

CuFeAl-composite catalysts of oxidation of gasification products of solid fuels: In situ study by XAS and XRD

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Catalytic oxidation of gasification products of solid fuels is allows utilizing low-grade fuels such as lignite, peat, and firewood as well as various industrial wastes. At the same time catalytic combustion produces a significantly lower amount of harmful emissions then “traditional combustion” of fuels. CuFeAl-composite catalysts demonstrate high activity and stability in catalytic oxidation of gasification products of solid fuels. Moreover, the catalysts are inexpensive and ecologically clean. Here we present our results of in situ investigations of the catalyst state in reaction conditions. Since carbon monoxide is the main product of gasification of solid fuels we performed investigation CuO, Fe₂O₃, and CuFeAl-composite catalysts in CO and CO+O₂ mixture in a wide temperature range. We applied three methods: XANES, EXAFS, and XRD. *In situ* XAS experiments were performed at the Structural Materials Science station at Kurchatov Center for Synchrotron Radiation. The spectrometer is equipped with high temperature chamber that allows collecting XAS spectra within temperature range from RT to 600°C in the gas mixture at atmospheric pressure [1]. *Operando* XRD/MS experiments were carried out at the “High Precision Diffractometry II” station at “Siberian Synchrotron and Terahertz Radiation Center”. The diffractometer is equipped with XRK 900 reaction chamber (Anton Paar GmbH) that allow observing the diffraction patterns within temperature range from RT to 900°C in the reactant mixture at atmospheric pressure [2]. XANES is very useful for identification of different chemical states of copper and iron and allows us to study the chemistry of the catalysts under reaction conditions. X-ray diffraction techniques allow us to study the phase composition, but, unfortunately, the technique cannot identify nanoparticles and amorphous phases. This shortcoming can be eliminated by EXAFS which may clarify the structure of local environment of copper and iron atoms even when their concentration is extremely low.

We found that fresh CuFeAl-composite catalysts consist of CuFe_2O_4 , CuO , Fe_2O_3 , and Al_2O_3 . In a CO flow, the reduction of copper from Cu^{2+} to Cu^{1+} and Cu^0 started at temperature about 200°C ; at 600°C copper is mainly in the metallic state. At the same time the reduction of iron started at temperature about 400°C and at 600°C about 20% of iron is in the metallic state. *Operando* XRD study allows us to determine the phase transition of iron-containing phase during the reduction in a CO flow. The reduction process occurs in the next manner: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ and Fe^0 . In $\text{CO}:\text{O}_2 = 2:1$ mixture, the reduction of copper from Cu^{2+} to Cu^{1+} started at temperature about 400°C and at 600°C about 50% of copper is in the Cu^{1+} state, whereas iron is slightly reduced to Fe^{2+} state at 600°C . The following increase the partial pressure of O_2 leads to shift initial reduction temperature to high temperature range.

Thus, the use of complimentary methods (XANES, EXAFS, and XRD) allows us to determine the chemical state of copper and iron, phase composition in the catalyst during the oxidation of CO. The data presented can facilitate to clarify the mechanism of oxidation of CO.

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References:

- [1] A.A. Chernyshov, A.A. Veligzhanin, Ya.V. Zubavichus, Nucl Instrum Methods Phys Res A 603 (2009) 95.
- [2] A.A. Saraev, Z.S. Vinokurov, V.V. Kaichev, A.N. Shmakov, V.I. Bukhtiyarov, Catal. Sci. Technol. 7 (2017) 1646.