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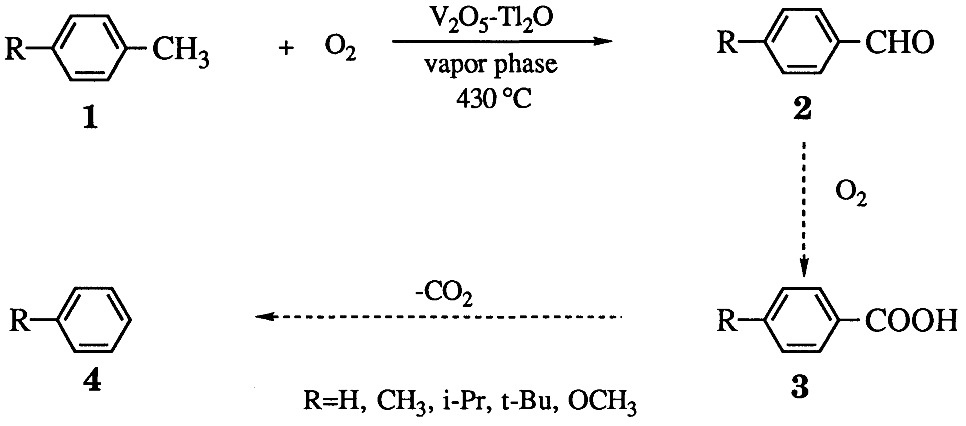
Partial Oxidation of *p*-Substituted Toluenes to Corresponding Benzaldehydes in Vapor Phase over V_2O_5-Tl_2O Catalyst

Michio UESHIMA* and Noboru SAITO
Central Research Laboratory, Nippon Shokubai Co., Ltd., 5-8 Nishi Otabi-cho, Suita, Osaka 564

The selective oxidation of *p*-substituted toluenes to corresponding aromatic aldehydes were effectively performed by vapor phase oxidation reaction over V_2O_5-Tl_2O combination catalyst with high activity and selectivity.

It is known that the partial oxidation of *p*-substituted toluenes to corresponding benzaldehydes in the liquid phase are carried out in the presence of a Co salts in acetic acid with oxygen[1,2] or by the anodic oxidation.[3] However, efficiencies of these reactions are not so high. On the other hand, the vapor phase catalytic oxidation of *p*-substituted toluenes to the *p*-substituted benzaldehydes has not been reported except the oxidation of *p*-methoxy toluene to *p*-methoxy benzaldehyde using V_2O_5-P_2O_5-K_2SO_4 system catalyst.[4] The V_2O_5 has a strong oxidizing ability and has been often used as a catalyst in a partial oxidation of toluene wherein the resulting products are benzoic acid and benzaldehyde at around the same yield.[5] A partial oxidation is a reaction to get an intermediate selectively on the way of complete oxidation, therefore it is important to control the consecutive reaction of an intermediate.

We found that the partial oxidation of *p*-substituted toluenes to the corresponding benzaldehydes in the vapor phase could be performed by use of V_2O_5-Tl_2O combination catalyst with high activity and high selectivity. In the present paper we wish to report the effect of V_2O_5-Tl_2O combination catalyst on the partial oxidation of *p*-methyl, -isopropyl, -tertiarybutyl and -methoxy substituted toluene to the corresponding *p*-substituted benzaldehyde, respectively.



The catalyst was prepared as follows. Ammonium metavanadate (10.7 g) and oxalic acid (2.0 g) were dissolved in 200 ml of deionized water, to this solution thallium nitrate (9.7 g / 30 ml water) and diatomaceous earth (6.5 g) were added. The suspension was vigorously stirred and heated to evaporate water until the suspension become a slurry-like mixture. The mixture was dried at 120 °C in air. The dried mass was calcined at 600 °C for 2 hours in air and pulverized to 9 - 16 mesh. Atomic ratio of the catalyst prepared was V / Tl = 1 / 0.4.

The oxidation reactions were carried out as follows. 5 ml of a catalyst was filled up in a reaction tube (10 mm inside diameter). The reaction gas mixture comprising of *p*-substituted toluene and air at a mole ratio of 1 : 99 was flowed through the reaction tube at 430 °C and at a flow rate of 500 ml / min (STP). The products were analyzed by gas chromatography and ^{1}H-NMR spectroscopy.

The results of the vapor phase oxidation reaction of various *p*-substituted toluenes (**1**) over V_2O_5-Tl_2O at 430 °C are shown in Table 1. The products were corresponding benzaldehyde (**2**), benzoic acid (**3**), substituted benzene (**4**), CO, CO_2 and unknown products. The products **3** and **4** are formed by consecutive oxidation from **2** and the elimination of CO_2 from **3**, respectively.

The unknown products may be formed by the decomposition of each product. In these results, it is found that the methyl group of **1** is more activated by the addition of substituted groups to the *p*-position and is preferentially oxidized. However in the case of *p*-isopropyl toluene, the formation of toluic acid was observed. The isopropyl group is not so stable as other substituted groups. In the case of methoxy group which has a stronger electron donating ability than other substituted groups, the highest activity and selectivity to aldehyde were observed. The order of reactivity depending on substituted groups is as follows ; R = OCH_3 > CH_3, i-Pr, t-Bu > H. It is likely that in the oxidation reaction over V_2O_5-Tl_2O catalyst, the reactivity relates to the electron donating ability of substituted groups.

Table 1. Oxydation Reaction of *p*-Substituted Toluenes

Reactant **1**	Conversion / mol%	Selectivity / mol%					Ionization potential / eV	
R	**1**	**2**	**3**	**4**	CO+ CO_2	Unknown	**1**	**2**
H	4.0	44.2	21.4	0.4	30.3	3.7	9.34	10.02
CH_3		57.0	14.3	0.6	23.6	4.5	9.06	9.71
i-Pr	49.5	38.2	11.0	1.0	33.3	2.0 (14.5[a])	9.11	9.80
t-Bu	48.7	61.4	4.4	1.5	27.4	5.3	9.09	9.80
OCH_3	83.1	75.5	2.0	1.0	18.6	2.9	8.86	9.37

a) Toluic acid.

The values of ionization potential (Ip) of **1** and **2** calculated by Semi-Empirical Molecular Orbital Method MOPAC Ver. 6. (PM 3) , are shown in Table 1. The order of Ip is as follows ; R = OCH_3 < CH_3, i-Pr, t-Bu < H. This means the electron donating ability of methoxy group is stronger than that of other substituted groups, namely *p*-methoxy toluene is easily activated on the catalyst by donating an electron to the acidic sites on the catalyst which are supposed to be Lewis acid. There is a good relationship between the Ip value of reactant and an activity in these reactions. On the other hand, the selectivity to **2** enhanced with decreasing its Ip value. This suggests that the elimination of **2** from the surface of the catalyst is promoted with decreasing its Ip value. These results coincided well with the correlation observed between the Ip value of reactant and reactivity in the vapor phase oxidation of hydrocarbons by Dadyburjor et al.6) The V_2O_5-Tl_2O combination catalyst has a proper acidic property for these *p*-substituted toluenes. In XRD study of V_2O_5-Tl_2O, the multi crystal structures of mainly TlV_3O_8 and $Tl_3V_5O_{14}$ were observed. From DTA measurement, it was found this catalyst (mp. about 400 °C) was in melted state at reaction temperature (430 °C). Therefore, it is difficult to examine the correlation between the crystal structure and catalytic performances. However, it is suggested that the well-balanced combination catalyst between acidic oxide, V_2O_5 and basic oxide, Tl_2O, is effective in this partial oxidation of *p*-substituted toluenes to *p*-substituted benzaldehydes.

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