraction as a function of reaction time for the investigated catalysts (right panel).
the 5Cu catalyst, a dramatic increase in the initial catalytic activity is observed (9 and 6.5 \% propylene conversion for 5CuCa and 5Cu catalysts, respectively) with trace (below 0.5 \%) PO selectivity. Acrolein and CO\textsubscript{x} selectivities remain very similar to the unmodified 5Cu catalyst.

CONCLUSION

Based on the research done, we propose that Cu\textsuperscript{+} is not crucial for PO formation; instead the electropositive Na\textsuperscript{+} and K\textsuperscript{+} decrease the nucleophilic strength of oxygen in CuO\textsubscript{x}, making its attack on the allylic hydrogen of propylene less invasive. Alkali (K and Na) modification produces finely dispersed alkali metal cations, associated with the CuO\textsubscript{x} phase, resulting in a greatly stabilized morphology and catalytic activity. The stifling effect of Ca on the nucleophilic character of oxygen species in CuO\textsubscript{x} is negated by charge compensation by strongly adsorbed hydroxyl groups. As a result, Ca modification for PO selectivity is inefficient.

REFERENCES