

Formation of stilbene by oxidative coupling of toluene over lead oxide modified with lithium

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The oxidative coupling of toluene to bibenzyl and stilbene has been studied over lithium-modified lead oxide under anaerobic conditions. The selectivity for the coupled products can be improved by the addition of lithium metals to lead oxide. In order to understand the effect of the reaction conditions on the selectivity, kinetic studies have also been carried out.

KEY WORDS: toluene; oxidation; coupling; stilbene.

1. Introduction

Coupled products have been obtained when the partial oxidation of toluene is carried out under anaerobic conditions, while benzaldehyde and benzoic acid are the main products under aerobic conditions. It was reported by researchers at Monsanto [1,2] that the oxidative coupling of toluene to stilbene was considered to be the first step in the production of styrene. In this process, cheaper toluene was used instead of benzene and only half the amount of ethylene was required compared to the conventional process. Hupp and Swift [1] judged that PbO was the most active and selective based on previous results, so they examined PbO in a fluidized-bed reactor. The components of the reactant gas were toluene and steam, and no molecular oxygen was contained therein. The fluidized-bed reactor was separated into reduction and oxidation zones. The reaction was carried out under anaerobic conditions. Lead oxide reduced by the reaction was oxidized in the oxidation zone in the fluidized bed. The main and desirable product was stilbene. The other main products were bibenzyl, benzene and carbon dioxide. Carbon dioxide was produced by the oxidative dealkylation of toluene and the combustion of hydrocarbons.

King [3] carried out the oxidative coupling of toluene under anaerobic conditions to study the reaction of the organic reactant with the surface and lattice oxygen. It was found that the metal oxides on the left side of the periodic table catalyzed the methyl–aryl coupling and the metal oxides on the right side of the periodic table catalyzed the methyl–methyl coupling. Possible reaction mechanisms were proposed. In the case of PbO, which is an easily reducible metal oxide on the right side of the periodic table, the first step in the reaction is the

abstraction of an α -hydrogen to form water rather than proton transfer. Lead oxide is reduced to the metallic form, and metal lead has a weak interaction with the benzyl radical. Therefore, benzyl radicals may couple among themselves into bibenzyl.

Dubuis *et al.* [4] carried out the coupling of toluene under periodic condition over Pb/Li/MgO. The operation involved toluene oxidation in the absence of oxygen and regeneration of the catalyst by gas-phase oxygen. This operation permitted one to obtain bibenzyl at a selectivity of 0.9.

Although the research on toluene coupling is very limited, some studies concerning the oxidative coupling of toluene with methane have been published [5–13]. For the cross-coupling of methane and toluene, lithium-promoted basic oxides enhanced the activity of the formation of methyl and benzyl radicals [5–7]. Khan and Ruckenstein [8] carried out this reaction under aerobic conditions. They used alkali–metal-compound-promoted MgO catalysts. Their results showed that the selectivity for the coupling products was enhanced by the alkali metals. A high performance was especially obtained by promoting MgO with binary alkali metal compounds.

For the oxidative coupling of toluene, the selectivity for the coupled products decreased due to the presence of oxygen in the gas phase. Therefore, lattice oxygen from metal oxides should be used for the selective toluene coupling [2]. In addition, as described above, the type of metal oxide is also limited to increase the selectivity. In this paper, we carried out the oxidative coupling of toluene over PbO under anaerobic conditions. The effect of the second component on the selectivity for the coupled products was investigated. We also studied the concentration dependence of the reaction rates to determine the optimum reaction conditions.

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2. Experimental

The lead oxide used in this study was a commercial material manufactured by Wako Pure Chemical Co. The alkali, alkaline earth and rare earth metal compounds were deposited on this reagent-grade lead oxide by the conventional impregnation method. An aqueous solution of the salt was added to PbO followed by vigorous stirring. The initial loading of the metal compounds was 10 mol%. After drying in an oven overnight at 383 K, the powder was pressed, crushed, and sieved to a 32–48 mesh particle size. After the powder was oxidized in flowing air, the reaction runs were carried out in the temperature range of 798–843 K under almost atmospheric pressure in a fixed-bed tubular reactor. A 10.0-mm i.d. stainless tube enclosed within an aluminum block was used as the reactor. The block was heated on its surface by a flexible electrical heater.

Toluene was supplied at a constant rate to an evaporator from a micro-feeder. The inert gas, nitrogen, was passed through the evaporator. Oxygen content in the inert gas was below 1 ppm and the oxidation by gas-phase oxygen was ignored. The flow rate of nitrogen was in the range of 8.2×10^{-4} – 1.28×10^{-3} mol min⁻¹. The feeding rate of toluene varied from 2.74×10^{-5} to 1.41×10^{-4} mol min⁻¹. The initial pressure of toluene was varied from 10^3 to 10^4 Pa. Product vapor from the reactor was passed through a cooling trap of mesitylene. The trapped products were analyzed off-line by a gas chromatograph using a column packed with 5%-SILAR 10C Chromosorb WEW. The gas component separated from the condensed products was also analyzed on-line by a gas chromatograph that contained a Porapak N column.

The experiment was carried out as follows: After 5.0 g of the oxide was packed in the reactor by being sandwiched between quartz wool plugs, it was heated at 843 K in flowing air for 2 h. The gas supply was changed to nitrogen to remove oxygen in the reactor and the temperature was set to the reaction temperature. Toluene was then supplied to the evaporator and the reaction was carried out. The conversion of toluene was expressed as the fraction of moles of reacted toluene. The selectivity was the ratio of the number of moles of toluene converted to a specific product to the total number of moles of the reacted toluene.

3. Results and discussion

The main products of the reaction were stilbene, bibenzyl, benzene and carbon dioxide. Dubuis *et al.* [4] reported that benzaldehyde was not detected in the absence of gas-phase oxygen. In our case, the formation of oxygenated products was also not detected. Carbon dioxide detected in the product was formed by the oxidation of the methyl group of toluene and by the complete

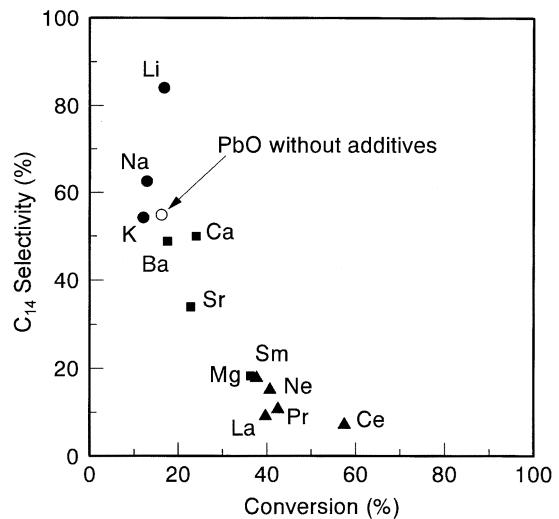


Figure 1. The relationship between toluene conversion and selectivity of bibenzyl and stilbene. Reaction conditions: reaction temperature, 843 K; catalyst, 5.0 g; molar flow rate of nitrogen, 4.69×10^{-4} mol min⁻¹; molar flow rate of toluene, 4.74×10^{-5} mol min⁻¹. Reference (○), alkaline (●), alkaline earth (■), lanthanide (▲).

oxidation of organic compounds. Hupp and Swift [1] considered the same reaction paths in their analysis. Because benzene was formed but methane and hydrocarbons containing oxygen were not detected, we also considered that the methyl group of toluene was oxidized to carbon dioxide.

We studied the effect of the addition of alkali metals on the selectivity for the coupling products (C_{14}). The alkaline earth and lanthanide metals were also tested. All of the metals were added in the form of nitrates. Figure 1 shows the relationship between the toluene conversion and the sum of the selectivity for stilbene and bibenzyl. When the additives were not added to PbO, the C_{14} selectivity was 54.8% under this condition. This figure implied that the selectivity for the coupling products decreased with increasing conversion. However, the selectivity was not much influenced by the space-time, whereas the conversion increased with the space-time. Therefore, the selectivity was not affected by the conversion but was affected by the type of additives. This point shall be discussed in a later section.

The conversion was not significantly influenced by the addition of alkali metals. When lithium was used, the C_{14} selectivity significantly increased and exceeded 80% under this condition. A similar tendency was confirmed under several different conditions. In the case of alkaline earth metals, the C_{14} selectivity decreased. In the case of methane coupling, PbO supported on MgO exhibited excellent characteristics under anaerobic conditions [14]. However, the results of toluene coupling over PbO modified with MgO showed a large decrease in the selectivity for the coupled products. It was observed that MgO increased the reaction activity; the oxidation and benzene production were especially catalyzed because the methyl group of

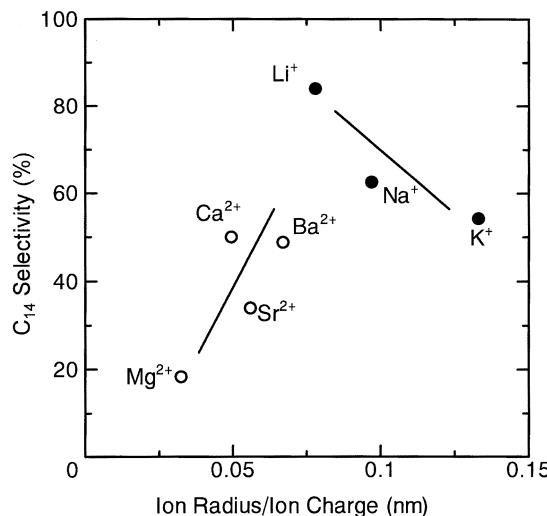


Figure 2. Effects of ion radius per charge on C_{14} selectivity. Reaction conditions are the same as those in figure 1.

toluene was easily oxidized. The addition of lanthanide metals showed a similar tendency to MgO . These metals promoted the formation of benzene, and the C_{14} selectivity was below 20%.

Figure 2 shows the comparison between the C_{14} selectivity and the ion radius/ion charge. The relationship shown in this figure is quite similar to that obtained by Ohno *et al.* [15] for the oxidative coupling of methane. The selectivity decreased with this increasing ratio for alkali metals, while the reverse relationship was obtained for alkaline earth metals. The maximum selectivity for coupling products was observed for lithium.

Some researchers reported that the selectivity for coupled products was enhanced over the catalysts containing alkali metals in the cross-coupling of methane and toluene [5–12]. In the oxidative coupling of methane, lithium-doped MgO is one of the best catalysts that exhibit high catalytic activity and the selectivity for coupled products [16–22]. Ito *et al.* [16] reported that the $[Li^+ - O^-]$ species were the active sites for methane activation. DeBoy and Hicks [23] carried out methane coupling and reported that Li_2O exhibited the highest selectivity for C_2 hydrocarbon among alkali, alkaline earth and rare earth oxide. Khan and Ruckenstein [8,9] investigated the effects of bi-alkali-promoted catalysts on the reaction performance of cross-coupling of methane and toluene. They described that it was important to increase the surface basicity for higher performance in the oxidative methylation. The amount of surface lattice oxygen having a nucleophilic character was increased by the addition of alkali metals. These oxygen sites facilitate the abstraction of hydrogen from both methane and toluene. While these studies were conducted under aerobic conditions, King [4] stated that alkali oxides did not catalyze the coupling of toluene under anaerobic conditions due to their high reduction potentials. Therefore, formation of bibenzyl using PbO

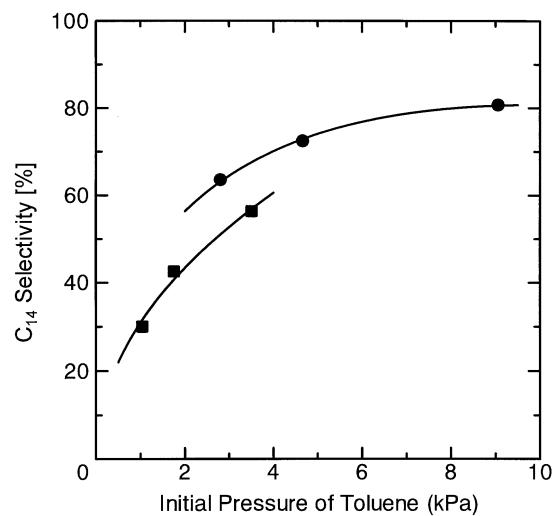


Figure 3. Effect of initial pressure of toluene on C_{14} selectivity for PbO modified with lithium nitrate. Reaction conditions: reaction temperature, 843 K; catalyst, 5.0 g; molar flow rate of nitrogen, $9.79 \times 10^{-4} \text{ mol min}^{-1}$ (●), $2.68 \times 10^{-3} \text{ mol min}^{-1}$ (■).

is not due to the base-catalyzed proton abstraction but due to hydrogen abstraction. On the other hand, Kim *et al.* [6] reported that a non-crystalline Pb – Li – O material acted as an oxygen supplier when they carried out cross-coupling of methane and toluene over Pb – Li – MgO catalyst. Taking the above into consideration, we suppose that toluene coupling proceeds with high C_{14} selectivity over Li_2O , even under anaerobic conditions due to the oxygen supply from PbO and/or Pb – Li – O .

In the case of PbO modified with lithium, the selectivity for the coupled products was stable at about 63%, whereas the conversion decreased from 6.5% to 5.1% after 5 h. The calculation based on the feed rate of toluene and the conversion shows that about 3% of the PbO was reduced to its metallic form during the 5 h reaction.

Figure 3 shows the effects of the initial pressure of toluene on the C_{14} selectivity. The selectivity increased with the toluene pressure for each nitrogen flow rate. Under the experimental temperature condition, the C_{14} selectivity slightly increased with temperature. On the contrary, the selectivity for benzene slightly decreased. We studied the influence of the partial pressure of toluene on the reaction rate. By assuming that the bibenzyl formation and benzene formation are parallel reactions, we analyzed the reaction-rate equations. Figure 4 shows the relationship between the partial pressure of toluene and initial formation rates of the coupled products and benzene. The order of the reaction can be obtained from the slope of the lines. The order of the reaction was found to be 1.7 for the bibenzyl formation and 0.75 for the benzene formation. These results indicated that the rate-determining step for the bibenzyl formation was not the adsorption of toluene. The

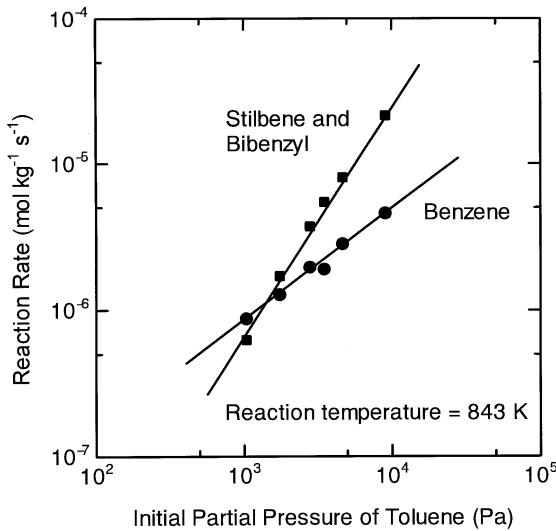


Figure 4. Relationship between initial partial pressure of toluene and reaction rates for PbO modified with lithium nitrate.

difference in the reaction order between these reactions is discussed in the next section.

Otsuka *et al.* [5] reported that the coupled products and benzene were formed in a parallel reaction of the benzyl radical in the cross coupling of methane and toluene because the yields of these compounds were proportional to the contact time. We obtained the reaction equations based on the following assumptions: (1) Toluene adsorbs on the active site of the catalyst. (2) Langmuir isotherm rules can be used to describe the adsorption. We take into account the vacant site and the site on which the toluene adsorbs. (3) The reaction between the adsorbed toluene and the surface lattice oxygen produces the benzyl radical. (4) The benzyl radical reacts with the surface lattice oxygen and forms benzene. This reaction is the rate-determining step for the benzene formation. (5) The benzyl radicals couple among themselves into bibenzyl. This reaction is the rate-determining step for the coupling reaction.

Based on this assumption, the reaction rates were derived for bibenzyl and benzene:

$$r_1 = \frac{k_1 P_T^2}{(1 + K_1 P_T)^2} \quad (1)$$

$$r_2 = \frac{k_2 P_T}{(1 + K_2 P_T)} \quad (2)$$

where P_T is the partial pressure of toluene, r_1 and r_2 are the formation rates of bibenzyl and benzene, respectively, k_1 and k_2 are the reaction-rate constants, and K_1 and K_2 are the equilibrium constants. Rearrangement of the above equations gives the following equations:

$$\frac{P_T}{r_1^{0.5}} = \frac{1}{k_1^{0.5}} + \left(\frac{K_1}{k_1^{0.5}} \right) P_T \quad (3)$$

$$\frac{P_T}{r_2} = \frac{1}{k_2} + \left(\frac{K_2}{k_2} \right) P_T. \quad (4)$$

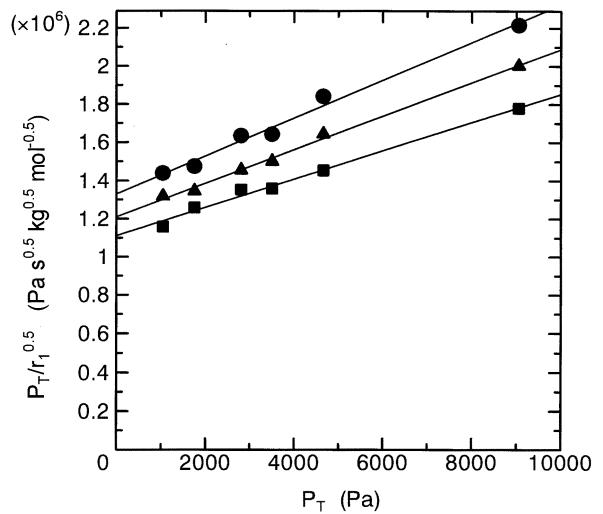


Figure 5. Partial pressure of toluene *versus* parameter $P_T/r_1^{0.5}$ in equation (3) for PbO modified with lithium nitrate. Reaction temperature: 853 (■), 843 (▲), 823 K (●).

These equations can be used to evaluate the kinetic parameters k_1 , k_2 , K_1 and K_2 . Figure 5 shows the plot of P_T *versus* $P_T/r_1^{0.5}$ for the formation of the coupled products. Figure 6 shows the plot of P_T *versus* P_T/r_2 for the formation of benzene. It is clearly shown that the experimental data are well fitted by equations (3) and (4). The kinetic parameters obtained from the slope and intercept are given in table 1.

Figure 7 shows the Arrhenius plot for the reaction-rate constants given in table 1. The activation energy was calculated to be 150 kJ mol⁻¹ for the coupling reaction and 129 kJ mol⁻¹ for the benzene formation. This result proved the increase in the C₁₄ selectivity with reaction temperature as mentioned above.

Based on the rate equation obtained and the values of parameters given in table 1, we calculated the conversion

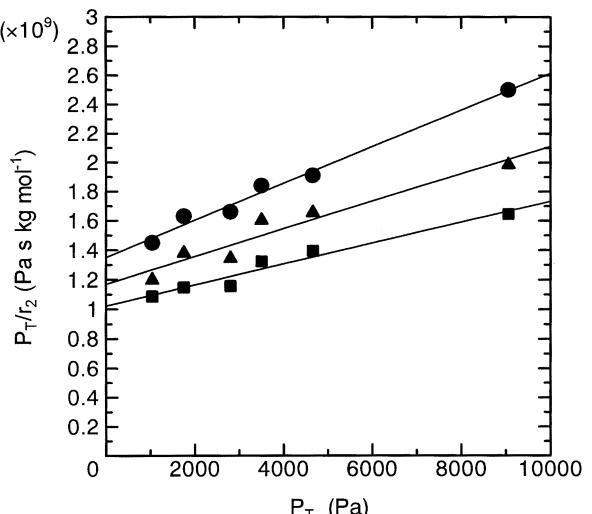


Figure 6. Partial pressure of toluene *versus* parameter P_T/r_2 in equation (4) for PbO modified with lithium nitrate. Reaction temperature: 853 (■), 843 (▲), 823 K (●).

Table 1
Estimated parameter values.

Parameters	Temperature (K)		
	833	843	853
k_1 (mol s ⁻¹ kg ⁻¹ Pa ⁻²)	5.4×10^{-13}	6.5×10^{-13}	7.8×10^{-13}
K_1 (Pa ⁻¹)	6.6×10^{-5}	6.3×10^{-5}	6.2×10^{-5}
k_2 (mol s ⁻¹ kg ⁻¹ Pa ⁻¹)	3.5×10^{-5}	3.7×10^{-5}	3.9×10^{-5}
K_2 (Pa ⁻¹)	6.9×10^{-5}	6.9×10^{-5}	6.8×10^{-5}

and selectivity for each product. The comparison of the experimental results with the calculations for the relationship between the conversion and the selectivity for the coupled products is shown in figure 8. This figure shows that the high selectivity for the coupled products was not affected by the toluene conversion as described above. Therefore, the selectivity shown in figure 1 was considered to be due to the type of additives and was not affected by conversion.

4. Conclusions

Lead oxide has been known as an excellent catalyst for the formation of stilbene in the oxidative coupling reaction of toluene under anaerobic conditions. In the present study, we showed that the selectivity for stilbene and bibenzyl could be improved by the addition of lithium nitrate to PbO. We also obtained the reaction-rate equation over the Li-modified PbO. The apparent reaction order was 1.7 for the coupling reaction and 0.75 for the benzene formation. This result was explained by the Langmuir isotherm rules, and the reaction-rate equations were obtained. The activation energy was larger for the coupling than for the benzene formation. The experimentally obtained relationship between the

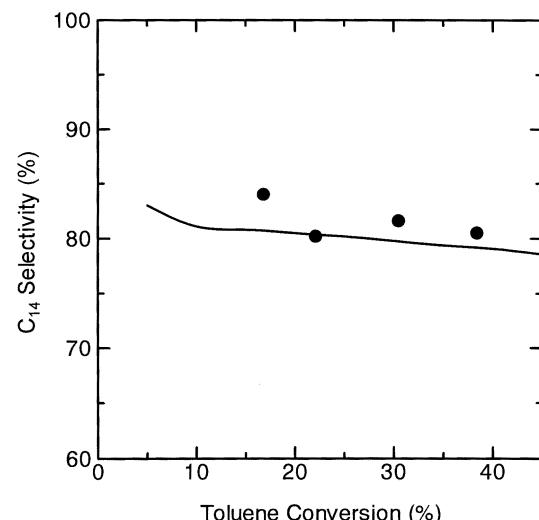


Figure 8. Comparison of calculated selectivity (solid line) with experimental data for PbO modified with lithium nitrate. Reaction conditions: reaction temperature, 843 K; molar flow rate of nitrogen, 4.69×10^{-4} mol min⁻¹; molar flow rate of toluene, 4.74×10^{-5} mol min⁻¹.

selectivity and conversion was confirmed by the calculation using these equations. The results indicate that the reaction temperature and partial pressure of toluene should be raised in order to increase the selectivity for the coupled products.

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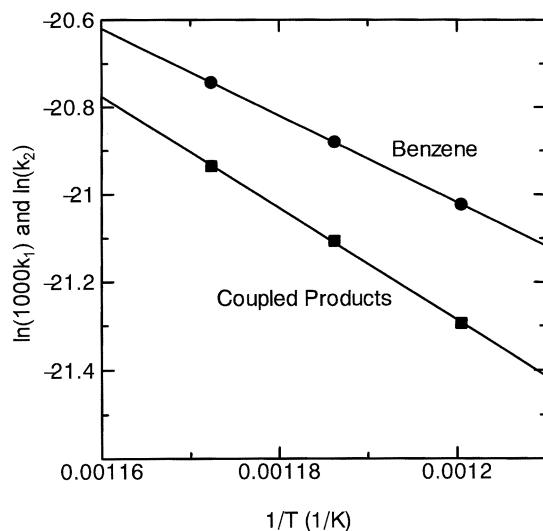


Figure 7. Arrhenius plots for bibenzyl formation (●) and benzene formation (■) for PbO modified with lithium nitrate.

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