

Nanocomposites and nanomaterials

Nanostructured Zn-La-Zr-Si-oxide catalysts for one step synthesis of 1,3-butadiene from ethanol

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1,3-Butadiene (BD) is the most important monomer in the production of a wide variety of synthetic rubbers, elastomers and polymer resins. BD can be produced from bioethanol (obtained from renewable sources) by the Lebedev process. The catalysts of the process should have multifunctional active sites with acid, base and redox properties [1].

We have shown that La_2O_3 -based catalysts have high activity and stability over time in the ethanol conversion to BD. The results of some tested catalysts are displayed in Table 1.

Table 1. Catalytic results in the butadiene synthesis from ethanol ($T = 648 \text{ K}$, $\text{WHSV} = 0.82 \text{ g}_{\text{ethanol}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, time-of-stream = 3 h)

Catalyst*	Ethanol conversion (%)	BD selectivity (%)	BD yield on fed alcohol basis (%)
$\text{ZrO}_2\text{-La}_2\text{O}_3\text{-SiO}_2$	30.2	58.6	17.7
$\text{ZnO-L}_2\text{O}_3\text{-SiO}_2$	30.1	44.1	13.3
$\text{ZrO}_2\text{-ZnO-L}_2\text{O}_3\text{-SiO}_2$	80.0	65.7	52.6

* Methods of the catalysts preparation are available at [2].

The effect is achieved by nanoparticles interaction of the catalyst components on its interphase. The sites of dehydration (ZnO , La_2O_3), aldol condensation ($\text{La}_2\text{O}_3/\text{SiO}_2$, $\text{ZrO}_2/\text{SiO}_2$), Meerwein–Ponndorf–Verley reduction (ZrO_2) and dehydration (SiO_2 , ZnO/SiO_2 , $\text{ZrO}_2/\text{SiO}_2$) are formed. We have firstly shown that doping of the catalyst with lanthanum improves its redox properties and provides the required stability in the process.

1. Makshina E. V., Dusselier M., Janssens W. et al. Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene // Chem Soc Rev. – 2014. – **43**. – P. 7917–7953.
2. An application for a patent of Ukraine #u2015 04490 Method for

producing catalyst for synthesis of 1,3-butadiene from ethanol // *Kyriienko P. I., Larina O. V., Soloviev S. O.* – 07.05.2015 (in Ukrainian).