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Oxidation of Acetic Acid on Co–Bi Composite Oxide Catalysts

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The complete oxidation of acetic acid on Co–Bi composite oxide catalysts was investigated with a comparison of their activity for the oxidation of toluene. Co–Bi composite oxides (Co/Bi · ox) with Bi contents of 10–20 mol% exhibited high activity for the oxidation of acetic acid, and a reduced Co–Bi composite oxide catalyst (Co/Bi · red) containing as much as 55 mol% of Bi had the same activity as a reduced Co catalyst. However, both catalysts were not as active for the oxidation of toluene as for the oxidation of acetic acid. Temperature-programmed desorption experiments showed that the high activity of Co/Bi · ox for the oxidation of acetic acid was due partly to the strong affinity of Bi for acetic acid. The addition of Bi up to 20 mol% increased the surface area of Co/Bi · ox which was another factor contributing to the high activity of the catalyst for the oxidation of acetic acid. Both Co/Bi · ox and Co/Bi · red exhibited larger compressive strength than the corresponding Co catalyst without Bi.

1. INTRODUCTION

Emission of organics from stationary and automobile sources is a serious environmental problem. Catalytic oxidation is an effective means of controlling organic emissions and achieving odor control. Generally, two types of oxidation catalysts are available—noble metal catalysts and metal oxide catalysts. Although noble metals such as platinum and rhodium are highly active (*1–4*), their supplies are limited. Therefore, the use of plentiful and inexpensive metal oxide catalysts is preferred. The activity of existing metal oxide catalysts, however, is relatively low compared with that of noble metal catalysts; therefore, the development of more effective oxide catalysts is necessary. Most of the metal oxide catalysts used for the complete oxidation of organics have utilized first-series transition metals (*5–7*). Few studies have been reported for combustion catalysts containing non-transition elements such as Bi (*8*) although Bi has been frequently utilized as a co-catalyst for various molybdate catalysts for the partial oxidation of olefins such as propylene (*9–11*). Co has also been used as a co-catalyst for some of these Mo–Bi catalysts (*12, 13*). However, there have been no reports on the catalytic activity of Co–Bi composite oxide catalysts for vapor-phase oxidation of organics to CO_2 and H_2O.

Previously, we carried out an aqueous-phase oxidation of acetic acid and found that Co–Bi composite oxide catalysts have high activity (*14*). This paper deals with the vapor-phase oxidation of acetic acid to CO_2 and H_2O on Co–Bi composite oxide catalysts. The activities of the catalysts for acetic acid oxidation are compared with their activities for the oxidation of toluene.

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2. EXPERIMENTAL

Catalyst Preparation

(*a*) *Oxidized catalyst* (*Co/Bi · ox*). Cobalt(II) nitrate and bismuth(III) nitrate at known molar ratios were dissolved in concentrated nitric acid (ca. 30 g/100 ml acid); this solution was poured into 500 ml of a 3 *M* sodium hydroxide solution. The resultant precipitate was washed with water until no nitrogen component was detected in the washings by a total-nitrogen analyzer. The precipitate was then dried in air at 100°C. The dry precipitate was molded into a bar (0.5 × 1 × 5 cm), and calcined at 450°C for 2 h in air. On the basis of the weight change of the catalysts, Bi appeared to be present as Bi_2O_3, and Co, as Co_3O_4. Single-component oxide catalysts prepared from bismuth(III) nitrate and cobalt(II) nitrate also showed apparent compositions corresponding to Bi_2O_3 and Co_3O_4, and they were designated as Bi_2O_3 and Co_3O_4, respectively. The catalysts were crushed into about 20-mesh size before use.

(*b*) *Reduced catalyst* (*Co/Bi · red*). Bars of the oxidized catalysts prepared by the above procedure were reduced in a hydrogen stream at 450°C for 2 h. They were crushed into about 20-mesh size and stored under a nitrogen atmosphere.

Apparatus and Procedure

Reactions were carried out using an ordinary flow reactor under atmospheric pressure. Saturated vapors of acetic acid or toluene were obtained by passing dried air through saturators containing G. R.-grade acetic acid or toluene, respectively. Two flow lines, one from the saturator and the other from an air pump, were connected to a mixing chamber, and the outlet tube from the mixing chamber was connected to the reactor via a preheater tube. The concentrations of acetic acid and toluene entering the reactor were 3000 and 2000 ppm, respectively. The catalysts were supported in the 7-mm-o.d. quartz tube reactor by glass wool plugs. The temperature of the catalyst bed was monitored with a Chromel–alumel thermocouple placed at the center of the catalyst bed. Unless otherwise stated, space velocities were 10,000 h^{-1} for toluene oxidation and 20,000 h^{-1} for acetic acid oxidation. Space velocity was defined by $V(\text{feed})/V(\text{cat}) \cdot h$, where V(feed) and V(cat) were the volumes of the feed gas and the catalyst used at STP, respectively. The temperature of the catalyst bed was raised from room temperature at a constant rate of 3.75°C/min with an electric furnace. The temperature of the initiation of oxidation (T_1) and the temperature where conversion to CO_2 reached 95% (T_2) based upon whether acetic acid or toluene was being fed into the reactor were recorded. T_1 was defined as the temperature where the concentration of CO_2 at the outlet of the reactor exceeded 200 ppm. Complete oxidation of acetic acid and toluene was confirmed by the attainment of approximately 100% yield of CO_2 and from the absence of any possible by-products other than CO_2 such as formic acid, formaldehyde, methanol, acetone, and methyl formate at the outlet of the reactor as determined by a Hitachi 063 gas chromatograph equipped with a flame ionization detector using Chromosorb 101 (3 mm diam × 1 m length). However, T_2 was preferred to the temperature of complete oxidation for the evaluation of the activity of the catalysts because of the possibility that trace amounts of other by-products might have escaped detection using the above analytical technique. Therefore, complete oxidation was defined as the point where approximately 100% conversion to CO_2 from acetic acid or toluene was attained and no increase in the CO_2 concentration at the outlet of the reactor was observed as the temperature of the catalyst bed was further increased.

The temperature-programmed desorption experiments were carried out by adsorbing acetic acid or toluene onto the catalysts at 50°C and then heating the sample at a rate of 3.75°C/min under a nitrogen atmosphere.

Analysis

Acetic acid, toluene, carbon dioxide, and acetone were analyzed using a Shimadzu GC-3BT gas chromatograph. The column packing consisted of activated charcoal (3 mm diam × 1 m length) for the analysis of carbon dioxide and Chromosorb 101 (3 mm diam × 1 m length) for acetic acid, toluene, and acetone. Total nitrogen was determined with a Sumitomo GCT-12N total-nitrogen analyzer. Differential thermal analysis (DTA) and X-ray analysis were carried out using a Rigaku Denki Thermoflex 8001 DTA analyzer and a Rigaku Denki Geigerflex 2012 X-ray analyzer, respectively. Compressive strengths of the catalysts were measured by the use of a Shimadzu P-100 Autograph. BET surface areas of the catalysts were measured with a Shimadzu Sorptgraph ADS-1B surface area analyzer.

3. RESULTS AND DISCUSSION

(*a*) *Effect of the Composition of Co/Bi · ox and Co/Bi · red on the Catalytic Activity*

Figure 1 shows the effects of the composition of the Co/Bi · ox and Co/Bi · red catalysts on T_1 and T_2 in the oxidation of acetic acid. Both T_1 and T_2 were lowered by addition of Bi to Co in the case of Co/Bi · ox catalysts and a minimum was reached at 10–20 mol% Bi (metal ion basis). This is the same behavior observed in the aqueous-phase oxidation of acetic acid where a Co/Bi · ox catalyst containing 16.7% of Bi was found to have the highest activity (*14*). It is interesting to note that Bi_2O_3 alone was effective for the oxidation of acetic acid. On the other hand, the activity of Co/Bi · red was affected very little by the incorporation of Bi into the catalyst since catalyst with as much as 55 mol% of Bi showed even a slightly higher activity than the Co catalyst.

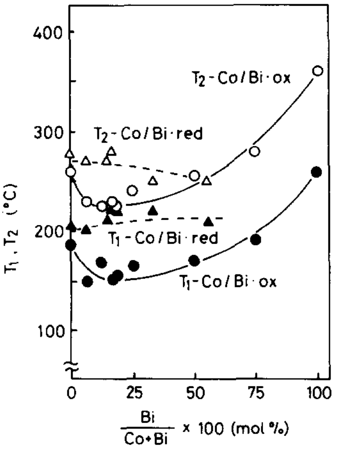

FIG. 1. Oxidation of acetic acid over Co/Bi · ox and Co/Bi · red. [AcOH] = 3000 ppm, SV = 20,000 h^{-1}.

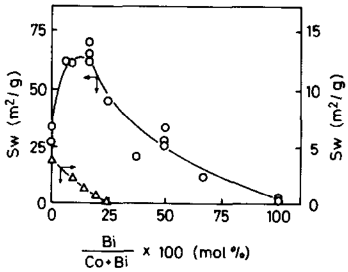

FIG. 2. BET surface area of (○) Co/Bi · ox and (△) Co/Bi · red.

Figure 2 shows the change in BET surface areas due to changes in the composition of the catalysts. The surface area of the Co_3O_4 catalyst was considerably larger than that of the Bi_2O_3 catalyst. However, addition of Bi to Co increased the surface area of the oxidized catalyst to a maximum when the Bi content was 10–20 mol%. Therefore, an increase in surface area is one of the most important factors contributing to the apparent high activity of the Co/Bi · ox catalysts with 10–20 mol% Bi. On the other hand, the surface area of the Co/Bi · red catalyst decreased monotonically with an increase in Bi content. However, the activity of the Co/Bi · red catalyst was almost the same irrespective of the Bi content even up to 55 mol% showing that surface area alone is not the controlling factor for the activity of the Co/Bi · red catalyst and that Bi has as much activity for oxidizing acetic acid as the Co catalyst.

As shown in Fig. 3, the incorporation of Bi into catalysts did not enhance the catalytic oxidation of toluene. A small amount

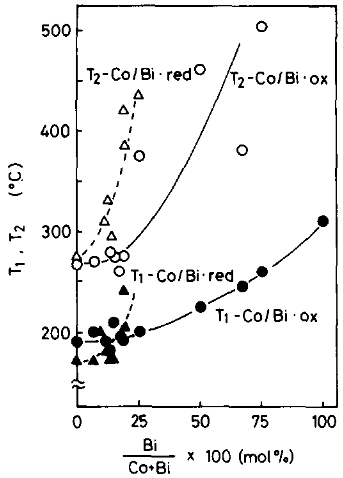

FIG. 3. Oxidation of toluene over Co/Bi · ox and Co/Bi · red. [Toluene] = 2000 ppm, SV = 10,000 h^{-1}.

of Bi in the reduced catalyst decreased the activity significantly. The retarding effect of Bi in the oxidized catalyst, however, was not so pronounced; Co/Bi · ox with 10–20 mol% Bi had almost the same activity as Co catalyst without Bi. It seems that an increase in the surface area of the Co/Bi · ox catalysts with 10–20 mol% of Bi compensates for the retarding effect of Bi toward toluene oxidation. The catalytic activity was relatively unaffected by the addition of 10–20 mol% Bi to the catalysts.

Details about the effect of less than 20 mol% of Bi on the surface area of the oxidized catalysts are unknown. It was found that Co/Bi · red catalysts with a high Bi content (e.g., 55 mol%) had a metallic appearance and a silver-gray color. Since the mp of Bi (271°C) is much lower than that of Co (1492°C), it seems that the bismuth metal produced by the reduction of Bi_2O_3 with hydrogen during the preparation of the Co/Bi · red catalysts aggregates and decreases the surface area of the catalysts monotonically as Bi content is increased.

It seems that the catalysts undergo oxidation or reduction during the reaction. The oxidation states of copper catalysts change during the oxidation of propylene, but they attain steady states within 20 min after the start of the reaction (*15*). The steady states are different depending upon the initial oxidation states of the copper catalysts employed. Changes in the oxidation state of Co/Bi · red catalysts with 15.4 mol% of Bi were investigated after the oxidation of toluene at 400°C for 1 h ([toluene] = 2000 ppm, SV = 10,000 h^{-1}). During the reaction, the color of the catalyst changed from dark gray to black which is typical of the oxidized catalyst. A 10.2% increase in weight was observed and was probably due to an incorporation of oxygen. If the catalyst is in a completely reduced state at the beginning of the reaction, and the final state is Co_3O_4–Bi_2O_3, the weight increase is 36.5%. Although the initial state of the catalyst was not analyzed, it seems that a considerable portion of the catalyst was oxidized during the reaction. However, BET surface area of the catalyst scarcely increased: 0.9 m^2/g before and 2.0 m^2/g after the reaction (compare with 50–70 m^2/g for Co/Bi · ox catalysts with similar Bi contents). These facts indicate that, although the oxidation states of the catalysts change during the reaction, this change differs depending upon the initial oxidation states of the catalysts employed, as, for example, with copper catalysts (*15*). Two types of catalysts, Co/Bi · ox and Co/Bi · red, were employed in this experiment in order to determine the effects of the initial oxidation states of the catalysts on their subsequent activities. Judging from the results shown in Figs. 1 and 3, oxidized catalysts in general exhibit greater catalytic activity than reduced catalysts.

Table 1 shows the compressive strength of the Co/Bi · ox and Co/Bi · red catalysts. As the content of Bi was increased, the compressive strengths of both catalysts increased. This was especially true of the Co/Bi · red catalysts for which addition of even a small amount of Bi produced a large increase in compressive strength. Therefore, addition of Bi to the Co catalysts increases their mechanical strength.

From this point on, we confine our discussion to the catalytic behavior of a Co/

TABLE 1

Compressive Strength of Catalysts[a]

Compressive strength of: (kg/cm²)	Bi (mol%)				
	0	17	37	50	100
Co/Bi · ox	8.5	25	36	60	140
Co/Bi · red	44	116	—	—	—

[a] Conditions for preparation of the catalysts are described in the experimental section.

Bi · ox catalyst with a Bi content of 16.7 mol% which was one of the oxidized catalysts with the highest activity for the oxidation of acetic acid. This catalyst with a molar ratio of Co to Bi of 5 was designated as Co/Bi · ox(5/1).

(*b*) *Acetic Acid and Toluene Oxidation over Co/Bi · ox(5/1)*

The deactivation of the Co/Bi · ox(5/1), Co_3O_4, and Bi_2O_3 catalysts was investigated. All catalysts retained the ability to completely oxidize acetic acid and toluene after reaction for 10 h at temperatures slightly higher than the corresponding temperature for complete oxidation: Co_3O_4, toluene: 285°C; AcOH: 270°C; Bi_2O_3, AcOH: 370°C; and Co/Bi · ox(5/1), toluene: 310°C; AcOH: 250°C.

Deactivation of the catalysts was also investigated at still higher reaction temperatures. Co_3O_4 previously used in the reaction at 500°C for 2 h catalyzed the complete oxidation of acetic acid at 270°C. Co/Bi · ox(5/1) was also active at 250°C after the same treatment (510°C for 2 h). However, 7–17% of acetic acid remained unconverted in the oxidation over Bi_2O_3 at 375°C after the reaction at 500°C for 2 h.

Co_3O_4 and Co/Bi · ox(5/1) lost some of their oxidizing activity for toluene after high-temperature reactions. Conversion of toluene to CO_2 over Co_3O_4 previously used in the reaction at 435°C for 2 h was 80% at 285°C and was 65% at 285°C with Co/Bi · ox(5/1) previously used in the reaction at 450°C for 2 h. These results indicate that both Co/Bi · ox(5/1) and Co_3O_4 have good thermal stability for the oxidation of acetic acid but are rapidly deactivated during the oxidation of toluene at elevated temperature.

The effect of variations in calcination temperature in the preparation of Co/Bi · ox(5/1) was investigated, and the results are summarized in Table 2. As the calcination temperature was lowered, BET surface areas (Sw) of the catalysts increased. Catalysts calcined at 350 and 450°C had higher activity for the oxidation of acetic acid than catalysts calcined at higher temperatures. However, the catalyst calcined at 350°C lost activity when used at 550°C; acetic acid conversion to CO_2 was about 30% after 1 h. The catalyst calcined at 650°C also lost activity during the reaction at 550°C for 2 h; acetic acid conversion to CO_2 was 50% when the reaction temperature was lowered to 270°C. The other two catalysts exhibited no deactivation under similar reaction conditions; therefore, calcination temperatures of 450–550°C appear to produce the most stable catalysts.

Complete oxidation of acetic acid was obtained on Co/Bi · ox(5/1) calcined at 450°C at a space velocity even as high as 307,500 h^{-1} although the required reaction temperature (290°C) was much higher than the temperature, 235°C, required for complete oxidation when the space velocity was 20,000 h^{-1}.

TABLE 2

Effect of Calcination Temperature of Co/Bi · ox(5/1)

Calcination temp. (°C)	Sw (m²/g)	T_1[a] (°C)	T_2[a] (°C)
350	69	150	240
450	65	150	230
550	18	170	250
650	6.5	180	265

[a] Oxidation of AcOH. [AcOH] = 3000 ppm; SV = 20,000 h^{-1}.

(*c*) *DTA and X-Ray Analysis of Co/Bi · ox(5/1)*

Precipitated $Co(OH)_2$ and $Bi(OH)_3$, and co-precipitated Co–Bi mixed hydroxide with a Co-to-Bi molar ratio of 5 were dried at 100°C and subjected to DTA (Fig. 4). $Co(OH)_3$ showed a sharp endothermic peak at 265°C corresponding with its change to Co_3O_4 (*16*). $Bi(OH)_3$ exhibited two peaks, one at 130°C and the other at 740°C. The latter was considered to be attributable to the conversion of α-Bi_2O_3 to δ-Bi_2O_3 (*17*). Although the intermediate states between $Bi(OH)_3$ and α-Bi_2O_3 are not clear, the peak at 130°C might be due to the conversion of $Bi(OH)_3$ to $BiO(OH)$ (*18*). The endothermic pattern of co-precipitated Co–Bi mixed hydroxide was quite different from those of $Co(OH)_2$ and $Bi(OH)_3$; peaks at 130, 265, and 740°C observed for $Co(OH)_2$ or $Bi(OH)_3$ disappeared and new peaks appeared at 350 and 280°C.

X-Ray diffraction patterns of Co/Bi · ox(5/1) and a mixture of Co_3O_4 and Bi_2O_3 with a Co-to-Bi molar ratio of 5, each prepared from the corresponding hydroxide at 450°C, are shown in Fig. 5. Bi_2O_3 had a high degree of crystallinity although Co_3O_4 was considerably amorphous. The X-ray diffraction pattern of Co/Bi · ox(5/1) was different from that of the mixture of Co_3O_4 and Bi_2O_3; the intensity of its peaks was very weak, and the linewidths were broad. The peak at $d = 2.79$ Å ($2\theta = 32.1°$) of Bi_2O_3 disappeared indicating that irregularities at the (123) and/or (202) planes of Bi_2O_3 had occurred. Also, the peak at $d = 3.39$ Å ($2\theta = 26.3°$) of Bi_2O_3 was split into a doublet indicating that the (121) plane of Bi_2O_3 had been distorted in the catalyst. Thus, DTA and X-ray analysis seem to indicate that Co/Bi · ox(5/1) is different from a physical mixture of Co_3O_4 and Bi_2O_3 and that Bi interacts with Co in the catalyst.

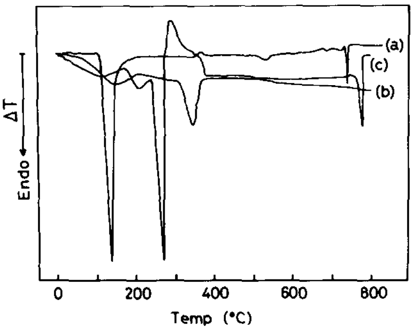

FIG. 4. DTA curves of (a) $Bi(OH)_3$, (b) $Co(OH)_2$, and (c) Co–Bi mixed hydroxide with a Co-to-Bi molar ratio of 5. All hydroxides were prepared by precipitation and dried at 100°C.

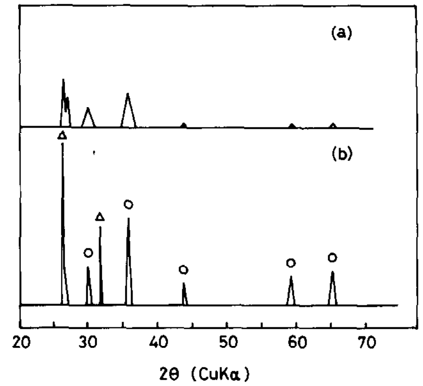

FIG. 5. X-Ray diffraction patterns of (a) Co/Bi · ox(5/1) and (b) a mixture of Co_3O_4 and Bi_2O_3 with a Co-to-Bi molar ratio of 5. All oxides were prepared by calcinating the corresponding hydroxides at 450°C. Δ: Bi_2O_3, ○: Co_3O_4.

(*d*) *Adsorption Properties of Co/Bi · ox(5/1) for Acetic Acid and Toluene*

Figure 6 shows the temperature-programmed desorptions (TPD) for acetic acid and toluene adsorbed on Bi_2O_3, Co_3O_4, or Co/Bi · ox(5/1). Three peaks were observed in the desorption profile for acetic acid on Bi_2O_3 (Fig. 6a). The first desorption peak appeared at the very beginning of the TPD time; the second peak appeared at 180–300°C. The third desorption occurred at around 290°C and was due to acetone. Carboxylic acids undergo dehydration and decarboxylation to produce ketones by an interaction with basic metal salts such as BaO (*19*). Since CO_2 was detected during the desorption of acetone, the following reaction is suggested:

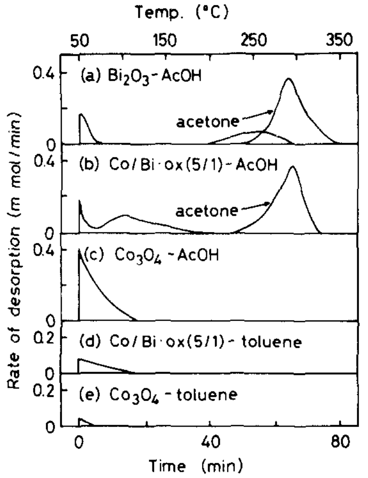

FIG. 6. TPD of adsorbed acetic acid and toluene. Sw = 4.6 m²/g [Bi_2O_3], 46 m²/g [Co_3O_4], 62 m²/g [Co/Bi · ox(5/1)].

$$2CH_3COOH \xrightarrow{Bi_2O_3} (CH_3)_2C{=}O + H_2O + CO_2.$$

The amount of acetic acid desorbed from Co_3O_4 was far less than the total amount of desorbed species from Bi_2O_3 despite the larger surface area of Co_3O_4 (Fig. 6c). Note that one molecule of acetone corresponds to two molecules of acetic acid. Interaction between acetic acid and Bi_2O_3 played an important role in the adsorption process. Co/Bi · ox(5/1) gave a TPD pattern somewhat similar to that of Bi_2O_3; desorption occurred at three different temperature ranges and the desorbing species at the highest temperature range was acetone (Fig. 6b). However, desorption of acetic acid occurred differently compared with its desorption from Bi_2O_3 and Co_3O_4. This supports the results of DTA and X-ray analysis that some interaction exists between Co and Bi. From the comparison of the amounts of desorbed species and the temperature of their desorption, it was suggested that Co/Bi · ox(5/1) had almost the same ability to adsorb acetic acid as Bi_2O_3.

Desorption of toluene occurred at low temperature from both Co/Bi · ox(5/1) and Co_3O_4 (Figs. 6d,e). The amount of toluene desorbed from Co/Bi · ox(5/1) was much smaller than that of acetic acid plus acetone desorbed from the same catalyst. This result, together with the fact that Co_3O_4 adsorbed much smaller amounts of acetic acid than Co/Bi · ox(5/1), indicated that Bi increases the affinity of Co/Bi · ox catalysts for acetic acid.

The catalytic action of Mo–Bi catalysts for the oxidation of olefins has been investigated extensively (*20–23*). For example, Batist *et al.* reported that the oxidizing component in these catalysts is Mo and that Bi acts as an oxygen carrier to reoxidize the reduced Mo and therefore promotes the oxidation of 1-butene (*24*). Co has much higher activity for oxidation reactions than Mo (*25*), and it is improbable that Bi improves the oxidizing ability of Co as in the case of the Mo–Bi catalyst reported by Batist *et al.* This is suggested by the fact that the activity of Co for the oxidation of toluene is decreased by addition of Bi. Ai and Ikawa reported that the addition of Bi to Mo increases the selectivity of the catalyst to produce unsaturated aldehyde (e.g., acrolein) during the oxidation of olefins by decreasing the affinity of the catalyst for aldehydes thus promoting their desorption from the surface of the catalyst to avoid their further oxidation (*26*). The role of Bi of the Co/Bi · ox catalysts in the oxidation of acetic acid seems to be opposite to that of the Mo–Bi catalyst reported by Ai and Ikawa. The strong affinity of Bi for acetic acid promotes the interaction of acetic acid with the catalysts in the first step of the reaction and, consequently, accelerates the whole reaction.

4. CONCLUSION

The catalytic activities of Co/Bi · ox and Co/Bi · red for the complete oxidation of acetic acid and toluene were investigated. The salient findings of this study are the following:

(1) Bi has an inherent activity for oxidizing acetic acid as indicated by the facts that Bi_2O_3 was significantly active in the oxida-

tion of acetic acid and that Co/Bi · red with a Bi content as high as 55 mol% exhibited the same activity as the reduced Co catalyst.

(2) One of the promoting effects of Bi in Co/Bi · ox for the oxidation of acetic acid is the strong affinity of Bi for acetic acid; acetic acid is rapidly adsorbed onto the surface of the catalyst in the first step of the reaction.

(3) Another important action of Bi is to increase the surface area of the Co/Bi · ox catalysts and increase their apparent activity, so long as its content is less than 20 mol%.

(4) Both the Co/Bi · ox and Co/Bi · red catalysts are not as active for the complete oxidation of toluene as for the complete oxidation of acetic acid. The low activity of the Co/Bi · ox catalysts is due partly to their weak affinity for toluene compared to their affinity for acetic acid.

(5) The addition of Bi increases the mechanical strength of both the Co/Bi · ox and Co/Bi · red catalysts.

Although it is suggested that Bi interacts with Co in the Co/Bi · ox catalyst, the details of the interaction and its effect on the properties of the catalysts remain unknown.

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