JOURNAL OF CATALYSIS **137**, 487–496 (1992)

Oxidative Cross-Coupling of Methane and Toluene over LiCl-Added Co_3O_4

KIYOSHI OTSUKA, MASAHARU HATANO, AND TOHRU AMAYA

Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan

Received January 16, 1992; revised May 8, 1992

A LiCl-added Co_3O_4 has been found to be one of the most active catalysts for oxidative cross-coupling of methane and toluene. The reaction was examined at temperatures higher than 823 K and at a higher methane/toluene ratio than 10. In order to understand the whole network of this reaction, the kinetic studies on the homocoupling of each reactant have been carried out. The results suggested a Langmuir–Hinshelwood type mechanism for both reactants; i.e., the rate-determining step is at the abstraction of hydrogen from methane or from toluene, forming methyl or benzyl species on the surface, respectively, or liberating the corresponding alkyl radicals into the gas phase. The coupling of the alkyl intermediates produces each coupling product, i.e., C_2 and C_{14} compounds. Under methane and toluene cofeed conditions, the formation of C_8 compounds (ethylbenzene and styrene) can be explained in terms of the coupling of methyl and benzyl intermediates. Although a large difference between the reactivities of methane and toluene made it difficult to carry out the kinetic studies on the cross-coupling of methane and toluene, the results were well interpreted in terms of the reaction mechanisms proposed for the oxidation of methane and that of toluene. © 1992 Academic Press, Inc.

INTRODUCTION

A new method of synthesizing ethylbenzene and styrene directly from toluene and methane by oxidative cross-coupling was first demonstrated by Khcheyan *et al.* (*1*) and Yakovich and Bakareva (*2*). Recently, a wide variety of metal oxides has been screened as potential methane oxidative coupling catalysts (see reviews (*3–6*) and references therein). On the basis of these studies, several groups have applied some methane-coupling catalysts to the oxidative methylation of toluene with methane (*7, 8*). The favorable catalysts for the latter reaction are the ones based on the alkali-promoted alkaline earth and rare-earth oxides. The activation of methane over these catalysts, however, requires temperatures higher than 973 K, which causes a considerable gas-phase conversion of toluene to by-products. Therefore, in order to understand the catalytic conversion of toluene and methane in detail, it is necessary to carry out the reaction at lower temperatures.

We have reported that LiCl-added Co_3O_4 (designated LiCl/Co_3O_4 hereafter) is one of the most active catalysts for the oxidative coupling of methane at <900 K (*9*). Preliminary experiments have shown that this catalyst is active and selective also for the oxidative cross-coupling of toluene and methane. Therefore, in this report we describe kinetic studies of this reaction and propose a general picture of the reaction network. The oxidative coupling of methane and that of toluene on LiCl/Co_3O_4 are investigated in advance to gain understanding of the activation of methane and of toluene independently.

EXPERIMENTAL

Materials

The cobalt oxide catalyst (Co_3O_4) used in this study was a commercial material manufactured by Wako Pure Chemical Co. The

0021-9517/92 $5.00

LiCl/Co_3O_4 was prepared by wet impregnation using an aqueous solution of LiCl. The catalyst was calcined at 673 K for 2 hr and then at 973 K for 2 hr. The lithium loading was adjusted to 17 and 30 mol% relative to moles of metals (Li + Co). The LiCl (30 mol%)/Co_3O_4 was used for the reactions of toluene with and without methane. The LiCl (17 mol%)/Co_3O_4 was used for the kinetic studies of the oxidative coupling of methane. The Y_2O_3–CaO was prepared from a mixture of Y_2O_3 and $CaCO_3$ (Y_2O_3/MgO = 1/9) by calcining in air at 1023 K for 2 hr. The Li (7 wt%)/MgO and Li(3 wt%)/Y_2O_3–CaO were prepared by wet impregnation MgO and Y_2O_3–CaO, respectively, by Li_2CO_3. These catalysts were calcined in air at 1023 K for 2 hr. Methane (>99.97%), helium (>99.99%), and oxygen (99%) were used without further purification. The toluene was purified by distillation.

Procedure

All the experiments in this work were carried out using a tubular fused-alumina reactor having an internal diameter of 0.60 cm. A 0.50- to 2.0-g catalyst sample was mixed with 20- to 40-mesh quartz sand and sandwiched by quartz wool. A chromel–alumel thermocouple centered in the catalyst bed was used for temperature measurement and control. The catalyst bed was ca 1.5 cm long for a 2.0-g sample. The center of the bed was positioned at the hottest area in the furnace. The temperature gradient was less than 1°C · cm^{-1} at 923 K for 5 cm length of the furnace at the position of the catalyst bed.

The catalyst was pretreated in the reactor at 973 K for 1 hr under a flow of oxygen and He (1 : 4) at a flow rate of 100 ml (STP) · min^{-1}. All the studies were carried out at atmospheric pressure using helium as a diluent; i.e., the total pressure was adjusted to 101.3 kPa by balancing with helium. The total flow rate was 100 ml (STP) · min^{-1} unless otherwise stated. The analysis of products was performed by means of on-line gas chromatography. The quantitative analysis of chlorine in the LiCl/Co_3O_4 was carried out as follows: A part of the catalyst before or after the reaction was immersed in distilled water and stirred for 1 hr at 298 K. The quantity of the Cl^- anion extracted from the water was measured by a pH meter equipped with a Cl^- electrode. The Li^+ content was analyzed by an atomic absorption spectrometer.

The yields of C_8 compounds (ethylbenzene + styrene) and C_{14} compounds (bibenzyl + stilbene) were evaluated on the basis of the toluene converted.

RESULTS AND DISCUSSION

Favorable Catalysts for the Coupling of Methane and Toluene

The rare-earth and alkaline-earth oxides and the first series transition metal oxides with and without lithium dopant have been tested for the oxidative cross-coupling of methane and toluene at temperatures lower than 923 K. Some examples of the results obtained in the range of time on stream between 2 and 3 hr are shown in Table 1. The products not shown in Table 1 are ethane, ethylene, CO, CO_2, H_2O, benzene, and benzylchloride (for LiCl/Co_3O_4 and LiCl/NiO). The results indicate that LiCl/Co_3O_4 gives the most C_8 and C_{14} compounds under the experimental conditions shown in the caption of Table 1. Moreover, the styrene/(ethylbenzene + styrene) ratio was the highest for this catalyst. Among the catalysts tested in this work, the LiCl(30 mol%)/Co_3O_4 was the most active and selective for the formation of the coupling products (C_8 and C_{14}). Therefore, we have chosen this catalyst for further study.

The Contribution of Noncatalytic Reactions

The reactions in the same reactor with and without LiCl/Co_3O_4 catalyst were carried out in order to examine the contribution of the gas-phase reactions to the catalytic one. The results are compared in Fig. 1. The reaction in the empty reactor gave only CO and CO_2 at <973 K. A trace of benzene

TABLE 1

C_8 and C_{14} Formations over Different Catalysts

Catalyst	Conversion (%)			Yield (%)		Styrene/C_8 ratio
	Toluene	CH_4	O_2	C_8	C_{14}	
LiCl (30 mol%)/Co_3O_4	61	6.2	53	23.0	14	0.62
Li (7 wt%)/MgO	50	<1	43	13.8	0	0.28
$Y_2O_3 \cdot CaO$	87	8.0	70	8.9	0.4	0.43
Li (7 wt%)/$Y_2O_3 \cdot CaO$	45	7.0	45	12.5	0.3	0.26
LiCl (20 mol%)/NiO	9	<1	3	0.9	0	0
None	5	<1	<1	0	0	0

Note. Reaction conditions: $T = 923$ K, P(toluene) = 0.78, $P(CH_4) = 50$, $P(O_2) = 10$ kPa, catalyst weight = 2.0 g.

probably due to the cracking of toluene was observed at >973 K. For the reaction in the presence of LiCl/Co_3O_4, the rates of formation of carbon oxides ($CO + CO_2$) and of benzene are plotted in Fig. 1 for comparison with the results of the noncatalytic reaction. The formation of the other products in the catalytic reaction is described later. The results in Fig. 1 show that there is only a slight contribution of the gas-phase reaction to the catalytic one.

Kinetic Curves and Product Distribution

The changes in the distribution of products at 873 K for the catalytic reaction of the gas mixture (toluene : methane : O_2 = 0.8 : 50 : 10 kPa) over LiCl(30 mol%)/Co_3O_4 are shown in Fig. 2. Although the rates of formation of carbon oxides ($CO + CO_2$) and of benzylchloride increase gradually with time on stream, fairly good steady-state for-

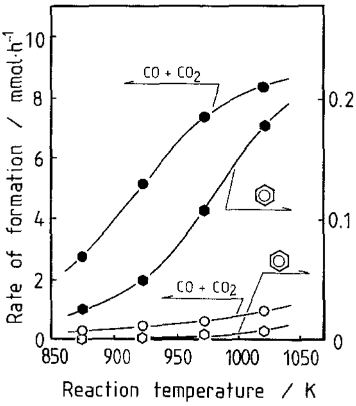

FIG. 1. Comparison between catalytic and noncatalytic reactions. (●, ⬢) Catalytic; (○, ⬡) noncatalytic; (●, ○) formation rate of carbon oxides; (⬢, ⬡) formation rate of benzene. Reaction conditions: P(toluene) = 0.8, $P(CH_4) = 50$, $P(O_2) = 10$ kPa, weight of catalyst (LiCl(30 mol%)/Co_3O_4) = 2.0 g.

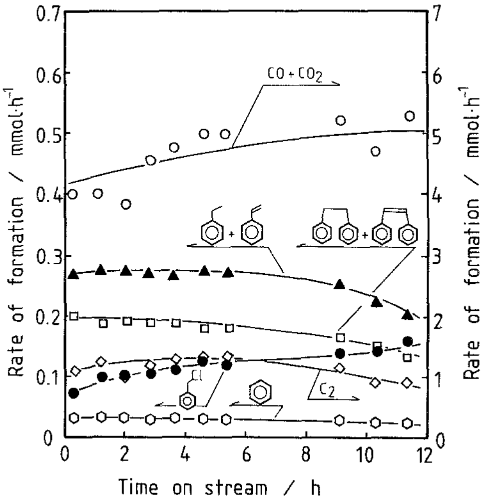

FIG. 2. The changes in the distribution of products over LiCl(30 mol%)/Co_3O_4 with reaction time. The rates of formation of each product were plotted. Reaction conditions: P(toluene) = 0.8, $P(CH_4) = 50$, $P(O_2) = 10$ kPa, $T = 873$ K.

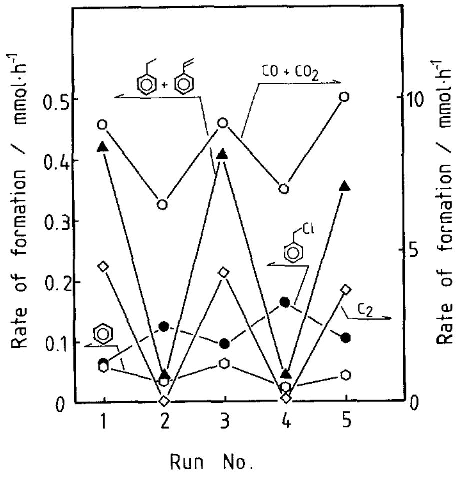

FIG. 3. Toluene oxidation in the presence and absence of methane. The rates of formation of each product were plotted. Reaction conditions: P(toluene) = 0.8, $P(O_2)$ = 10 kPa, T = 923 K. Runs 1, 3, and 5; with methane ($P(CH_4)$ = 50 kPa), runs 2 and 4; without methane. C_{14} products were not measured in these experiments.

mations are observed for the other products at time on stream less than 9 hr. However, the reaction at 973 K showed that the formation rates of C_8, C_{14}, and C_2 compound and of benzene decreased considerably with time on stream at >3 hr. In contrast with this, the rate of carbon oxides increased after 3 hr. These observations indicate that the deactivation of catalysts for partial oxidation is unavoidable at higher temperatures or after the use of catalyst for several hours. Therefore, the experiments were usually carried out at temperatures lower than 923 K and the data, especially for the kinetic studies, were collected within 5 hr of time on stream for each fresh catalyst. The catalyst deactivation is discussed later.

The formation of ethylbenzene and styrene in Fig. 2 suggests the cross-coupling of toluene and methane. This has been supported by the results in Fig. 3. Runs 1, 3, and 5 in Fig. 3 are the results obtained under the cofeeding of toluene and methane. Methane was replaced by helium for runs 2 and 4. As can be seen in Fig. 3, the rate of formation of C_8 compounds dropped abruptly with the turning off of methane feed. The coupling product of methane (C_2 compounds) was, of course, not observed for runs 2 and 4. These observations strongly suggest that the C_8 compounds are formed through the coupling of toluene and methane.

Before we describe the kinetic results for the cross-coupling of toluene and methane, the studies on the homocoupling of each reactant are discussed below.

Kinetic Studies on the Coupling of Methane

Kinetic studies on the methane coupling over LiCl(17 mol%)/Co_3O_4 have been carried out at temperatures between 823 and 973 K and at the partial pressures of reactants of 5 to 40 kPa for methane and of 1 to 20 kPa for oxygen. All the kinetic studies have been carried out at conversions of reactants lower than 10%. The rate of conversion of methane and those of C_2 and carbon oxides ($CO + CO_2$) were measured at different temperatures under constant initial pressures of reactants ($P(CH_4)$ = 20, $P(O_2)$ = 10 kPa). The plot of the logarithm of the rates against the inverse of temperature showed good straight lines for methane conversion and C_2 and CO_2 formations. The apparent activation energies were evaluated as follows: conversion of methane (143 kJ · mol^{-1}), C_2 formation (272 kJ · mol^{-1}), and CO_2 (105 kJ · mol^{-1}).

The rate of methane conversion was measured at different reactant pressures and at three different temperatures (853, 873, and 888 K) to determine the rate equation. Under a constant initial pressure of oxygen (5.1 kPa), the values of $P(CH_4)/R_m$, where R_m is the rate of methane conversion, are plotted against $P(CH_4)$ in Fig. 4. Good linear correlation was observed for all the temperatures examined. Similar analyses were carried out for the data obtained at different initial pressures of oxygen under a constant methane pressure (20.2 kPa). The plot of $P(O_2)/R_m$ vs $P(O_2)$ showed a better linear correlation at

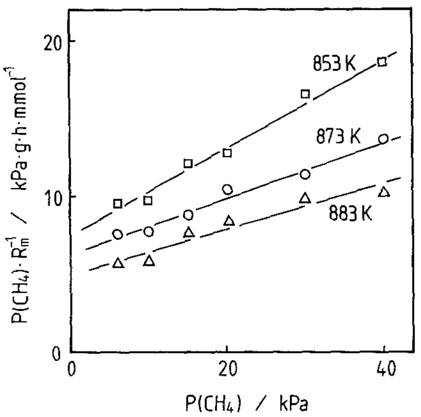

FIG. 4. Methane coupling. Plot of $P(CH_4)/R_m$ vs $P(CH_4)$.

each temperature. These kinetic results indicate that the experimental rate equation for the methane conversion can be expressed as

$$R_m = k_0 \frac{k_1 P(CH_4)}{k_2 + k_3 P(CH_4)} \cdot \frac{K_0 P(O_2)}{1 + K_0 P(O_2)}, \quad \text{(i)}$$

where k_0, k_1, k_2, k_3, and K_0 are the constants at a fixed temperature. A very similar rate equation has already been reported for the conversion of methane over Sm_2O_3 (*10*), Li/MgO, $BaCeO_3$, CeO_2 (*11*), and LiCl/NiO (*12*). Therefore, we believe that the following reaction mechanism, which has been proposed previously (*10–12*), is also suitable for the oxidation of methane over LiCl/Co_3O_4.

$$CH_4 + S \xrightarrow{k_1} CH_4^* \cdots S \quad (1)$$

$$CH_4^* \cdots S \xrightarrow{k_2} CH_4 + S \quad (2)$$

$$CH_4 + CH_4^* \cdots S \xrightarrow{k_3} 2CH_4 + S \quad (3)$$

$$O_2 \overset{K_0}{\rightleftarrows} O_2^*(a) \quad (4)$$

$$CH_4^* \cdots S + O_2^*(a) \xrightarrow{k_0} CH_3 + HO_2 \quad (5)$$

$$CH_3 + CH_3 \xrightarrow{k_6} C_2H_6 \quad (6)$$

$$CH_3 + O_2 \xrightarrow{k_7} CH_3O_2 \twoheadrightarrow CO, CO_2, \quad (7)$$

where CH_4^* is a thermally exited methane formed on the surface upon impact of the molecule having high translational kinetic energy and O_2^* is an active diatomic oxygen responsible for the abstraction of hydrogen from CH_4^*. The experimental rate equation (eq. (i)) can be derived by assuming the steady-state approximation for the concentration of CH_4^* and the rate-determining step is reaction (5) (*10–12*). C_2 products and carbon oxides are produced via a common reaction intermediate (probably an adsorbed CH_3 group (*13*) or $CH_3\cdot$ radical in the gas phase (*5*, *14*)) through reactions (6) and (7), respectively.

Kinetic Studies on the Coupling of Toluene

The oxidation of toluene over LiCl (30 mol%)/Co_3O_4 occurred at temperatures higher than 700 K. However, a temperature higher than 823 K was needed for the oxidative coupling of methane. The products for the oxidation of toluene at a conversion level less than 10% were C_{14} compounds (stilbene and bibenzyl) > benzylchloride > carbon oxide > benzene. The coupling of toluene occurred with fairly high selectivity (>50%). The formation of benzylchloride shows that the chlorine added to the catalyst as LiCl reacts with toluene during the reaction. The rates of formation of each product were measured at different temperatures (873 to 800 K) and at constant initial pressures of toluene (2.3 kPa) and oxygen (2.0 kPa). The apparent activation energies evaluated from these data are as follows: conversion of toluene (92 kJ · mol^{-1}), formation of C_{14} compounds (201 kJ · mol^{-1}), carbon oxides (83 kJ · mol^{-1}), benzylchloride (58 kJ · mol^{-1}), and benzene (71 kJ · mol^{-1}). It is interesting to compare these activation energies with the values obtained for the oxidation of methane. The activation energy for the conversion of toluene (92 kJ · mol^{-1}) is quite low compared to that of methane (143 kJ · mol^{-1}). This is true between the homocoupling of toluene (201 kJ · mol^{-1}) and that of methane (272 kJ · mol^{-1}). These

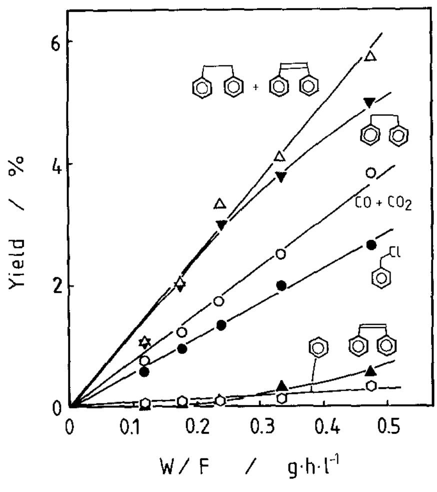

FIG. 5. Toluene coupling. Yields of each product were plotted against W/F. Reaction conditions: T = 873 K, weight of catalyst = 0.70 g, P(toluene) = 2.0, $P(O_2)$ = 2.0 kPa.

observations are quite reasonable on the basis of common knowledge that the reactivity of toluene should be much greater than that of methane.

In order to know the reaction paths for each product of the toluene oxidation, the effect of gas–catalyst contact time on the yields of products has been investigated over LiCl(30 mo.%)/Co_3O_4. The results are shown in Fig. 5. The yields were calculated on the basis of the toluene converted. The yields of C_{14} compounds (stilbene + bibenzyl), carbon oxides, benzylchloride, and benzene increased proportionally to contact time. This observation suggests that these products are formed in parallel probably through a common reaction intermediate. The yield of stilbene was accelerated with contact time, in contrast with deceleration in the yield of bibenzyl. This result strongly suggests that stilbene is formed from bibenzyl through oxidative dehydrogenation.

The effects of the partial pressure of oxygen on the formation rate of each product are shown in Fig. 6. The conversion of toluene did not occur in the absence of oxygen ($P(O_2)$ = 0). This fact suggests that the activation of toluene is initiated by oxygen. The rate of formation of C_{14} compounds increased sharply at low oxygen pressure, but reached a plateau at >5 kPa of oxygen.

The effect of the partial pressure of toluene on the formation rates of products is indicated in Fig. 7. Only a trace of benzene was formed under the pressure of toluene less than 2.3 kPa. Therefore, the formation rate of benzene was not plotted in Fig. 7. Steady-state results were not able to be obtained when the pressure of toluene was greater than 3 kPa.

The dependence of the toluene conversion rate on reactant pressures in Figs. 6 and 7 suggests a Langmuir–Hinshelwood type mechanism. Let us assume that the oxidative coupling of toluene occurs on the same active site and via a reaction mechanism similar to that proposed for methane coupling; i.e., the rate-determining step is the abstraction of hydrogen from the methyl

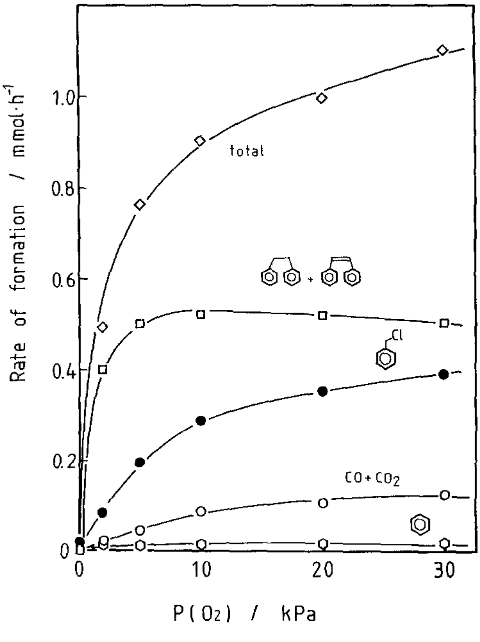

FIG. 6. Toluene coupling. Effect of $P(O_2)$ on the rates of formation of each product. Conversion rate of toluene, ◇; formation rate of C_{14}, □; benzylchloride, ●; carbon oxides, ○; benzene, ⬡. Reaction conditions: T = 833 K, catalyst weight = 0.70 g, P(toluene) = 2.3 kPa.

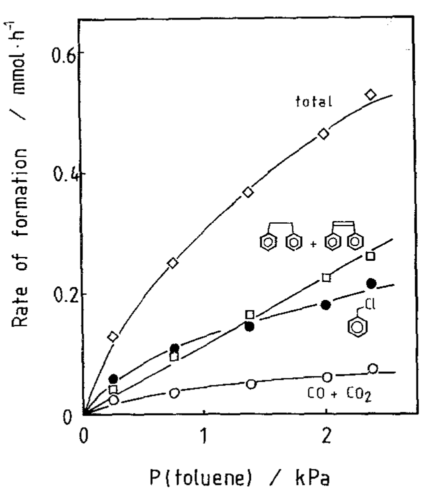

FIG. 7. Toluene coupling. Effect of P(toluene) on the rates of formation of product. The meaning of symbols are same as those of Fig. 6. Reaction conditions: T = 833 K, $P(O_2)$ = 2.0 kPa, catalyst weight = 1.50 g.

group of toluene by the action of diatomic oxygen, generating benzyl radicals (or adsorbed benzyl groups). The coupling of benzyl radicals produces bibenzyl. Further oxidation of the benzyl radical gives CO and CO_2. The benzyl radical reacts with chlorine on the surface of the catalyst, producing benzylchloride as a by-product. This tentative mechanism can explain the kinetic results for the cross-coupling of methane and toluene which is presented later.

The results in Figs. 5 to 7 indicate that benzylchloride is one of the major products. Therefore, one may consider this to be a major intermediate in the formation of C_{14} compounds; i.e., the coupling of benzylchloride or the cross-coupling of toluene and benzylchloride may give C_{14} compounds. However, this cannot be accepted for the following reasons. The results in Fig. 5 showed that the yield of coupling products and that of benzylchloride were proportional to contact time. If benzylchloride is the precursor of C_{14} molecules, the increase in the yield of coupling products should be accelerated with contact time. Moreover, the results in Figs. 6 and 7 showed that the rate of C_{14} formation did not depend on the second order of that of benzylchloride formation.

Cross-Coupling of Methane and Toluene

As described earlier, a temperature higher than 823 K was required for the activation of methane. The cross-coupling of methane and toluene occurred at temperatures >873 K. However, the conversion of toluene at such high temperatures exceeded more than 30%. Thus, it is difficult to find appropriate reaction conditions for the kinetic studies. Therefore, we describe qualitatively the reaction profile of the cooxidation of toluene and methane over LiCl/Co_3O_4. In general, a $P(CH_4)/P$(toluene) ratio greater than 10 was needed to obtain a steady-state reaction and a high yield of C_8 compounds.

Figure 8 shows a typical example of the temperature effect on the rate of formation of each product. The methane/oxygen/toluene ratio of the feed gas was 50/1/0.8 kPa. The results in Fig. 8 indicate that a temperature higher than 850 K is needed for the production of C_8 compounds. The rates of

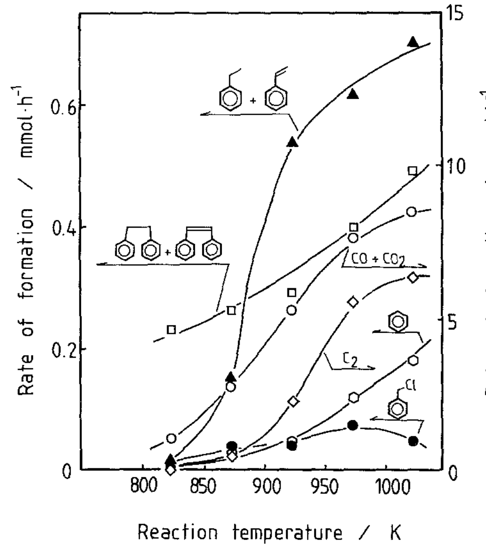

FIG. 8. Methane–toluene cross-coupling. Formation rates of products vs reaction temperature. C_8 formation rate, ▲; C_{14}, □; carbon oxides, ○; C_2, ◇; benzene, ⬡; benzylchloride, ●.

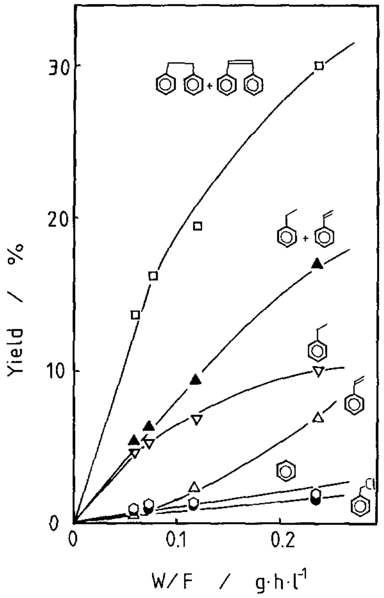

FIG. 9. Methane–toluene cross-coupling. Yield of products were plotted vs W/F. Reaction conditions: $T = 873$ K, P(toluene) = 2.3, $P(CH_4) = 50$, $P(O_2) = 10$ kPa, catalyst weight = 0.70 g.

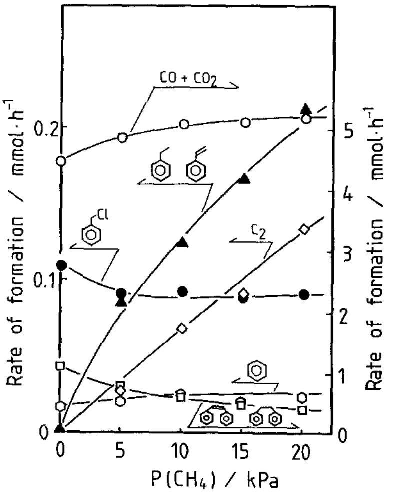

FIG. 10. Methane–toluene cross-coupling. Formation rates of products as functions of $P(CH_4)$. The meaning of symbols are the same as those of Fig. 8. Reaction conditions: T = 903 K, P(toluene) = 2.0 $P(O_2) = 10$ kPa, catalyst weight = 0.70 g.

C_8 and of C_2 increase in parallel with a rise in temperature, suggesting that the two reactions proceed via a common reaction intermediate (CH_3 group or $CH_3\cdot$ radical). The yields of C_{14} compounds, C_8 compounds, benzene, and benzylchloride, on the bases of the toluene converted, are plotted as functions of contact time in Fig. 9. At a conversion of toluene <20%, the yields increased proportionally to contact time. It is to be noted that the yield of styrene is accelerated with a rise in contact time as that of ethylbenzene is decelerated. This fact indicates that styrene is formed through oxidative dehydrogenation of ethylbenzene.

The effects of partial pressure of methane on the rate of formation of the products are plotted in Fig. 10. The formation rates of C_8 and C_2 compounds increased roughly in proportion to the pressure of methane. In contrast, the formation rate of C_{14} compounds decreased appreciably with the increasing methane pressure.

Figure 11 demonstrates the effect of tolu-

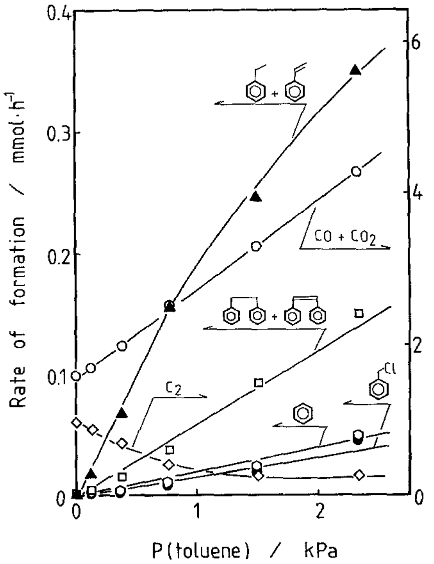

FIG. 11. Methane–toluene cross-coupling. Formation rates of products as functions of P(toluene). The meaning of symbols are the same as those of Fig. 8. Reaction conditions: $T = 873$ K. $P(CH_4) = 30$, $P(O_2) =$ 10 kPa, catalyst weight = 1.0 g.

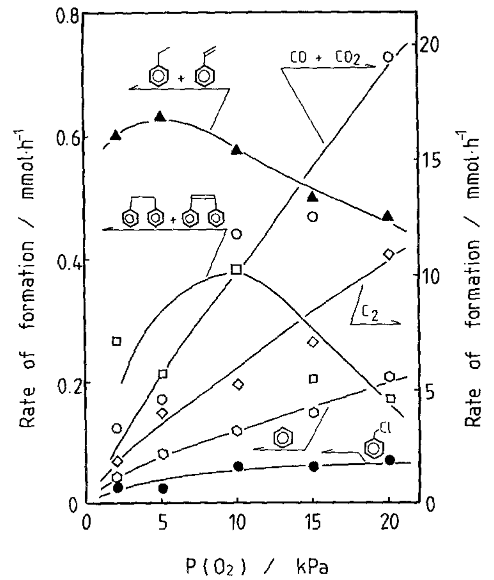

FIG. 12. Methane–toluene cross-coupling. Effect of $P(O_2)$ on the formation rates of products. The meaning of symbols are the same as those of Fig. 8. Reaction conditions: $T = 923$ K, P(toluene) = 0.78, $P(CH_4) = 50$ kPa, catalyst weight = 2.0 g.

ene pressure. The formation rates of C_8 compounds and C_{14} compounds increased proportionally to the pressure of toluene at a low-pressure range (<1 kPa). This is true also for the formations of benzylchloride and benzene. In contrast, the rate of C_2 production decreased sharply with a rise in the pressure of toluene.

The effects of the partial pressure of oxygen are shown in Fig. 12. The formation rate of C_2 compounds (methane coupling) increased linearly with a rise in oxygen pressure, but those of C_8 and C_{14} compounds decreased with the pressure of oxygen at >10 kPa, indicating that the coupling products of toluene are vulnerable to the deep oxidation by oxygen into CO and CO_2.

Overall Reaction Scheme

The results in Figs. 9 to 11 can be explained in terms of the observations for the oxidations of methane and toluene described earlier. Considering the reaction mechanisms for methane and toluene we propose the overall reaction scheme in Fig. 13 for the cooxidation of methane and toluene. Here, the reaction intermediates for the oxidations of toluene and methane are hypothesized to be benzyl and methyl radicals, respectively, for simplification. The observations that the yields of C_{14} compounds, benzylchloride, benzene, and C_8 compounds were proportional to the contact time (Figs. 5 and 9) support the proposal that these products are formed in parallel in steps 1 to 4 in Fig. 13. Stilbene and styrene are formed in steps 6 and 7, respectively, by oxidative dehydrogenation as described previously. It is generally accepted that ethylene is formed through dehydrogenation of ethane (step 8) (*3–6*).

The increase in the partial pressure of toluene would enhance the rate of formation of benzyl radical, thus increasing the rate of C_8 formation in step 4. Under constant partial pressure of methane, however, the increase in the rate of step 4 would inevitably decrease the steady-state concentration of methyl radicals. Therefore, the rate of formation of C_2 compounds should be reduced with a rise in the toluene pressure, which was observed in Fig. 11. On the other hand, the increase in the partial pressure of methane enhances the rate of C_8 formation in step 4, which decreases the steady-state concentration of benzyl radicals, lowering the rate of formation of C_{14} and of benzyl-

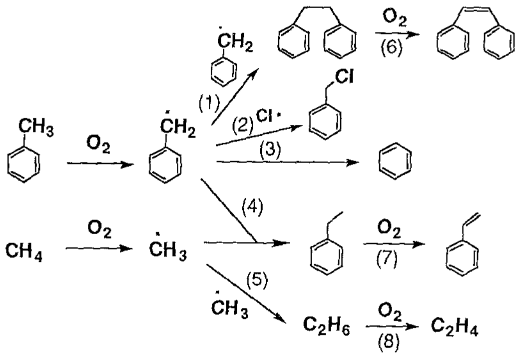

FIG. 13. Reaction mechanism of the cross-coupling of methane and toluene.

chloride. For the formation of benzene, however, the rate was slightly enhanced with a rise in the pressure of methane. We speculate that benzene is produced not only in step 3 but also from ethylbenzene and styrene. The carbon oxides (CO and CO_2) must be formed from all the products as well as directly from methane and toluene. However, the reaction paths for the carbon oxides were not indicated in Fig. 13.

Deactivation of Catalyst

As described earlier, although the catalytic activity of LiCl/Co_3O_4 for the cross-coupling of methane and toluene is highest among the catalysts tested so far, the deactivation of this catalyst is a serious problem. The formation of benzylchloride under all the experimental conditions examined in this work suggests that the deactivation of the catalyst is unavoidable during the reaction. For example, the LiCl (30 mol%)/Co_3O_4 catalyst used for the cooxidation of methane and toluene lost about 50% of the chlorine, but the loss of Li was only 10%, after the reaction for 8 hr at 973 K under the following reaction conditions; $P(CH_4)$ = 50 kPa, P(toluene) = 0.8, $P(O_2)$ = 10, the flow rate is 100 ml min^{-1}, the weight of the catalyst is 2.0 g (fresh). However, if the reaction was carried out at temperatures lower than 923 K, the addition of LiCl greater than 15 mol% retained a steady state of the catalyst for a relatively longer time (>10 hr).

X-ray diffraction analysis of a fresh LiCl (30 mol%)/Co_3O_4 showed only the diffraction pattern due to Co_3O_4. No compound oxide between Li and Co_3O_4 was observed. Therefore, we speculate that amorphous LiCl is deposited on the surface of the host Co_3O_4. Probably, molten LiCl (melting point 878 K) covers or poisons the active sites for deep oxidations of the reactants and products on Co_3O_4 because the Co_3O_4 without LiCl did not produce any partial oxidation products except for CO and CO_2. Further studies are definitely needed to clarify the catalytic active species, the active oxygen species, the reaction zone (on the surface or in the gas phase), the reaction intermediates (adsorbed species or radicals in the gas phase), the deactivation mechanism of the catalyst, and the roles of Li and chlorine.

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