Supported transition metals oxides and N-hydroxyphthalimide in catalysis of the liquid-phase oxidation of cumene

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Abstract – The heterogeneous catalysts based on single active component such as* V_2O_5, MnO_x *and* CuO_x *and bi-components* V_2O_5-MoO_3 V_2O_5-WO_3 *and* V_2O_5-SbO_x *supported onto* TiO_2, TiO_2-SiO_2 *and* Al_2O_3-SiO_2 *was prepared, characterized and their cataalitic activities measured.

Keywords – cumene, liquid-phase oxidation, catalysts, transition metal oxide, N hydroxyphthalimide

Introduction Based on the principles of „green chemistry“, molecular oxygen is the most preferable oxidant for production of hydroperoxide compounds via liquid-phase oxidation of hydrocarbons. However, utilizing of molecular O_2 in oxidation processes requires application of efficient catalysts in order to achieve high yields of the target products at sufficient reaction rates. Most often various salts of transition metals (TM) were used as homogeneous catalysts of oxidation with molecular oxygen. In this work, we report on the synthesis and characterization of series of heterogeneous catalysts comprising the Mn, Cu and V oxides supported on TiO2, TiO_2-SiO_2 and SiO_2-Al_2O_3 (as a commonly used industrial support materials), their catalytic effect on the rates of liquid-phase cumene oxidation with molecular oxygen in the presence of radical catalyst N-hydroxyphthalimide (NHPI).

Catalysts preparation. The oxide catalysts such as V_2O_5-TiO_2 (6 wt. % V), V_2O_5-MoO_3/TiO_2 (4.5% V and 9.2 wt. % Mo) and V_2O_5-SbO_2/TiO_2 (4 wt.% V and 9.7 wt.% Sb) were prepared by spray-drying method. Cu and Mn containing catalysts supported on TiO2 modified with silica were prepared by wet-ness impregnation of support materials with aqueous solution of manganese nitrate or copper nitrate respectively. V_2O_5/TiO_2-WO_3 catalysts, containing 0.2 or 2.2 wt.-% of V are industrial TiO_2-WO_3 samples and were provided by Ebinger Katalysorservice Ltd.

Table 1. Composition, textural and physico-chemical properties of heterogeneous catalysts based on transition metal oxide supported on TiO_2, TiO_2-SiO_2 or γ-Al_2O_3-SiO_2.

	Abbr.	Catalyst composition	Content of TM/ wt. % $^{a)}$	$A_{BET/}$ m^2g^{-1} $^{b)}$	PD/ nm $^{c)}$	TA/ mmol g^{-1} $^{d)}$	$H_2{}^{cons}$/ μmol g^{-1} $^{e)}$
1	TiO_2		0.00	105	10,0	0.12	225
2	Mn/Ti-Si	MnO_x/TiO_2-SiO_2	Mn: 17.0	141	10,5	5.6	2178
3	Cu/Al-Si	CuO_x /Al_2O_3-SiO_2	Cu: 15.0	246	6,5	3.1	1670
4	V/Ti	V_2O_5/TiO_2	V: 6.0	92	9.3	4.45	2180
5	V-Mo/Ti	V_2O_5-MoO_3/TiO_2	V: 4.5; Mo: 9.2	86	9.8	0.53	3750
6	V-Sb/Ti	VO_x-SbO/TiO_2	V: 4.0: Sb: 9.7	83	10.5	0.49	3920
7	0.2VWTi	V_2O_5-WO_3/TiO_2	V: 0.2; W: 5.8	69	20.1	0.16	285
8	2.2VWTi	V_2O_5-WO_3/TiO_2	V: 2.2; W: 5.5	68	19.1	0.29	970

Content of TM (a) was determined by RFA analysis; b) the specific surface area (A_{BET}) and the average pore diameter (PD) $^{c)}$, determined by N_2 adsorption/desorption method; d) the total number of acidic sites (TA) determined by TPD of ammonia; e) total hydrogen consumption determined by TPR experiment with hydrogen at the temperature range between 100 and 700 °C.

Catalytic activity experiments. Catalytic activity test of liquid-phase cumene oxidation in the presence of NHPI and heterogeneous catalyst was carried out at atmospheric pressure in a manometric homemade closed temperature-controlled gasometric device. The oxidation experiments were conducted using pure oxygen in a glass microreactor (V=5 mL) equipped with magnetic stirring. The catalyst content was incrementally varied between 0.01 and 0.04 g mL-1 of the charged cumene (1 mL of RH). Solvent in all experiments was acetonitrile, the volume ratio of oxidized mixture : solvent 1:1. Oxidation was carried out under constant pressure of oxygen of 0,101 Mpa.

The effect of TMO on reaction rate of oxidation. Two groups of supported transition metal oxides were studied as catalysts: one active component V_2O_5/TiO_2, MnO_x/TiO_2-SiO_2, CuO_x/Al_2O_3-SiO_2 and binary mixtures of TMO containing e.g. V_2O_5-MoO_3,V_2O_3-SbO or V_2O_5-WO_3 supported on titanium dioxide. In our preliminary tests it was found that oxidation of pure cumene with molecular oxygen at 70°C and oxygen pressure of 0,101 MPa in the absence of the catalyst or the initiator was not observed for a time of more than 2 h. It was also found that in the presence of solely one catalyst (0.04 g mL^{-1}) in cumene oxygen uptake at temperature 70 °C occurs with pretty low reaction rates. In all cases the rate was less than 1×10^{-6} M s^{-1} and only in the case of the most active magnesium oxide it was about 2×10^{-6} M s^{-1}. It allows us to conclude, that under the conditions of our experiments, the reaction rate of cumene C-H bond activation and the free radicals formation are very small.

The calculated initial reaction rates of the oxygen consumption for catalytic oxidation of cumene for the first 800 second reaction time at the constant reaction condition are presented in Fig.1

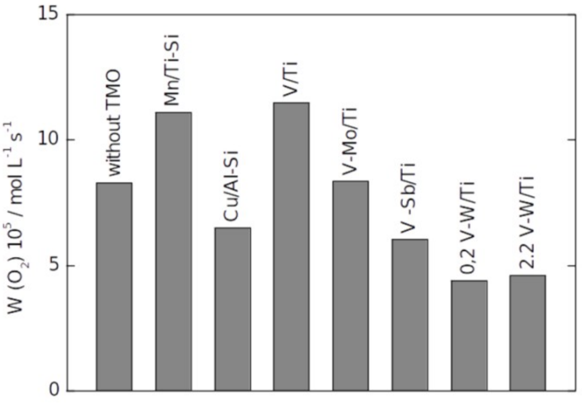

Fig.1. Comparison of the initial reaction rate of oxidation in the presence of AIBN, NHPI and different TMO loaded on various support materials.

Conclusion In the oxidation of cumene, the most catalytically active are systems containing manganese and vanadium oxides, where in the presence of NHPI a significant synergistic effect is observed.