Selective oxidation of hydrocarbons has great importance in chemical technology because it offers a possibility of obtaining oxygenates which are used as intermediates in organic syntheses. One of the important copper-catalyzed reactions is the partial oxidation of propene with molecular oxygen to produce propene oxide and acrolein [1]. In the last years gold catalysts have been also studied in propene oxidation [2] and epoxidation [3] and the nature of the support was found to be a very important factor influencing the catalyst selectivity.

The focus of this work was on the effect of the SBA-15 support structure (SBA-15 with long vs SBA-15 with short channels) and the introduction of niobium species in the framework of the matrix on the surface properties and the activity of bimetallic Au-Cu catalysts in propene oxidation with oxygen.

Two kinds of SBA-15 materials, with short and long channels, were prepared [3,4]. Nb was introduced by impregnation (10 wt. %). The modification with gold and copper was performed in two steps: i) grafting with 3-aminopropyl-trimethoxysilane on SBA-15 and next ii) Au (1 wt.%) and Cu (0.5 wt.%) introduction. The materials prepared were calcined at 773 K.

XRD, TEM, UV-Vis, XPS and XAS techniques were used for identification of the oxidation state of Au, Cu and Nb in the calcined samples and the samples reduced in hydrogen; i.e. under the conditions used for the activation of catalysts, prior to the catalytic oxidation of propene. It was found that gold on the surface of calcined AuCu-SBA-15 samples was present in the form of metallic gold particles (BE ca 84.0 eV – XP spectra). The treatment of bimetallic samples with hydrogen (at 573 K) shifted the Au4f7/2 BE to a lower value (83.5 eV) indicating the presence of negatively charged metallic gold species (Au^{0}) and implying that the gold had a great tendency to accept electrons through interaction with copper. (Au^{0}) species (BE ca 83.4 eV) were present on the surface of calcined AuCu-Nb/SBA-15. It indicates that the presence of niobium (BE = 207.7 eV – Nb^{5+}) changes the electronic state of gold in comparison to that in AuCu-SBA-15. Moreover, the changes in XANES spectra observed for bimetallic samples in comparison to references showed that Cu^{2+} and Cu^{+} species were found in calcined AuCu-samples, whereas metallic copper was found in the reduced ones. The EXAFS data for the latter samples indicated the gold-copper interactions. There were no differences in surface properties between the catalysts based on SBA-15 with long and short channels.

The results of catalytic activity of AuCu-SBA-15 with short and long channels after activation in H2 clearly showed the effect of SBA-15 structure on the selectivity of the catalysts in propene oxidation. AuCu-SBA-15 with short channels and AuCu-SBA-15 with long channels exhibited similar activity at 573 K (19 and 18 %, respectively). However, it is important to note that much higher selectivity to acrolein was achieved over the AuCu-SBA-15 with short channels than over that with long channels (35 and 19 %, respectively). It points out the crucial role of pore length in the reaction studied. The presence of niobium in the framework of AuCu-Nb/SBA-15 with long channels decreased the activity of the catalyst (10% of propene conversion), but increased the selectivity to acrolein (from 19 to 24%). To sum up, the presented results of propene oxidation on reduced bimetallic gold-copper catalysts supported on SBA-15 showed better catalytic performance of AuCu-SBA-15 with short channels. This catalyst is more selective to acrolein. Niobium in the framework of SBA-15 with long channels also has positive effect on the selectivity of AuCu-Nb/SBA-15 to acrolein.

References

Acknowledgements National Science Center in Poland (Grant No. 2014/15/B/ST5/00167) and "EURASIACAT: Advanced Education European-Asiatic Exchange Programme in Materials Science and Catalysis" are acknowledged for the financial support

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