

Effect of metal catalysts on the oxidation of *p*-xylene and *p*-methyltoluate

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

Monomeric and polymeric forms of metal phthalocyanines have been studied as co-catalysts of the cobalt-catalyzed oxidation of *p*-xylene and *p*-methyltoluate at 160 °C and 0.7 MPa of total pressure. Their influence is dependent upon the central atom, crystalline modification, and coordinated ligands, however, it is different for cobalt and mixed cobalt—manganese catalysts. The results suggest that metal phthalocyanines act as hydroperoxide decomposers and not as activators of the molecular oxygen.

Изучались мономерные и полимерные формы фталоцианидов металлов как сокатализаторов окисления смеси *p*-ксилола и *p*-метилтолуилата катализированого кобальтом при температуре 160 °C и давлении 0,7 МПа. Их влияние зависит от центрального атома, кристаллической модификации и координированных лигандов, причем наблюдались различия для кобальтовых и смешанных кобальто-марганцовых катализаторов. Результаты назначают, что изучаемые фталоцианиды металлов, правдоподобно, действуют как разрушители гидроперекисей, но не как активаторы молекулярного кислорода.

The process of dimethylterephthalate (DMT) production based on the oxidation of a mixture of *p*-xylene (PX) and *p*-methyltoluate (PMT) in the liquid phase has undergone many improvements since its commercial application [1—3]. In the

original process using only cobalt catalyst, higher oxidation temperatures were inappropriate for reaching higher yields. By the introduction of mixed cobalt—manganese catalysts the selectivity was improved and, moreover, over the temperature range 140—170 °C the yield of the oxidation products was almost not affected [4]. However, lower yields of DMT reached in this process in comparison with other technologies of terephthalic acid (TA) production lead to a systematic search for the possibilities of process improvements [5—13].

The present paper deals with the study of the effect of metal phthalocyanines as co-catalysts of the cobalt-catalyzed oxidation of *p*-xylene in a mixture with *p*-methyltoluate at conditions of the commercial DMT-process.

Experimental

Chemicals

p-Xylene (99.8 %) and *p*-methyltoluate (87.3 %) containing methylbenzoate (9.5 %) and DMT (1.9 %) were used without purification. Catalyst (Co—N) containing 10.1 % of cobalt was a commercial product "Nuodex". Monomeric phthalocyanines (PCM) and their derivatives containing —SO₃H or —SO₂NH₂ groups were synthesized by the method [14]. Polymeric forms of metal phthalocyanines (PPCM) or their metal mixtures (PPCM₁—M₂) were synthesized at 300 °C and 3.0 MPa of total pressure in a nitrogen atmosphere by the procedure described in [15, 16]. For the preparation of polymeric types dianhydride of pyromellitic acid (PPCM-1 type) or tetranitrile of pyromellitic acid (PPCCu-2, PPCCu—Fe-2) and 3,4,3',4'-benzophenonetetracarboxylic acid (PPCCu-3, PPCCu—Fe-3) were used. Copper acetylacetonate, Cu(acac)₂, was prepared according to [17]. Manganese and copper naphthenate (M—N) were prepared from sodium salts of naphthenic acids and metal chlorides. The metal content (w/mass %) in the prepared catalyst was determined using atomic absorption spectroscopy (Varian-Techtron AA 6) and for the mentioned catalyst was the following: PPCCu-1 13.5 % (Cu); PPCCu-2 15.3 % (Cu); PPCCu-3 14.1 % (Cu); PPCCu—Fe-2 13.2 % (Cu), 2.3 % (Fe); PPCCu—Fe-3 11.5 % (Cu), 2.4 % (Fe); Cu—N 6.7 % (Cu); Mn—N 7.1 % (Mn). Other chemicals of anal. grade purity were used without purification.

Oxidation procedure

A mixture of *p*-xylene (60 g) and *p*-methyltoluate (120 g) was oxidized at 160 °C and 0.7 MPa of total pressure with air (18 dm³ h⁻¹) in a 250 cm³ stainless steel reactor by the method described previously [18].

Kinetic measurements

The kinetics of the oxidation of a mixture of *p*-xylene and *p*-methyltoluate with oxygen in the presence of various metal catalysts was studied at 140 °C and 0.7 MPa of total pressure

using the apparatus described in [18]. The maximal oxidation rate was calculated from the plot of absorbed oxygen vs. time, measured under vigorous agitation.

Analysis

Outlet gases were continually monitored for oxygen using Permolyt-2 instrument (Junkalor Dessau, GDR) and for carbon dioxide using a gas chromatograph with a TC detector. The oxidation products as free acids were analyzed with a Hewlett-Packard 5830 gas chromatograph by doping with internal standard amylbenzoate. The content of terephthalic acid in the oxidation product was calculated as a solid undissolved in acetone after drying (2 h at 100 °C) and correction on solubility due to other oxidation products. The acid value of the reaction mixture was determined by acidometric titration with an alcohol solution of KOH.

Results

From kinetic measurements it follows (Table 1) that the Co—Mn—N catalyzed oxidation of *p*-xylene and *p*-methyltoluate is enhanced by some metal phthalocyanines. Their effect is demonstrated by the increase of the maximal reaction rates, as well as by the increase of the overall amount of oxygen consumed in the first stage of the reaction.

Table 1

Influence of metal phthalocyanines on the oxidation rate of the mixture containing $w(p\text{-xylene}) : w(p\text{-methyltoluate}) = 1 : 1$ with oxygen at 140 °C and 0.7 MPa
Catalyst 150 p.p.m. Co—N + 10 p.p.m. PCM (metal)

Co-catalyst	Relative rate r_{\max}	mole O ₂ ^a
		mole (PX + PMT)
—	1.00	0.40
PCSB	0.83	0.48
PCCu	0.85	0.36
PCUO ₂	1.19	0.44
PCPb	0.75	0.35
PCVO ₂	0.79	0.47
PCTi	1.09	0.43
PCCe	1.31	0.43
PCCr	1.10	0.49
PCAg	1.03	0.43
PCFe	0.82	0.40

a) Amount of consumed oxygen after 1 h of reaction.

The effect of metal phthalocyanines as co-catalysts was also studied from the point of the final oxidation products formation, *i.e.* terephthalic acid, its monomethylester (MMT) and by-product carbon dioxide, decreasing the selectivity of the process. At temperature 160 °C the influence of studied co-catalysts on the activity of Co—N catalyst is dependent upon the central atom (Table 2), crystalline modification of phthalocyanine and coordinated ligands

Table 2

Influence of monomeric forms of metal phthalocyanines as co-catalysts of PX and PMT oxidation catalyzed by 100 p.p.m. Co—N + 10 p.p.m. PCM (metal); reaction time 8 h

Co-catalyst	Acid value	w/mass %	
		MMT	TA
—	211	16.6	6.2
PCFe	208	14.4	5.0
PCNi	218	16.7	6.5
PCMn	201	14.9	5.2
PCCr	202	16.1	6.2
PCCu	219	15.9	6.0
PCCe	133*	7.5	Traces
PCSb	220	17.0	6.7

* Oxidation spontaneously stopped in the 6th hour of reaction.

Table 3

Influence of ligand on the activity of copper compounds
100 p.p.m. Co—N + 10 p.p.m. co-catalyst (metal)

Co-catalyst	Reaction time <i>t/h</i>	Acid value	w/mass %	
			MMT	TA
α -PCCu	8	219	15.9	6.0
α -PCCu ^a	8	217	16.9	6.8
β -PCCu	6 ^d	147	9.9	1.4
β -PCCu ^b	8	202	17.9	7.4
PCCuPy ₂	6 ^d	157	11.3	2.1
PCCu—SO ₃ H	8	209	15.0	5.6
PCCu—SO ₂ NH ₂	8	166	11.8	2.5
Cu(acac) ₂	8	211	14.7	4.7
Cu—N	5 ^d	168	12.2	2.8
Cu—N ^b	8	197	15.3	6.1
Cu(en) ₂ Ni(CN) ₄	8	222	17.5	7.2

a) 30 p.p.m.; b) in the presence of 10 p.p.m. Mn—N; c) complex with pyridine; d) oxidation spontaneously stopped.

(Table 3). The spontaneous stop of the oxidation after 5–6 h of reaction is observed for PCCe, β -modification of PCCu and copper phthalocyanine complex with pyridine. In addition to it, the substitution of the phthalocyanine ligand by the $-\text{SO}_2\text{NH}_2$ group decreases the rate of oxidation.

Despite the fact that metal co-catalysts are present in very low concentrations, their effect is significantly dependent upon their ligands. From Table 3 can be seen that the action of copper co-catalysts is also different in the system with cobalt and mixed Co—Mn catalyst, with both copper phthalocyanine and naphthenate. In the case of mixed Co—Mn catalyst the spontaneous stop of the oxidation in the presence of these types of co-catalysts is eliminated.

The polymeric forms of copper phthalocyanines prepared from various aromatic tetracarboxylic acids or their nitriles possess no synergistic effect (Table 4). In addition to it,

Table 4
Influence of polymeric forms of metal phthalocyanines
100 p.p.m. Co—N + 10 p.p.m. PPCM (metal); reaction time 8 h

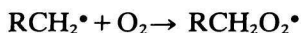
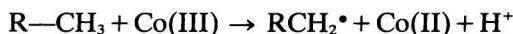
Co-catalyst	Acid value	w/mass %	
		MMT	TA
PPCCu-1	131 ^a	8.1	0.8
PPCCu-2	211	16.1	5.9
PPCCu-3	209	15.1	5.3
PPCCu—Fe-2	192	13.6	3.5
PPCCu—Fe-3	190	13.6	3.4
PPCMn-1 ^b	195	15.3	5.7

a) Reaction spontaneously stopped; b) in the presence of 100 p.p.m. pyridine.

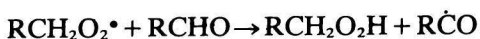
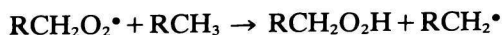
bimetallic Cu—Fe polyphthalocyanines have a negative influence on the oxidation reaction. In contrast to monomeric phthalocyanines, no negative influence of pyridine was observed for the polymeric forms.

Discussion

The oxidation of *p*-xylene and *p*-methyltoluate mixture catalyzed by transient metals proceeds via a radical chain mechanism [12]. It is proposed that in the first step hydrocarbon reacts with the catalyst in a higher valence state, forming a radical

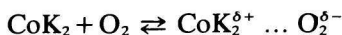


Peroxy radicals regenerate the active form of the catalyst and abstract a hydrogen atom from the hydrocarbon or aldehyde

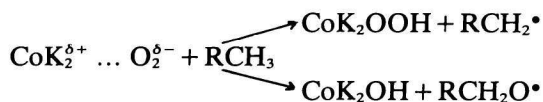


This leads to new types of radicals and a complex reaction system.

The formation of free radicals during the oxidation of *p*-xylene and *p*-methyltoluate mixture is described also by a mechanism including the formation of an intermediate complex of metal catalyst with oxygen [19]



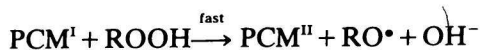
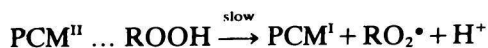
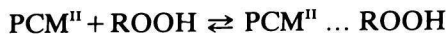
where K is a caprylate anion. Such a complex is more reactive towards hydrocarbon



The activation of oxygen was also proposed [20] in the oxidation of mesitylene in acetic acid solvent in the presence of manganese phthalocyanine catalyst.

The assumption that the metal phthalocyanines function as oxygen activators was postulated in various mechanisms concerning the oxidation of hydrocarbons [21—23], however, there still is criticism for such explanation [24, 25]. There are doubts that at temperatures above 120 °C the activation of oxygen by metal phthalocyanines proceeds [26].

The function of metal phthalocyanine catalysts and co-catalysts is probably in the homolytic cleavage of hydroperoxides [24] which proceeds via a complex formation between hydroperoxide and catalyst



As we have found out experimentally, all studied phthalocyanine catalysts act as effective decomposers of cumenehydroperoxide already at temperature 100 °C. In the course of decomposition a change of the modification of phthalocyanine structures occurs [27] but more frequently its destruction to metal oxides proceeds [28]. The results of kinetic measurements (Table 1) also refer to the course of these catalyst changes, since the effect of PCM to enhance the rate of oxygen consump-

tion successively decreases in the first hours of oxidation and after 8 h its influence on the yield of final products is small. The studied types of catalysts have no influence on the distribution of oxidation products, i.e. in their presence the ratio of $w(\text{TA})$ to $w(\text{MMT})$ does not change. The differences in the catalytic effect of α - and β -modifications of PCCu (Table 3) do not show the possibility of oxygen activation suggested in the case of α -PCCu which is more active in the oxidation of α -methylstyrene [29]. Though a higher activity of α -PCCu has been noticed also in the oxidation of *p*-xylene and *p*-methyltoluate catalyzed by Co—N catalyst, these differences were almost eliminated using a mixed Co—Mn—N catalyst. Furthermore, in the presence of the last mentioned catalyst, also the negative influence of Cu—N co-catalyst which is an effective scavenger of radicals [30] is substantially suppressed. In both of the last mentioned cases, this function of copper catalyst is hindered, probably due to a formation of mixed manganese—copper complexes.

During the study of metal phthalocyanines as co-catalysts of cobalt- and cobalt—manganese-catalyzed oxidation of *p*-xylene and *p*-methyltoluate mixture, the main attempt was focused on the investigation of the influence of these catalysts on the oxidation rate and formation of oxidation products. The obtained results suggest that the metal phthalocyanines act as hydroperoxide decomposers and not as activators of molecular oxygen.

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