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The Wet Oxidation of Organic Compounds Catalyzed by Co–Bi Complex Oxide

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Synopsis. The wet oxidation of various organic compounds was carried out in the presence of the Co–Bi (5:1) complex oxide catalyst. The catalyst was especially effective for the oxidation of all refractory lower carboxylic acids, which are intermediates in the wet oxidation of many organic compounds.

Wet oxidation, carried out in air under a high pressure and at an elevated temperature, is particularly effective for the purification of wastewaters which are resistant to biological treatment,[1] and the recovery of mechanical energy is possible when the process is applied to a highly contaminated wastewater.[2] The severe operating conditions, however, limit the application of this process, and so the development of various catalysts has been attempted in order to mitigate the reaction conditions.[3–6] Although homogeneous copper salts are highly active,[7] heterogeneous catalysts are recommended in actual waste-water treatment. The available data on active heterogeneous catalysts, however, seem to be meagre.[8]

Previously, it was found that cobalt–bismuth complex oxide with a molar ratio of Co to Bi of 5 was remarkably active in the wet oxidation of acetic acid.[9] In this work, the activity of this catalyst in the wet oxidation of various water-soluble organic compounds was investigated.

Experimental

Reagent. Commercial polyethylene glycol with a molecular weight of 4000 (PEG-4000) and other commercial reagents were used without further purification.

Preparation of the Catalyst. Co–Bi complex oxide with a molar ratio of Co to Bi of 5 (Co/Bi[5/1]) was prepared as follows. Corresponding amounts of cobalt(II) nitrate and bismuth(III) nitrate (total amount: *ca.* 30 g) were dissolved in 100 ml of concentrated nitric acid, and the solution was poured into 500 ml of 3 mol/dm^3 sodium hydroxide. The resultant precipitate was washed with water until no nitrogen component was detected by means of a total-nitrogen analyzer. After drying at 100 °C, the precipitate was calcined at 350 °C for 2 h in air. On the basis of the weight change of the catalyst, the Bi was regarded as BiO(OH), and the Co, as Co_3O_4. The catalyst had a BET surface area of 64 m^2/g and a particle size smaller than 200 mesh.

Procedure. The catalyst, deionized water, nitrogen (3.8 MPa), and oxygen (1.0 MPa) were charged into a 270 cm^3 autoclave equipped with a sample injector and a valve for sampling. After the autoclave had been heated to a prescribed temperature by means of an electric furnace, a known amount of the reactant was injected through an injector under pressure. At appropriate time intervals, an aliquot of the solution was then withdrawn and submitted to analysis. Unless otherwise stated, the pH of the solution was not adjusted.

The oxidation of ammonia was carried out in the same way (Reaction conditions: $[NH_3]=1200$ ppm, $[Co+Bi]=2.0\times10^{-2}$ mol/dm^3, $P(O_2)=1.0$ MPa, $P(N_2)=3.0$ MPa, temp=270 °C, pH=11.0). In this case the determination of total nitrogen (TN) in the solution was carried out when the autoclave was cooled down to room temperature after the reaction for 1 h, because analysis during the reaction at a high temperature (270 °C) might be inaccurate due to the escape of ammonia into the vapor phase.

The total organic carbon (TOC) and TN were determined by means of a Sumitomo GCT-12N TOC-TN analyzer.

Results and Discussion

Table 1 shows the results of the wet oxidation of various organic compounds. R_{cat} and $R_{\text{no cat}}$ show the initial rates of TOC-decrease in the presence and in the absence of Co/Bi[5/1] respectively. The ratio of the initial rates, $R_{\text{cat}}/R_{\text{no cat}}$, indicates the effect of the catalyst under the present reaction conditions. From the values of $R_{\text{cat}}/R_{\text{no cat}}$, it is shown that Co/Bi[5/1] was effective for the wet oxidation of various compounds. In the cases of the oxidation of 1,2-propanediol and acetonitrile, the induction periods were observed, and the effect of the catalyst was not shown by $R_{\text{cat}}/R_{\text{no cat}}$. However, the percentage decrease in TOC after 20 min shows that the both reactions were accelerated in the presence of the catalyst (Runs 24 and 25). Co/Bi[5/1] was also effective for the oxidation of refractory pyridine, although the effect was not so large. The oxidation of some compounds, such as phenol, glutamic acid, and urea, proceeded so rapidly, even in the absence of Co/Bi[5/1], that the effect of the catalyst could not be evaluated (Runs 15—17 and 27). The effect of the catalyst might be seen by carrying out the reaction at lower temperature. However, as can be seen from the temperature-dependence of the oxidation of acetic acid (Runs 2—5), the effect of the catalyst was less remarkable at lower temperatures. The oxidation of oxalic acid at low temperatures (140 and 112 °C) was not accelerated by Co/Bi[5/1] (Runs 10 and 11). Thus, the appropriate temperature, depending upon

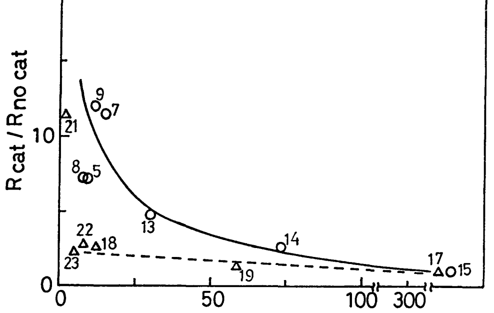

Fig. 1. Oxidation of organic compounds at 248 °C. Reaction conditions are shown in Table 1.
○: Carboxylic acids, △: compounds other than carboxylic acid. Numerals correspond to Run No. in Table 1.

TABLE 1. WET OXIDATION OF WATER-SOLUBLE ORGANIC COMPOUNDS IN THE PRESENCE AND ABSENCE OF Co/Bi[5/1][a]

			Without catalyst			With catalyst			
Run	Reactant	t/°C	pH	$R_{\text{no cat}}$[b] / ppm min^{-1}	ΔTOC[c] at 20 min / %	pH	R_{cat}[d] / ppm min^{-1}	ΔTOC[c] at 20 min / %	$R_{\text{cat}}/R_{\text{no cat}}$
1	Formic acid	112	2.8	17.7	17.3	2.9	27.8	25.9	1.6
2	Acetic acid	180	3.4	1.0	1.0	3.5	1.8	2.0	1.8
3	Acetic acid	200	3.4	2.6	2.4	3.4	6.8	7.1	2.6
4	Acetic acid	225	3.4	3.5	3.2	3.3	24.2	25.1	7.0
5	Acetic acid	248	4.0	9.2	8.3	3.4	70.5	67.0	7.2
6	Propionic acid	248	4.5	7.3	6.9	4.6	155	79.0	21.2
7	Butyric acid	248	3.5	15.0	17.5	3.8	173	83.4	11.5
8	Valeric acid	248	3.7	8.5	8.3	3.8	61.1	50.9	7.2
9	Hexanoic acid	248	3.5	11.7	12.4	3.4	140	80.6	12.0
10	Oxalic acid	112	1.4	0	0	1.4	0	0	—
11	Oxalic acid	140	1.4	35.6	27.0	1.4	35.6	31.9	1
12	Oxalic acid	160	2.5	$\simeq$330	90.0	2.5	$\simeq$330	86.3	1[e]
13	Adipic acid	248	2.8	29.4	27.3	3.2	142	97.4	4.8
14	Succinic acid	248	3.2	73.2	58.6	3.2	200	100	2.7
15	Glutamic acid	248	8.1	$\simeq$360	72.5	7.4	$\simeq$360	82.5	1[e]
16	Phenol	180	3.3	$\simeq$220	83.1	5.2	$\simeq$280	92.7	1.3
17	Phenol	248	2.8	$\simeq$390	93.4	3.5	$\simeq$390	95.8	1[e]
18	Methanol	248	5.5	11.7	11.7	6.2	29.5	29.0	2.5
19	Acetaldehyde	248	3.2	58.3	46.6	3.5	75.3	69.4	1.3
20	PEG-4000	200	4.4	31.6	38.3	7.7	117	77.9	3.7
21	Acetamide	248	6.6	0.9	1.0	8.3	10.3	12.1	11.4
22	Propionamide	248	6.0	7.2	6.2	7.5	19.5	19.2	2.7
23	Valeramide	248	7.9	4.4	4.1	8.0	10.0	14.4	2.3
24	1,2-Propanediol	248	6.5	0[f]	9.3	3.9	170	79.5	—
25	Acetonitrile	248	8.2	0.5>[f]	0.6	7.0	0.5>[f]	5.8	—
26	Pyridine	270	7.4	0	0	7.4	3.4	4.0	—
27	Urea	248	9.4	400<	100	9.5	400	100	—

a) Reaction conditions: $[\mathrm{Co+Bi}]=2.0\times10^{-2}\ \mathrm{mol/dm^3}$, $P(\mathrm{O_2})=1.0$ MPa, $P(\mathrm{N_2})=3.0$ MPa. b) Initial rate of TOC decrease in the absence of Co/Bi[5/1]. c) Percentage decrease in TOC. d) Initial rate of TOC decrease in the presence of Co/Bi[5/1]. e) Inaccurate due to rapid reaction. f) Induction period appeared.

the kind of compound to be oxidized, is necessary for the catalyst to exert its activity.

In order to see the property of the catalyst more clearly, the values of $R_{\text{cat}}/R_{\text{no cat}}$ were plotted against $R_{\text{no cat}}$ in the oxidation of various compounds at 248 °C (Fig. 1). It is clear that the catalyst is especially effective for the oxidation of carboxylic acid; the more refractory the carboxylic acid is, the more effective the catalyst is. However, for compounds other than carboxylic acid, the effect of the catalyst is not so remarkable. Previously, it was deduced that the catalytic action of Co/Bi[5/1] was due to two of its properties; one was the presence of basic sites, induced by Bi, where acetic acid was adsorbed by an acid–base interaction in the first step of the reaction, and the other was its redox property which induced the decomposition of the adsorbed acetic acid.[9] From the results shown in Fig. 1, it is clear that the catalyst exhibited the former property more strongly; the acid-base interaction played an important role in the oxidation of all carboxylic acids. The catalyst was quite effective for the oxidation of acetamide. As acetamide is readily hydrolyzed to produce acetic acid under the present reaction conditions,[10] the catalyst is apparently highly active in the oxidation of acetamide.

Many organic compounds undergoing wet oxidation gradually degrade to low-molecular-weight compounds and, finally, to highly refractory lower carboxylic acids.[11] As Co/Bi[5/1] is remarkably active for the oxidation of all refractory lower carboxylic acids, it is quite useful as a catalyst for the wet oxidation of wastewater.

The contamination of wastewater by ammonia is a serious environmental problem; however, few active catalysts for the wet oxidation of ammonia have been reported.[12] The catalytic activity of Co/Bi[5/1] in the wet oxidation of ammonia was investigated, the reaction conditions being shown in the Experimental section. The percentage decrease in TN in the solution was 46.0%, compared with 20.5% in the absence of Co/Bi[5/1], showing that the catalyst was also effective in the wet oxidation of ammonia.

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