Oxidation of toluene to benzoic acid over modified $V_2O_5-TiO_2$ catalyst with SeO_2, TeO_2 and Sb_2O_3

Jun Miki [1], Yo Osada, Yakudo Tachibana and Tsutomu Shikada

Materials and Processing Research Center, NKK Corporation,
Kawasaki-ku, Kawasaki 210, Japan

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It was found that the addition of SeO_2, TeO_2 or Sb_2O_3 to a V_2O_5/TiO_2 catalyst greatly improved the catalytic activity in the vapor phase oxidation of toluene to selectively form benzoic acid.

Keywords: toluene oxidation; vapor phase; benzoic acid; V_2O_5; SeO_2; TeO_2; Sb_2O_3

1. Introduction

The yield of benzoic acid in the vapor phase oxidation of toluene remains low because of the low conversion of toluene and the poor selectivity to benzoic acid, although a great number of studies have been performed [1–10]. Recently, the mechanism of toluene oxidation in the vapor phase has been investigated and its reaction network has become apparent with the benzyl cation on the catalyst presumed to be the precursor [11,12]. On the other hand, further investigations of the structure and the chemical state of active vanadium species have also been performed using XRD, XPS, SIMS, and IR [13–22]. However, it is very difficult to enhance the benzoic acid yield which is about 30% at most in the vapor phase oxidation [8]. V_2O_5 catalyst, commonly used for partial oxidation of aromatic hydrocarbons, is the only active species found, thus far, to form benzoic acid from toluene. In the present work, we tried to modify V_2O_5 catalyst with some oxides in order to improve the catalytic performance and found that the higher benzoic acid yields could be obtained using a V_2O_5/TiO_2 catalyst modified by SeO_2, TeO_2 or Sb_2O_3.

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[1] To whom correspondence should be addressed, at: Research Institute of Innovative Technology for the Earth (RITE), 9-2, Kizugawadai, Kizu-cho, Soraku-gun, Kyoto, 619-02 Japan.

2. Experimental

The titania-supported catalysts were prepared by impregnating a commercially available granular titania (Dia Catalysts & Chem., particle size 20–40 mesh) with aqueous solutions of metal salts, followed by drying and then calcining in air at 500°C for 3 h. V_2O_5/Al_2O_3 and V_2O_5/SiC catalysts were also prepared to investigate the support effect. 2.0 g of catalyst was used and was diluted with quartz sand to 1/4 concentration by weight in order to maintain a homogeneous temperature distribution of the catalyst bed. The reactions were carried out at atmospheric pressure using a U-shaped fixed-bed flow reactor (12 mm i.d.) in salt bath furnace. Toluene and water were fed into a pre-heated zone at 250°C and vaporized before injection. The organic products were collected in two cooled trap systems at −70°C under steady reaction conditions, and analyzed by FID gas-chromatography. The gaseous products such as carbon monoxide and carbon dioxide were analyzed by TCD gas-chromatography.

3. Results and discussion

The activities and selectivities for various catalysts are summarized in table 1. The 5 wt% V_2O_5/TiO_2 catalyst produced higher conversion than 5 wt% V_2O_5/Al_2O_3 and 5 wt% V_2O_5/SiC catalysts, as well as higher selectivity to benzoic acid. The results show the effect of the support on the activity and selectivity of the catalyst. These results are consistent with the view that the combination of vanadium oxide and TiO_2 gives an effective catalyst for selective oxidation of toluene [8].

In order to achieve higher activity, K_2SO_4, SeO_2, Sb_2O_3, and TeO_2 were examined as additives to 5 wt% V_2O_5/TiO_2 catalyst. $V_2O_5-K_2SO_4$ catalyst is industrially used for vapor phase oxidation of *o*-xylene or naphthalene to phthalic anhydride. The addition of K_2SO_4 greatly improved the benzoic acid selectivity, while the conversion drastically decreased. On the other hand, the addition of SeO_2, Sb_2O_3, and TeO_2 to 5 wt% V_2O_5/TiO_2 was found to be very effective for increasing the catalytic activity and selectivity to benzoic acid compared to the 5 wt% V_2O_5/TiO_2 catalyst. As a consequence of the higher selectivity to benzoic acid, $CO + CO_2$ formation is inhibited compared to the 5 wt% V_2O_5/TiO_2 catalyst. Deactivation with the passage of time was observed when using the 5 wt% $V_2O_5-SeO_2/TiO_2$ catalyst, while the $V_2O_5-Sb_2O_3/TiO_2$ and $V_2O_5-TeO_2/TiO_2$ catalysts showed no deactivation after more than 100 h. Fig. 1 shows the effect of Sb_2O_3 content on the activity and selectivity of the 5 wt% V_2O_5/TiO_2 catalyst. 1 wt% of Sb_2O_3 content gave the highest benzoic acid selectivity and the lowest $CO + CO_2$ selectivity. Below 2 wt% of Sb_2O_3 content, toluene conversion increased with increasing Sb_2O_3 content and selectivities appeared to be independent of Sb_2O_3 content above 1 wt%.

The effect of TeO_2 content was also examined as shown in fig. 2. 1–2 wt% of

Table 1
Activities of various catalysts for vapour phase oxidation of toluene[a]

Catalyst[b]	Conversion (%)		Selectivity[c] (%)				
	toluene	O_2	benzoic acid	benzaldehyde	benzene	$CO + CO_2$[d]	others[e]
5 wt% V_2O_5/Al_2O_3[f]	9.8	19.0	17.9	27.8	0.6	42.5	11.2
5 wt% V_2O_5/SiC[g]	3.8	5.8	3.5	67.7	1.0	21.2	6.6
5 wt% V_2O_5/TiO_2[h]	58.6	94.9	50.8	3.0	1.1	45.1	tr
5 wt% V_2O_5–1 wt% K_2SO_4/TiO_2[h]	13.5	17.0	71.6	1.9	0	22.7	3.8
5 wt% V_2O_5–2 wt% SeO_2/TiO_2[h]	66.2	89.0	73.2	2.7	0.3	20.7	3.1
5 wt% V_2O_5–2 wt% Sb_2O_3/TiO_2[h]	83.4	88.7	75.0	1.0	0.8	21.0	2.2
5 wt% V_2O_5–2 wt% TeO_2/TiO_2[h]	79.8	93.0	74.4	1.1	0.8	22.4	1.3
5 wt% Sb_2O_3/TiO_2[h]	0.5	2.1	0	44.5	6.3	49.1	0.1
5 wt% TeO_2/TiO_2[h]	0.3	0.1	0	69.3	8.8	21.9	0.0

[a] Reaction conditions: toluene/$O_2/H_2O/N_2$ = 1/2.5/57/10 (molar ratio); reaction temperature = 350°C; SV = 15000 h^{-1}.

[b] Prepared by impregnation; calcination temperature = 450°C.

[c] Selectivity is calculated on the basis of moles of toluene converted.

[d] CO/CO_2 split is in the range from 0.010 to 0.045 (molar ratio).

[e] Maleic anhydride, phthalic anhydride, benzophenone, and anthraquinone.

[f] BET surface area of α-$Al_2O_3 < 1$ m^2/g.

[g] BET surface area of SiC = 21.1 m^2/g.

[h] BET surface area of TiO_2 = 23.0 m^2/g.

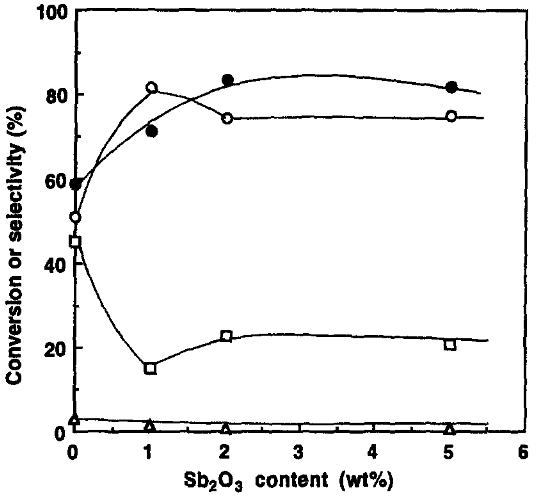

Fig. 1. Effect of Sb_2O_3 content on catalytic activity: catalyst, 5 wt% V_2O_5–Sb_2O_3/TiO_2; reaction conditions: temperature = 350°C; toluene/$O_2/H_2O/N_2$ = 1/2.5/57/10 (molar ratio); SV = 15000 h^{-1}. (●) Toluene conversion; (○) benzoic acid selectivity; (△) benzaldehyde selectivity; (□) CO + CO_2 selectivity.

TeO_2 content appeared to be effective for the optimization of benzoic acid selectivity and toluene conversion. Above 2 wt% of TeO_2 content, toluene conversion decreased rapidly and CO + CO_2 formation was depressed.

Fig. 3 depicts the effect of O_2/toluene ratio on conversion and selectivity over

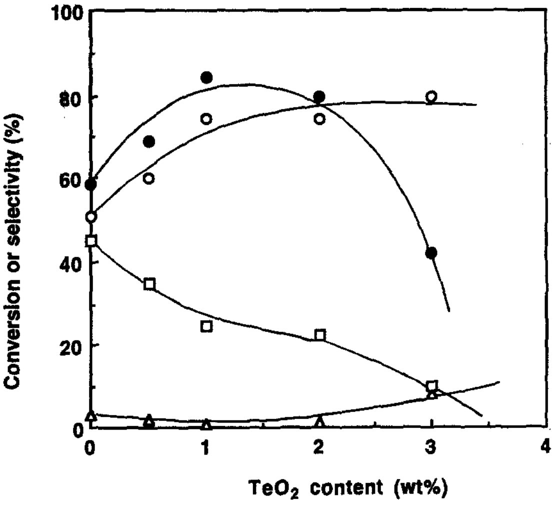

Fig. 2. Effect of TeO_2 content on catalytic activity: catalyst, 5 wt% V_2O_5–TeO_2/TiO_2; reaction conditions: temperature = 350°C; toluene/$O_2/H_2O/N_2$ = 1/2.5/57/10 (molar ratio); SV = 15000 h^{-1}. (●) Toluene conversion; (○) benzoic acid selectivity; (△) benzaldehyde selectivity; (□) CO + CO_2 selectivity.

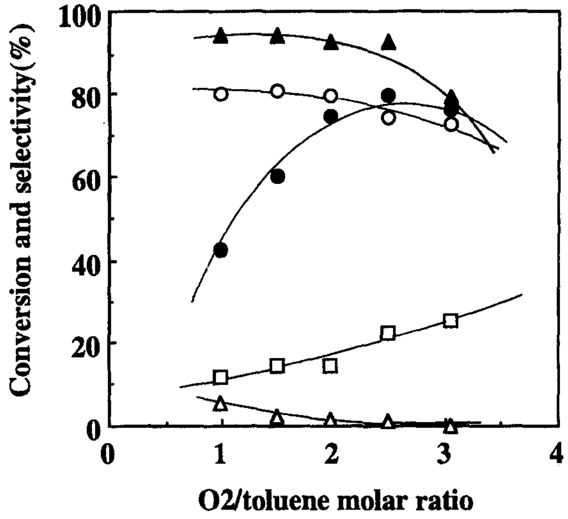

Fig. 3. Effect of O_2/toluene ratio on conversion and selectivity: catalyst, 5 wt% V_2O_5–2 wt% TeO_2/TiO_2 (2.0 g); reaction conditions: temperature = 350°C; H_2O/toluene = 55 (molar ratio); SV = 15000 h^{-1}. (●) Toluene conversion; (▲) O_2 conversion; (○) benzoic acid selectivity; (△) benzaldehyde selectivity; (□) CO + CO_2 selectivity.

5 wt% V_2O_5–2 wt% TeO_2 catalyst. The increase of O_2/toluene ratio up to 2.5 apparently gave a linear rise in toluene conversion, while a slight decrease in toluene conversion was observed above the O_2/toluene ratio of 2.5. The benzoic acid and benzaldehyde selectivities decreased gradually with increasing O_2/toluene molar ratio, while CO + CO_2 selectivity increased linearly. It could be concluded that an O_2/toluene molar ratio of about 2 is appropriate for the purpose of obtaining both high toluene conversion and high benzoic acid selectivity with depressing further oxidation of benzoic acid or benzaldehyde to CO_2.

The reason for the great improvement of catalytic activity by the additives is not clarified yet, but no complex oxide containing V and Sb or Te was detected in the XRD patterns. In addition, 5 wt% Sb_2O_3/TiO_2 and 5 wt% TeO_2/TiO_2 exhibited no activity for benzoic acid formation as shown in table 1, presumably indicating that SbO_2 and TeO_2 play a role of an inhibiter against complete combustion over V_2O_5/TiO_2, that is, these oxides are considered to regulate consecutive oxidation of benzyl cation on the V_2O_5/TiO_2 catalyst surface.

In conclusion, the modification by Sb_2O_3 and TeO_2 is considered to suppress further oxidation of benzoic acid to combustion products and that leads to the enhancement of toluene conversion and benzoic acid selectivity.

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