

**SUPPORTED METAL OXIDES AND N-HYDROXYPHthalIMIDE IN CATALYSIS OF THE OXIDATION OF BENZYLIC C-H BONDS**

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The aerobic liquid-phase oxidation of alkylarene (RH) in the presence of a binary catalytic system containing N-hydroxyphthalimide (NHPI) and supported V, Mn, and Cu oxides (TMO) was studied. The heterogeneous catalysts with single active component such as V<sub>2</sub>O<sub>5</sub>, MnO<sub>x</sub>, and CuO<sub>x</sub> and bi-components V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>-SbO<sub>x</sub> supported onto TiO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> were prepared and characterized. The kinetics of the aerobic oxidation of alkylarene in the presence of a binary catalytic system NHPI and TMO was studied using molecular oxygen (under 760 mm Hg) and acetonitrile (ACN) as a solvent, with volume ratio of cumene to ACN as 1:1, and the reaction temperature was 70 °C. The major product of cumene oxidation was cumene hydroperoxide. Correlation was found between the catalytic activity of the TMO + NHPI system and the acidic properties of TMO (measured by NH<sub>3</sub> TPD). The most active among the binary systems were MnO<sub>x</sub> ≅ VO<sub>x</sub>. It was found, that

synergistic effect promotes catalytic efficiency of Mn/Ti-Si + NHPI and V/Ti + NHPI systems.

Table. Oxidation of hydrocarbons catalyzed by [MnO<sub>x</sub>(TiO<sub>2</sub>SiO<sub>2</sub>)] = 5 g/L, [NHPI] = 30 mM

	Substrate	[RH] M	W*10 <sup>5</sup> mol/Ls	ΔH <sub>f</sub> kcal M <sup>-1</sup>
1	Cumene	3.59	17.0	-4.8
2	Tetralin	3.67	13.6	-1.7
3	o-Xylene	4.15	2.2	4.5

at [NHPI] = 0, for all oxide W < 0.2\*10<sup>5</sup> mol/Ls

A comparison of the catalytic properties of Mn and V oxides with their molecular hydrogen reduction profiles shows, that the supported Mn-oxide is more active due to its lower temperature of reduction.

The catalytic cumene oxidation was presented [1] with the reactions scheme identifying the role

of heterogeneous initiation and homogeneous propagation and termination steps for the oxidation proceeding via free-radical mechanism. In order to evaluate the efficiency of the binary catalytic system in the oxidation of various substrates and to find a relationship between catalytic activity and the chemical nature of TMO, we used a thermochemical approach with semi-empirical method for calculation of reaction enthalpies. Comparison of kinetic data and calculated enthalpies of key reactions of the main oxidation stages with their calculated enthalpies showed the following:

a) the reaction enthalpy for a certain alkylarene  $\text{PINO}^* + \text{RH} \rightarrow \text{R}^* + \text{NHPI}$ , which occurs in the liquid phase, contributes to the catalytic activity during the oxidation reaction;

b) the efficiency of the catalytic system with various oxides in the oxidation is proportional to the enthalpy of the reaction of the surface group  $\text{sM}=\text{O}$  on the of the oxide with the NHPI  $\text{sM}=\text{O} + \text{NHPI} \rightarrow \text{sMO-H} + \text{PINO}^*$  producing radical, which plays the main role in catalysis.

1. Opeida, I. A., Sheparovych, R. B., & Suprun, W. Y. (2023). Kinetic analysis of aerobic oxidation catalyzed by supported Mn and V oxides and N-hydroxyphthalimide. *Journal of Catalysis*, 424, 197–210.