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Liquid Phase Oxidation of 2,6-Di-*t*-butylphenol by Molecular Oxygen Using Magnesium Oxide Catalysts Modified with Metal Ion

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Mn(II), Co(II), Cu(II), or Fe(III) ion containing magnesium oxides catalyzed oxidation of 2,6-di-*t*-butylphenol to quinones by molecular oxygen. 98% Yield to 1,1'-bis(4-oxo-3,5-di-*t*-butylcyclohexadienylidene) was obtained with 16.7 wt% Mn ion containing magnesium oxide catalyst.

Recently, we developed novel catalytic process for the synthesis of α,β -unsaturated compounds using magnesium oxide catalysts modified with metal ion.[1,2] The additive metal ion in the catalysts may be coordinated by basic oxygen in the MgO lattice, and its circumstance is considered similar to that of metal ion incorporated into schiff's base complex. In this study, it is demonstrated that liquid phase oxidation of 2,6-di-*t*-butylphenol by molecular oxygen, which is extensively investigated using schiff's base complex,[3,4] is catalyzed by metal ion containing magnesium oxides(M-MgO).

Four kinds of metal ions, Mn(II), Co(II), Cu(II), and Fe(III), were chosen as additive elements because these ions are active elements for phenol oxidations. M-MgO catalysts were prepared by impregnation method reported in the previous paper.[1] The catalyst(0.6 g) treated in a nitrogen atmosphere for 2 h at 600 °C before the reaction was dispersed in organic solvent(100 ml) without exposure to air and then 2,6-di-*t*-butylphenol(0.01 mol) was added. The mixture was reacted for 24 h at room temperature under bubbled oxygen. The products were analyzed by gas chromatography(OV-1, 1 m, 100-280 °C). The results are given in Table 1.

Metal ion containing MgO catalysts were found to be very active for the oxidation of phenol. Mn-MgO catalyst promoted a coupling reaction of 2,6-di-*t*-butylphenol exclusively to form 1,1'-bis(4-oxo-3,5-di-*t*-butylcyclohexadienylidene)(DPQ). The catalytic activity and selectivity for DPQ formation increased steeply with increase of the content of added Mn ion up to 3 wt%(Runs 1-4). It should be noteworthy that the selectivity to DPQ is 100%. Further addition of Mn ion into MgO brought about no pronounced effects on both activity and selectivity. 2,6-Di-*t*-butylphenol oxidation to DPQ also took place over Co, Cu, and Fe-MgO catalysts(Runs 5-7). These catalysts, however, were less active and less selective than Mn-MgO catalyst, catalyzing 2,6-di-*t*-butylbenzoquinone(BQ) formation. Among the catalysts tested the maximum yield (98%) of DPQ was obtained with 16.7 wt% Mn-MgO catalyst.

Table 1. Oxidation of 2,6-Di-*t*-butylphenol over Metal Ion Containing MgO Catalysts

Run	Catalyst	wt%	Solvent	Yield of Quinones/%	Selectivity/%	
					DPQ	BQ
1	Mn-MgO	0.5	benzene	36	97	3
2	Mn-MgO	3.1	benzene	94	100	0
3	Mn-MgO	9.9	benzene	97	100	0
4	Mn-MgO	16.7	benzene	98	100	0
5	Co-MgO	3.1	benzene	42	95	5
6	Cu-MgO	3.1	benzene	7	83	17
7	Fe-MgO	3.1	benzene	19	81	19
8	$Mn(OH)_2$	-	benzene	tr	-	-
9	MgO	-	benzene	0	-	-
10	Mn-MgO	3.1	methanol	55	100	0
11	Mn-MgO	3.1	acetonitrile	82	100	0
12	Mn-MgO[a)]	3.1	benzene	tr	-	-

a) CO_2 was bubbled for 1 min before the reaction.

Since MgO and $Mn(OH)_2$ were completely inactive by themselves for oxidation of phenol(Runs 8,9), it is obvious that the incorporated metal ion in MgO lattice plays an important role in the course of reaction. In addition, the surface base seems to be affecting the activity of catalyst because benzene was found the most effective solvent for the formation of DPQ and the yield of the DPQ was low when a polar solvent, such as methanol(Run 10) or acetonitrile(Run 11) was used. In order to study the role of surface base of Mn-MgO catalysts, the catalytic oxidation was carried out using Mn-MgO of which surface base was poisoned with CO_2 before the reaction. CO_2 poisoned Mn-MgO catalyst showed no activity for the conversion of 2,6-di-*t*-butylphenol(Run 12). It seems, therefore, that the basic site on the MgO surface promoted the formation of phenolate anion which would be intermeditate of the reaction.

It is well-known that cobalt schiff's base complexs catalyze BQ formation mainly in the oxidation of 2,6-di-*t*-butylphenol. On the other hand, Co-MgO catalyst showed a high ability for coupling reaction to form DPQ. This difference may result from the property change of metal ion by the incorporation into MgO lattice. This might be the reason for 100% selectivity attained on Mn-MgO catalyst.

References

1) W. Ueda, T. Yokoyama, H. Kurokawa, Y. Moro-oka, and T. Ikawa, J. Jpn. Petrol. Inst., 29, 72(1986).
2) W. Ueda, H. Kurokawa, Y. Moro-oka, and T. Ikawa, 1985, 819.
3) M. Frostin-Rio, D. Pujol, C. Bied-Charreton, M. Perree-Fauvet, and A. Gaudemer, J. Chem. Soc., Perkin Trans. 1, 1984, 1971.
4) A. Nishinaga, K. Watanabe, and T. Matsuura, Tetrahedron Lett., 15, 1291(1974).

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