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

Janvit Teržan[1, 2], Petar Djinovic[1], Janez Zavašnik[3, 4], Iztok Arcon[2, 5], Gregor Žerjav[1], Matjaž Spreitzer[2, 6] and Albin Pintar[1]

[1]Department for Environmental Sciences and Engineering, National Institute of Chemistry, Slovenia
[2]Jožef Stefan International Postgraduate School, Slovenia
[3]Centre for Electron Microscopy and Microanalysis, Jožef Stefan Institute, Slovenia
[4]Max-Planck-Institut für Eisenforschung GmbH, Germany
[5]University of Nova Gorica, Slovenia
[6]Advanced Materials Department, Jožef Stefan Institute, Slovenia
E-mail: janvit.terzan@ki.si

ABSTRACT

We synthesized and investigated CuO_x/SiO_2 catalysts in the propylene partial oxidation. Ordered mesoporous silica (KIT-6, *Ia3d* morphology) was used to load 1-10 wt. % Cuand subsequently modified with Na, K and Ca. The synthesized materials were characterized by N_2 physisorption, XRD, TEM-EDS, CO_2-TPD, *operando* UV/Vis DRS, *operando* XANES and pyridine DRIFT spectroscopy. Regardless of the CuO_x loading, catalyst deactivation was observed during propylene oxidation in the presence ofnon-modified catalysts. The resulting bulk CuO_x promotes acrolein selectivity. Alkali (K and Na) modification produces finely dispersed alkali metal cations, associated with the CuO_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_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_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_2O_2 as an oxidant. HPPO process uses H_2O_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_2O_2), large quantity and a low price of the co-products (styrene 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_x/SiO_2 catalysts were prepared by precipitation of the copper-ammonia complex ($[Cu(NH_3)_4(H_2O)_2]^{2+}$) via dilution hydrolysis method (inspired by Meng*et al.*[7]). For the alkali and earth alkali modification, 30 mL of aqueous solutions of nitrate salts (0.1 M $NaNO_3$, 0.05 M $Ca(NO_3)_2$ and 0.1 M KNO_3) was used. The samples were marked as *x*Cu*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_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 mm^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 Brønsted 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.
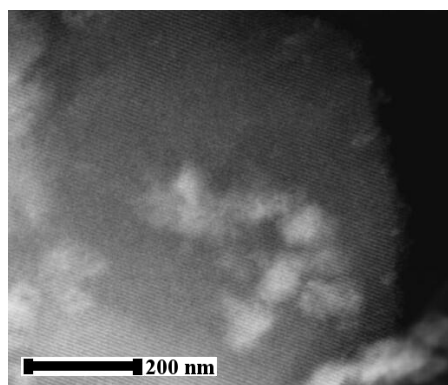
RESULTS AND DISCUSSION

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.

The BF-TEM micrographs show a well-ordered mesoporous structure in both the sodium modified and unmodified sample, which confirm the results of the N_2physisorption and XRD analyses. Additional morphological properties were tested with the UV/VIS DR analysis. The spectra revealed characteristic charge transfer bands between mononuclear Cu^{2+} and oxygen. A broad but less intense peak corresponding to the d-d transition of Cu^{2+} ions in an octahedral environment, which can be attributed to bulk CuO, was also observed.

In all samples a shoulder characteristic of $[Cu–O–Cu]_n$-type (oligomeric species) was present. *Ex-situ* and operando UV/VIS DR analyses of the unmodified samples showed a notable absorption red-shift along with the increase of band intensity related to bulk CuO, after the second calcination protocol (performedto simulate the alkali and earth alkali modification of the samples) and during catalytic conditions. Alkali as well as earth alkali modification of the CuO_x/SiO_2 catalysts noticeably stunted the sintering effect seen in the unmodified samples. Switching to a purely reductive atmosphere results in a progressive increase of light absorption in the whole range of wavelengths for both the modified and the unmodified catalysts. Returning to an oxidative atmosphere causes re-

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_2O-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.
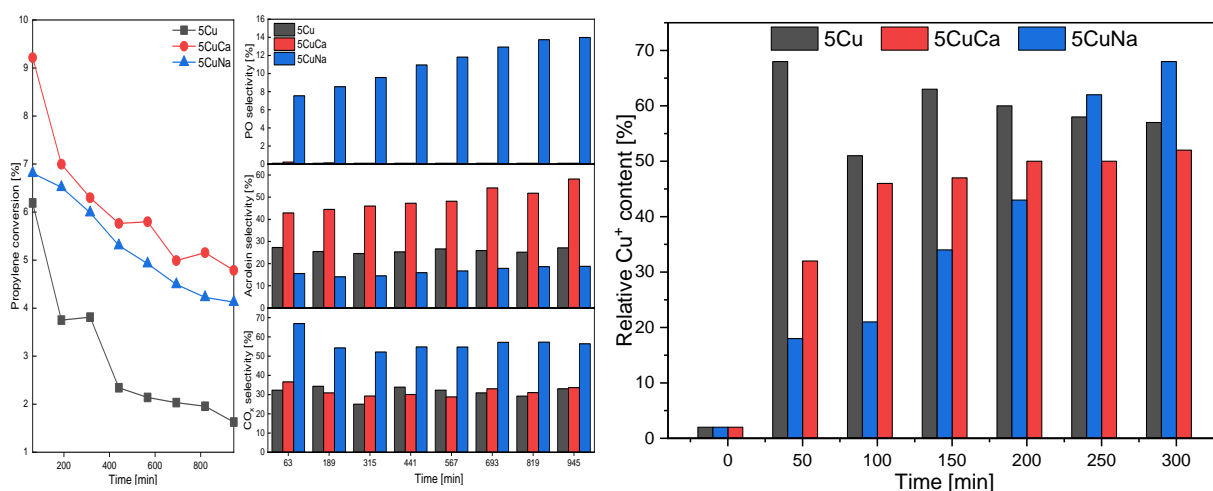

Figure 2. Temporal evolution of propylene conversion (left panel) and the selectivity (mid panels) and Cu^+ fraction as a function of reaction time for the investigated catalysts (right panel).

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 thatall 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

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_x selectivities remain very similar to the unmodified 5Cu catalyst.

CONCLUSION

Based on the research done, we propose that Cu^+ is not crucial for PO formation; instead the electropositive Na^+ and K^+ decrease the nucleophilic strength of oxygen in CuO_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_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_x is negated by charge compensation by strongly adsorbed hydroxyl groups. As a result, Ca modification for PO selectivity is inefficient.

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