

Supplementary Material

Selective Aerobic Oxidation of P-Methoxytoluene by Co(II)-Promoted NHPI Incorporated into Cross-Linked Copolymer Structure

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Abstract: A wide series of copolymer materials with various contents of 4-vinyl-diisopropyl-phthalate ester (10–90 mol%), divinylbenzene (1–11 mol%) and styrene, as monomers, were obtained by radical copolymerization. In the last steps of the synthesis, diisopropyl ester functionalities were converted into the form of N-hydroxyphthalimide (NHPI) rings. The obtained materials with the NHPI groups immobilized in the copolymer structure were studied by various physicochemical techniques, including FT-IR, UV-Vis-DR, XPS, elemental analysis, and tested as catalysts in aerobic oxidation of p-methoxytoluene in the presence of Co(II) acetate co-catalyst. Conversion of the aromatic substrate was correlated with the NHPI content and cross-linking degree. The best catalytic performance (conversions higher than 23%) was achieved for the copolymer catalysts containing 60% and 30% of 4-vinyl-diisopropyl-phthalate ester. At too high concentrations of NHPI and DVB, some of the NHPI groups were transformed into inactive (C=O)-N=O species or not available due to embedding inside the copolymer structure. The mechanism of the process involving both NHPI centers, forming phthalimide N-oxyl (PINO) radicals, and Co(II) cations was discussed. Stability of the developed catalysts was also tested. The opening of imide rings took place during the catalytic process, resulting in the formation of carboxyl groups and the release of hydroxylamine molecules. The deactivated catalyst could be easily regenerated by repeating two last steps of closing imide ring.

Keywords: copolymerization; 4-vinyl-diisopropyl-phthalate ester monomer; NHPI species; Co(II) co-catalyst; aerobic oxidation of p-methylanisole; reaction mechanisms; copolymer catalyst regeneration

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Table S1. Yield (%) and selectivity to p-anisyl alcohol (%; values given in brackets) in the presence of the copolymer catalysts with different NHPI loadings and cross-linking degrees measured after 6 h tests at 80 °C (0.1 g copolymer catalyst, 5.0 mg AIBN, 5.0 mg Co(OAc)₂·4H₂O, 2.0 mL PMT, p_{O₂} = 1 atm).

mol% of DVB	mol% of NHPI								
	10	20	30	40	50	60	70	80	90
1	2.8 (19.5)	0.9 (12.2)	2.6 (26.9)	4.2 (25.7)	0.9 (20.3)	1.6 (14.8)	0.8 (26.2)	0.2 (30.5)	0.8 (25.6)
3	2.9 (28.9)	1.6 (8.8)	2.9 (17.6)	3.0 (15.8)	4.0 (26.4)	3.9 (22.3)	0.5 (20.3)	2.1 (32.5)	0.7 (30.0)
5	1.7 (17.2)	2.9 (16.3)	5.3 (28.6)	2.4 (15.7)	4.5 (24.7)	3.7 (15.9)	0.6 (26.6)	0.3 (20.9)	0.3 (27.8)
7	2.3 (15.6)	5.3 (27.4)	3.9 (16.7)	4.3 (20.0)	4.1 (19.2)	1.8 (18.1)	0.9 (19.9)	0.9 (23.3)	0.4 (20.9)
9	3.4 (23.9)	3.8 (21.2)	4.2 (19.1)	1.6 (22.4)	1.2 (21.2)	1.6 (31.8)	2.0 (26.9)	0.7 (24.2)	0.5 (21.0)
11	2.1 (20.6)	0.4 (7.7)	2.1 (12.6)	1.3 (9.8)	0.6 (9.2)	n.m.	n.m.	n.m.	n.m.

The most active samples are highlighted by shading background.

Table S2. Yield (%) and selectivity to p-anisaldehyde (%; values given in brackets) in the presence of the copolymer catalysts with different NHPI loadings and cross-linking degrees measured after 6 h tests at 80 °C (0.1 g copolymer catalyst, 5.0 mg AIBN, 5.0 mg Co(OAc)₂·4H₂O, 2.0 mL PMT, p_{O₂} = 1 atm).

mol% of DVB	mol% of NHPI								
	10	20	30	40	50	60	70	80	90
1	6.0 (41.8)	2.8 (36.7)	3.3 (34.1)	5.9 (35.8)	2.1 (48.1)	5.4 (50.0)	1.1 (34.7)	0.3 (45.7)	0.9 (27.4)
3	2.9 (29.6)	5.8 (33.2)	5.0 (30.5)	6.2 (32.2)	4.6 (30.4)	4.8 (27.1)	0.9 (34.0)	3.3 (50.1)	1.2 (51.7)
5	2.7 (27.8)	6.1 (34.1)	4.5 (24.2)	3.5 (22.3)	5.9 (32.4)	4.6 (19.6)	0.8 (36.7)	0.8 (55.9)	0.6 (59.4)
7	5.2 (35.0)	4.8 (24.7)	5.7 (24.1)	6.9 (31.9)	7.1 (32.9)	3.6 (36.1)	1.5 (32.6)	1.9 (49.5)	0.7 (34.5)
9	4.9 (34.5)	7.4 (41.4)	7.2 (32.8)	3.5 (47.9)	2.5 (43.4)	2.9 (55.0)	3.4 (44.9)	1.5 (53.4)	1.0 (44.3)
11	3.7 (36.3)	1.5 (29.9)	5.6 (33.7)	4.4 (32.8)	1.5 (23.0)	n.m.	n.m.	n.m.	n.m.

The most active samples are highlighted by shading background.

Table S3. Yield (%) and selectivity to p-anisic acid (%; values given in brackets) in the presence of the copolymer catalysts with different NHPI loadings and cross-linking degrees measured after 6 h tests at 80 °C (0.1 g copolymer catalyst, 5.0 mg AIBN, 5.0 mg Co(OAc)₂·4H₂O, 2.0 mL PMT, p_{O₂} = 1 atm).

mol% of DVB	mol% of NHPI								
	10	20	30	40	50	60	70	80	90
1	4.2 (29.3)	3.2 (41.7)	2.9 (30.0)	5.3 (32.2)	1.1 (24.9)	2.9 (26.8)	0.9 (29.5)	0.1 (18.8)	1.2 (39.3)
3	3.5 (35.5)	9.2 (52.4)	8.1 (49.7)	9.4 (48.8)	5.5 (36.5)	8.3 (47.5)	1.1 (39.7)	1.0 (14.8)	0.2 (8.8)
5	4.9 (49.5)	7.3 (40.6)	7.6 (41.1)	8.5 (54.6)	6.6 (36.0)	14.2 (61.1)	0.7 (34.4)	0.3 (20.7)	0.1 (9.9)
7	6.0	8.3	12.8	9.1	8.4	3.7	1.9	0.7	0.8

	(40.1)	(42.4)	(54.3)	(42.0)	(39.2)	(37.5)	(42.3)	(18.2)	(40.4)
9	5.1	5.5	8.5	1.6	1.7	0.6	1.6	0.5	0.6
	(36.5)	(30.9)	(38.7)	(21.5)	(29.2)	(11.6)	(21.0)	(16.5)	(26.1)
11	4.2	3.1	7.5	6.5	3.9	n.m.	n.m.	n.m.	n.m.
	(41.2)	(62.3)	(45.1)	(48.7)	(59.7)				

The most active samples are highlighted by shading background.