



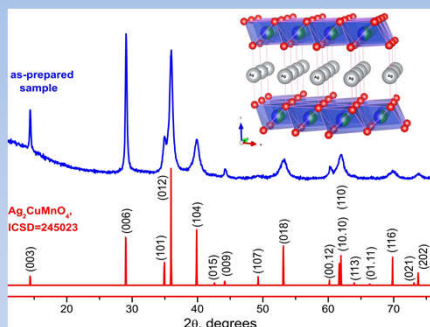
Ternary mixed oxide of silver, copper and manganese – novel catalytic material for oxidation reactions

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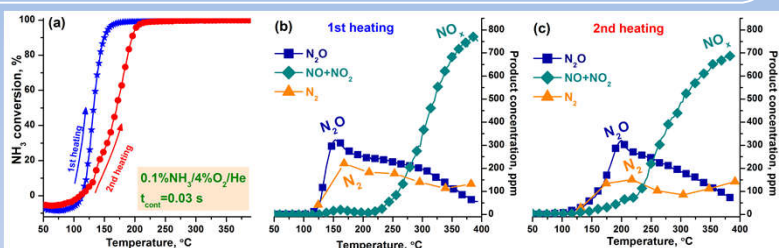
Introduction:

Cu- and Ag-containing systems are traditionally used as catalysts to perform various oxidation reactions. Great interest to such systems is caused by a need to search and develop cheap and highly efficient catalysts without noble metals. The structure of mixed oxides based on copper and silver provides the stabilization of particular oxygen species with modified reactivity and catalytic properties in comparison with single metal systems. In this work, ternary mixed oxide $\text{Ag}_2\text{CuMnO}_4$ was considered as catalyst for oxidation of CO, ethylene and ammonia.



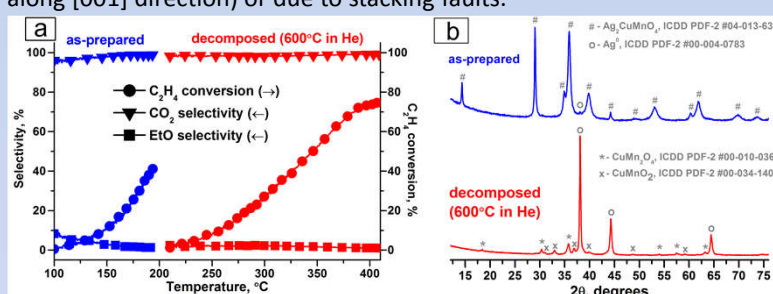
Synthesis and XRD:

Ternary oxide was prepared by hydrothermal method in alkaline medium in the presence of $\text{Na}_2\text{S}_2\text{O}_8$. $T = 140^\circ\text{C}$, $t = 24\text{ h}$. X-ray pattern corresponds to delafossite phase with $\text{Ag}_2\text{CuMnO}_4$ composition. Delafossite crystallites were found to be elongated up to 20-30 nm along [001] direction, while sizes along other crystallographic directions not exceed 10 nm. The Rietveld refinement revealed a discrepancy between the calculated and experimental curves for the 003, 006, 009, and 0012 reflections. It can be caused by disregarded anisotropy of particles shape (elongation along [001] direction) or due to stacking faults.



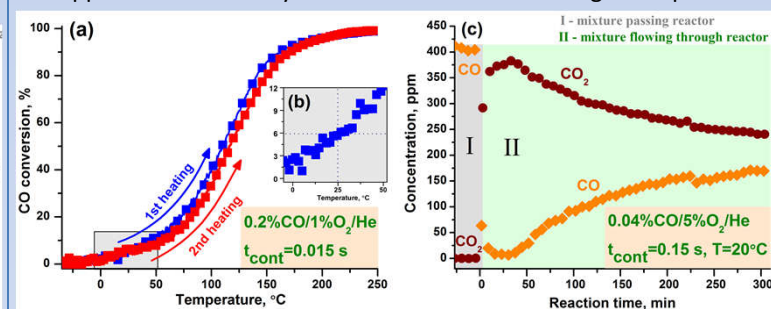
NH₃ oxidation:

Noticeable activity in NH_3 oxidation was observed at temperature above 100°C , reaching the conversion of 100% at 150°C . Dinitrogen (N_2) and nitrous oxide (N_2O) were mainly formed in the range of $100\text{--}250^\circ\text{C}$, while the contribution of NO and NO_2 was appeared above 250°C . The NO_x selectivity reached $\sim 70\%$ at 400°C . The destruction of delafossite structure in NH_3+O_2 mixture was not observed, although the appearance of weakly intense 111 reflection for Ag^0 took place.



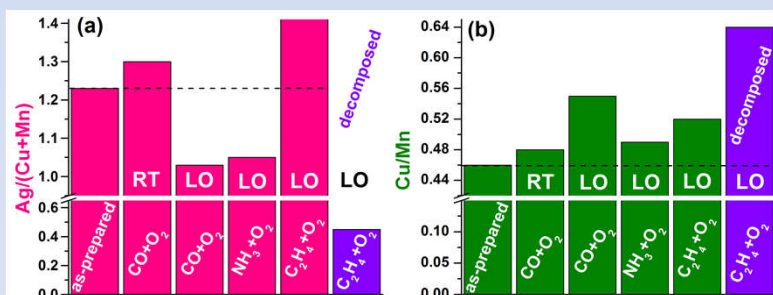
C₂H₄ oxidation:

As-prepared $\text{Ag}_2\text{CuMnO}_4$ demonstrated evident activity in C_2H_4 oxidation at $T > 120^\circ\text{C}$. The exposure in $\text{C}_2\text{H}_4+\text{O}_2$ mixture resulted in the appearance of Ag^0 traces with the preservation of the delafossite structure. The complete decomposition of $\text{Ag}_2\text{CuMnO}_4$ in He at 600°C resulted in the deterioration of activity in ethylene oxidation: (1) the shift of C_2H_4 conversion curve towards higher temperatures, (2) the CO_2 selectivity close to 100% in all observed temperature range.

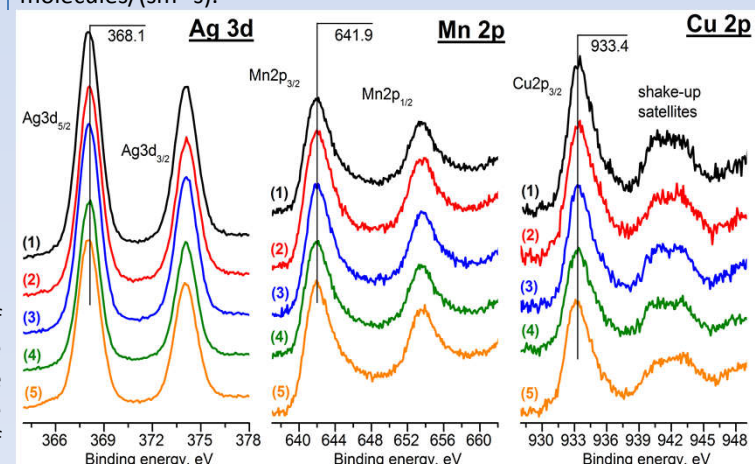


CO oxidation:

The activity was observed $T > 0^\circ\text{C}$. The curves of CO conversion obtained during 1st and 2nd heating in $\text{CO}+\text{O}_2$ mixtures were similar. During the isothermic experiment at 20°C the CO oxidation rate was decreased during 6 h reaching specific steady state value of $\sim 2 \cdot 10^{11}$ molecules/($\text{cm}^2 \cdot \text{s}$). The E_a value was estimated close to 20 kJ/mole. Note, that in the presence of water vapors in $\text{CO}+\text{O}_2$ mixture the specific steady state rate of CO oxidation was dropped to $\sim 3 \cdot 10^{10}$ molecules/($\text{cm}^2 \cdot \text{s}$).



XPS: The presence of O_2 in reaction mixture provides the preservation of pristine states of Cu, Ag and Mn at the $\text{Ag}_2\text{CuMnO}_4$ surface, while the relative metal ratios are varied in dependence on reaction conditions. The heating of $\text{Ag}_2\text{CuMnO}_4$ in catalytic media up to $200\text{--}400^\circ\text{C}$ resulted in the modification of its bulk and surface accompanied by the partial release of silver from the delafossite structure.



Conclusions:

Ternary oxide $\text{Ag}_2\text{CuMnO}_4$ with delafossite structure is a promising system for catalytic oxidation reactions. High activity in CO oxidation was observed at room temperature, while the efficient oxidation of C_2H_4 or NH_3 was occurred above 150°C only. Delafossite structure was preserved after the heating of ternary oxide up to 400°C in the various reaction mixtures with the excess of O_2 , while some changes in surface composition were detected. The complete decomposition of the delafossite structure led to a deterioration of catalytic activity.