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Amination of Phenols with Ammonia over Palladium Supported on Alumina

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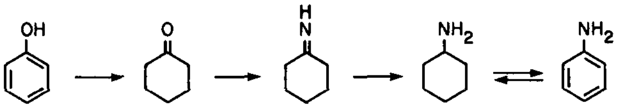
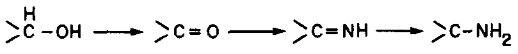
The amination of phenol with ammonia in the presence of hydrogen over palladium supported on alumina gives aniline effectively at 250°C. The presence of hydrogen is essential. The following reaction scheme is proposed:



The reaction rate is approximately first order with respect to the partial pressure of hydrogen, and zeroth order with respect to the partial pressure of ammonia. The rate-determining step of the reaction is concluded to be in the hydrogenation of phenol into cyclohexanone. The catalytic behavior of palladium is improved by making an alloy with gold or by cosupporting La^{3+} or Al^{3+} ions. The improvement may be caused by better dispersion of palladium.

INTRODUCTION

Amination of phenol with ammonia is usually carried out over acidic catalysts such as alumina or silica–alumina under high pressure and at high temperatures of about 450°C (*1*), and the industrial process using a Lewis-acid-type catalyst has been developed (*2*). In the case of amination of alcohols, though solid acid catalyst can be used, metals in cooperation with hydrogen can be a better alternative as catalyst, since the reaction can be carried out at much lower temperatures (*3, 4*). The reaction scheme proposed is (*3, 4*)



$$\overset{H}{>C}-OH \longrightarrow >C=O \longrightarrow >C=NH \longrightarrow >C-NH_2$$

The dehydrogenation of alcohols into ketones is the rate-determining step, in which metal catalysts play a decisive role. The subsequent steps, amination of ketone into amine, are rather facile reactions. Since the hydrogenation of phenol gives cyclohexanone, a ketone (*5, 6*), good hydrogenation catalysts such as metals could be effective for amination of phenol in the presence of hydrogen. In fact, Hamada *et al.* (*7, 8*) reported that phenol is aminated over palladium supported on carbon in the presence of cyclohexanone or cyclohexanol, a hydrogen-transfer agent.

This paper is to show that palladium supported on alumina can convert phenol into aniline in the presence of ammonia and hydrogen. The reaction proceeds under atmospheric pressure at much lower temperatures (~250°C) than the temperatures at which the amination is undertaken over acidic catalysts. The catalytic properties of palladium are improved by making an alloy with gold or by cosupporting trivalent metal cations. The effects of reaction temperature, and the partial pressures of ammonia and hydrogen are examined, the plausible reaction scheme and the rate-determining step being proposed.

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EXPERIMENTAL

Catalysts

Alumina used was Sumitomo-Activated Alumina of 10 to 20 mesh. Palladium supported on alumina was prepared by two different methods. In the first method, palladium–ammine complex solution was obtained by heating palladium chloride in aqueous ammonia at 70°C. Alumina was added to the solution, then dried over a water bath, followed by heating at 120°C for 1 h. The solid was then calcined at 400°C for 2 h and heated in a hydrogen stream at 400°C for 2 h. Most of the experiments were done with the catalysts prepared by this method, and no remarks will be given in the text. In the second method, alumina was added to the solution obtained by dissolving palladium chloride in hydrochloric acid. The procedures for drying and reduction were the same as those for the first method. Other alumina-supported metals were prepared by immersing alumina in the aqueous solution of a corresponding metal chloride. The procedures for drying and reduction were the same as those for palladium catalysts. Palladium with added metals or metal cations was prepared by immersing alumina in the hydrochloric acid solution containing palladium chloride and a corresponding metal chloride, except for palladium–gold and palladium–aluminum where chloroauric acid and aluminum nitrate were used, respectively.

Procedures

The reactions were carried out with a continuous flow reactor operating at atmospheric pressure. The reactor is a silica tubing (13 mm i.d.) placed in a vertical furnace. Phenol (10 g) was liquefied by adding 2 g of water. The phenol–water mixture was pumped by a motor-driven syringe to be vaporized in the preheating zone of the reactor containing 10 cm^3 quartz. Other liquid materials were fed without adding water. For *o*- and *p*-cresol, the syringe was kept at 80°C. Ammonia from a cylinder was dried with a sodium hydroxide column. The reaction products were trapped by two successive traps. The first trap was cooled by ice water, in the second trap, gases being led to a solvent, *N*,*N*-dimethylformamide.

Catalysts, which were once reduced in flowing hydrogen at 400°C for 2 h as described above, were further reduced in flowing hydrogen at 400°C for 1 h prior to the reaction, and the temperature was lowered to the reaction temperature in flowing hydrogen. Then, ammonia and phenol started to be fed consecutively. The products were analyzed by a gas chromatograph with a 60-cm column of PEG-20M (20 wt%) on Chromosorb AW-HMDS operating at 120°C.

The conversion, yield, and selectivity were defined as follows:

$$\text{Conversion (\%)} = \frac{\text{Phenol fed (mol)} - \text{Phenol recovered (mol)}}{\text{Phenol fed (mol)}} \times 100,$$

$$\text{Aniline yield (\%)} = \frac{\text{Aniline produced (mol)}}{\text{Phenol fed (mol)}} \times 100,$$

$$\text{Aniline selectivity (\%)} = \frac{\text{Aniline yield}}{\text{Conversion}} \times 100,$$

$$\text{Dicyclohexylamine yield (\%)} = \frac{\text{Dicyclohexylamine produced (mol)} \times 2}{\text{Phenol fed (mol)}} \times 100.$$

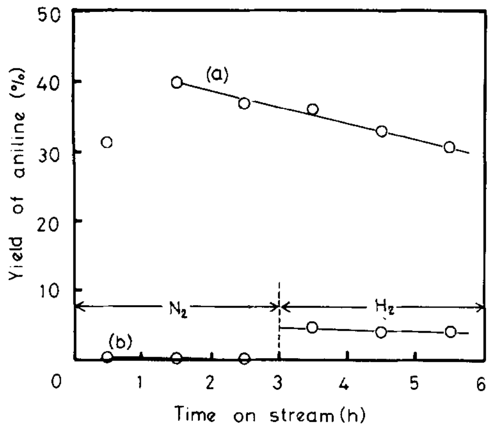


FIG. 1. Change in aniline yield with time on stream 250°C, W/F = 3.05 g h mol^{-1}. (a) Molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.2 : 1.1. (b) Same as (a) except that hydrogen was replaced by nitrogen for the first 3 h.

RESULTS AND DISCUSSION

Need of Hydrogen

The reaction was carried out at 250°C over Pd (2 wt%) on alumina with the feed of phenol : ammonia : hydrogen : water = 1 : 9.2 : 9.2 : 1.1 and a contact time of W/F = 3.05 g h mol^{-1}, where W is the weight of catalyst (g) and F is the total molar feed (mol h^{-1}). In Fig. 1a is shown the change in the aniline yield with time on stream. The aniline yield of about 40% was obtained initially and it decreased to 30% after 6 h of running. The selectivity to aniline was always about 70%. Thus, aniline is surely produced by the reaction of phenol and ammonia in the presence of hydrogen. When hydrogen in the feed was replaced by nitrogen, aniline was not obtained at all, as shown in Fig. 1b. Hydrogen was substituted for nitrogen after 3 h running of the reaction, and then aniline started to be produced, though the yield was lower than that in the case where hydrogen was fed from the beginning. The results clearly show that the presence of hydrogen is essential for the amination. It should be noted that the severe deactivation of the catalyst occurs in the absence of hydrogen.

TABLE 1

Catalytic Activities of Group VIII Metals Supported on Alumina for Amination of Phenol

Catalyst	Supported amount (wt%)	Conversion (%)	Aniline yield (%)	Selectivity (%)
Pd	0.5	43.0	30.9	71.8
Pd	5	48.0	28.8	60.0
Pt	0.5	53.2	28.3	53.2
Pt	5	97.7	0.8	0.8
Rh	0.5	28.3	10.5	37.1
Rh	5	91.4	1.1	1.2
Ru	0.5	2.2	0	0
Ru	5	1.6	0	0
Cu	6.0	0	0	—
Co	2.5	0	0	—
Ni	1.0	0	0	—
Fe	6.3	0	0	—

Note. Reaction conditions: 250°C; W/F = 3.05 g h mol^{-1}; phenol : ammonia : hydrogen : water = 1 : 9.3 : 9.3 : 1.1.

Catalytic Activities of Various Metals

The catalytic activities of various metals supported on alumina were compared in Table 1. As seen in Table 1, palladium is the best catalyst for the amination. Platinum and rhodium give aniline at low levels of supported metal (0.5 wt%), but the yield is very low when the amount of supported metal is larger (5 wt%). Other metals (Ru, Cu, Co, Ni, Fe) do not give aniline at all. The effect of the palladium loading on the catalytic behavior is shown in Fig. 2. The yield of aniline is maximum at the supported amount of 2 wt%, though the effect of the supported amount is not so significant. The effect of the loading amount on the selectivity was much more pronounced in the case of platinum and rhodium as shown in Table 1. The activity of the palladium depended greatly on the supporting material. The following activity order was observed:

$$Al_2O_3\ (44) > \text{carbon}\ (12) > SiO_2\ (3) > SiO_2\text{–}Al_2O_3\ (2) > \text{Y-zeolite}\ (0).$$

The numbers in parentheses indicate the aniline yield at 250°C.

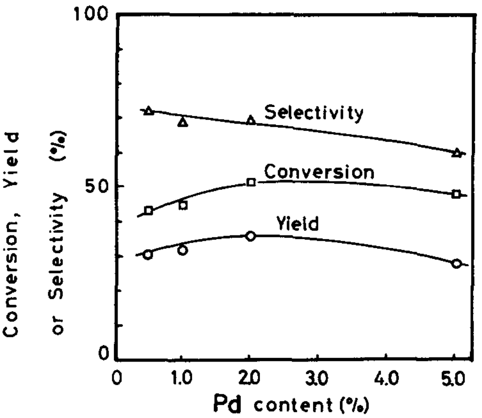


FIG. 2. Effect of supported amount of palladium on alumina on the catalytic properties. □, Conversion of phenol; ○, aniline yield; △, selectivity to aniline. Reaction conditions: 250°C; W/F = 3.05 g h mol^{-1}; molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.2 : 9.2 : 1.1.

Effect of Reaction Temperature

The effect of the reaction temperature on the product yield was examined in the temperature range of 140–300°C over Pd (2 wt%)-Al_2O_3. As shown in Fig. 3, the product selectivity substantially depends on the reaction temperature. Dicyclohexylamine and cyclohexylamine are the main products at 140 and at 170–200°C, respectively, aniline becoming the most predominant product only over 230°C. The selectivity to amination decreases over 250°C where the hydrocracking of phenol becomes significant. It should be noted that the total conversion of phenol decreases with reaction temperature. When the reaction temperature was lowered from 250 to 200°C at 2 h and then to 140°C at 3.5 h after starting the reaction, the conversion and the selectivity changed to the values which would be expected if the reaction had started at respective temperatures from the beginning. The decrease in the conversion by raising the reaction temperature is not caused by the catalyst deactivation, but by the kinetic effect.

Effect of Contact Time

In Fig. 4 is shown the effect of contact time on the conversion and the selectivity to aniline over Pd (2 wt%)-Al_2O_3 at 250°C. The aniline yield increases with contact time, and reaches 43% at W/F = 6.0 g h mol^{-1}, while the selectivity to aniline decreases slightly with contact time. The formation of cyclohexylamine and benzene accounts for part of the by-products. The effect of the contact time was examined also at 205°C (Fig. 5). As described above, the most predominant product is cyclohexylamine at this temperature, though aniline and dicyclohexylamine are also formed. The values of the apparent equilibrium constant, K, at three different contact times in Fig. 5,

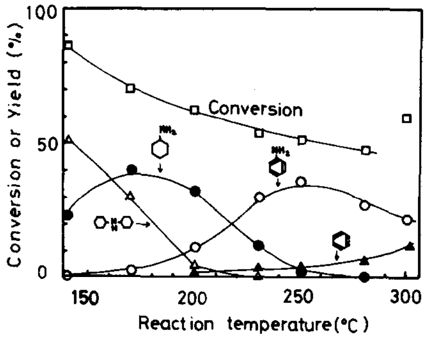


FIG. 3. Change in product distribution with reaction temperature in amination of phenol. □, Total conversion; ○, aniline yield; ●, cyclohexylamine yield; △, dicyclohexylamine yield; ▲, benzene yield. W/F = 3.05 g h mol^{-1}; molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.2 : 9.2 : 1.1.

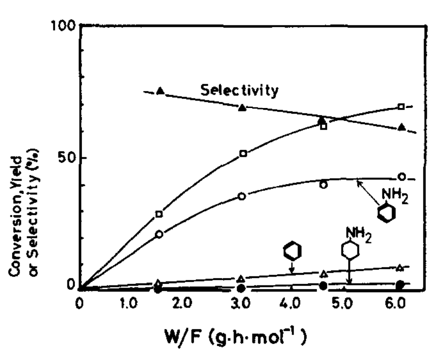


FIG. 4. Effect of contact time on phenol amination at 250°C. □, Total conversion of phenol; ○, aniline yield; ●, cyclohexylamine yield; △, benzene yield; ▲, selectivity to aniline. Molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.3 : 9.3 : 1.1.

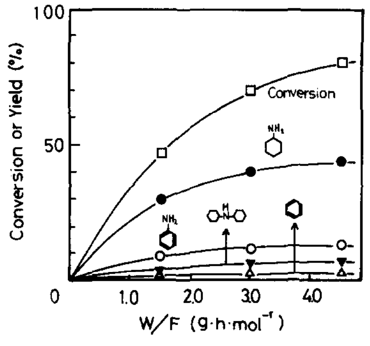


FIG. 5. Effect of contact time on phenol amination at 205°C. □, Total conversion of phenol; ○, aniline yield; ●, cyclohexylamine yield; ▼, dicyclohexylamine yield; △, benzene yield. Molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.3 : 9.3 : 1.1.

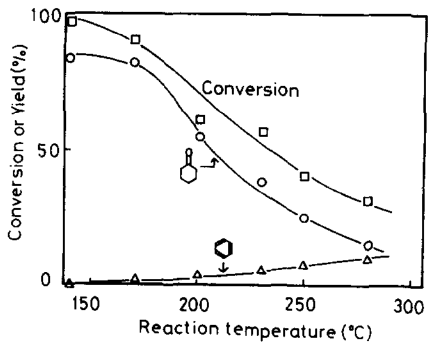
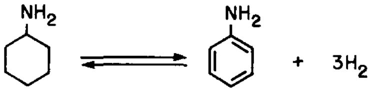


FIG. 6. Effect of reaction temperature on hydrogenation of phenol. □, Total conversion of phenol; ○, cyclohexanone yield; △, benzene yield. W/F = 3.05 g h mol^{-1}; molar feed ratio, phenol : nitrogen : hydrogen : water = 1 : 9.2 : 9.2 : 1.1.

K = (Molar product ratio,
cyclohexylamine to benzene)
× (Partial pressure of
hydrogen at reactor outlet),

are in good agreement with each other, indicating that cyclohexylamine and aniline are formed in equilibrium.

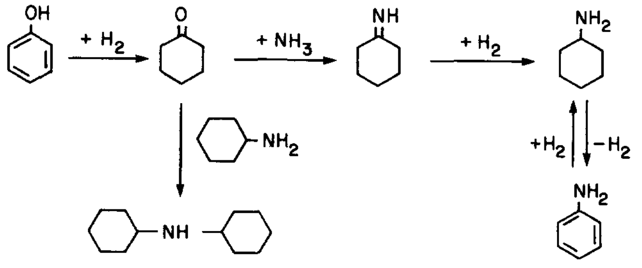


The equilibrium shifts to dehydrogenation at higher temperatures, explaining the shift of the main product from cyclohexylamine to aniline at higher temperatures.

Related Reactions

To get further insights into the reaction mechanism of the amination, several related reactions were studied.

The hydrogenation of phenol over Pd (2 wt%)-Al_2O_3 was examined at various temperatures. As shown in Fig. 6, the main product is cyclohexanone, benzene being also produced as a by-product. The conversion of phenol or the yield of cyclohexanone decreases with reaction temperature as in the case of phenol amination. Figure 7 shows the effect of the reaction temperature on the reaction of cyclohexanone with ammonia in the presence of hydrogen. The conversion of cyclohexanone is about 90% in the temperature range studied, indicating that the amination of cyclohexanone is a rather facile reaction, though the material balance shows that the hydrocracking or aldol condensation (9) of cyclohexanone also proceeds. The distribution of the amination products is quite similar to that in the phenol amination. Thus, at lower temperatures, dicyclohexylamine and cyclohexylamine are produced mainly, but over 250°C, aniline is the main product. It is also confirmed that cyclohexylamine is easily converted into aniline even in the presence of hydrogen at 250°C. From these facts, a plausible reaction scheme can be given as follows:



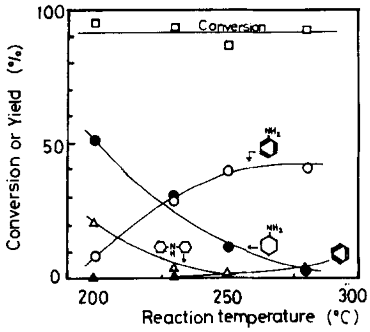


FIG. 7. Effect of reaction temperature on amination of cyclohexanone. □, Total conversion of cyclohexanone; ○, aniline yield; ●, cyclohexylamine yield; △, dicyclohexylamine yield; ▲, benzene yield. W/F = 3.22 g h mol^{-1}; cyclohexanone : ammonia : hydrogen = 1 : 8.9 : 8.9.

Dicyclohexylamine may be formed by the reaction of cyclohexanone with cyclohexylamine instead of ammonia. The surface concentration of adsorbed cyclohexylamine should be larger at lower temperatures, explaining the higher yield of dicyclohexylamine at lower temperatures.

Reaction Kinetics

The dependences of the rate on the partial pressures of hydrogen and ammonia were examined. The rate is approximately first order with respect to the partial pressure of hydrogen below 0.3 atm, while it does not depend on the partial pressure of ammonia between 0.15 and 0.45 atm. Therefore, it is concluded that the rate-determining step is the hydrogenation of phenol into cyclohexanone. This is in accord with the fact that the amination of cyclohexanone is a facile reaction, and cyclohexanone is not found in the reaction products of phenol amination. The conclusion is also supported by the fact that both amination and the hydrogenation of phenol have negative temperature dependence. The negative temperature dependence is often observed in the hydrogenation of olefins over metals (*10*).

Amination of Alkyl Phenols

The amination of various alkyl phenols was examined at 250°C with Pd (2 wt%)–Al_2O_3 as catalyst. From phenol, *o*-, *m*-, *p*-cresol, and 2,4-dimethylphenol, the corresponding anilines were obtained in the yields of 36.0, 20.0, 23.6, 17.5, and 10.2%, respectively. The selectivity to alkyl aniline was 60–70% in all cases. In the case of amination of cresols, both methylcyclohexylamines and toluene were produced in 3% yield. Similarly, in the amination of 2,4-dimethylphenol, both 2,4-dimethylcyclohexylamine and *m*-xylene were produced in 3% yield. The reactivity order for substituted phenols is

phenol > cresols > 2,4-dimethylphenol,
m-cresol > *o*-cresol > *p*-cresol.

The activity order for amination is in accord with that for hydrogenation of the corresponding aromatic compounds (benzene > toluene > *m*-xylene) (*11*). The activity order among cresols is in agreement with that for the hydrogenation of cresols over group VIII metals (*12*). This

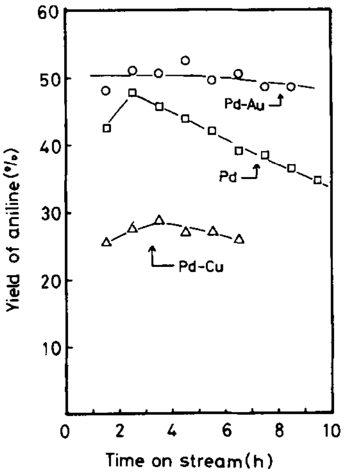


FIG. 8. Effect of alloying on the catalytic activity of palladium. Catalysts used were Pd (2 wt%), Pd (2 wt%)–Au (0.5 wt%), and Pd (2 wt%)–Cu (0.2 wt%) supported on alumina. Reaction conditions: 250°C; W/F = 2.98 (Pd, Pd–Au), 3.06 (Pd–Cu) g h mol^{-1}; molar feed ratio, phenol : ammonia : hydrogen : water = 1.7 : 5.7 : 5.7 : 1.1 (Pd, Pd–Au), 1 : 9.7 : 9.7 : 1.1 (Cu).

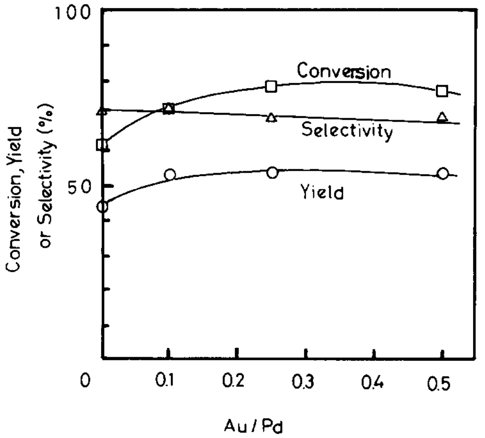


FIG. 9. Effect of addition of gold on the catalytic properties of palladium on alumina. Reaction conditions: 250°C; $W/F = 3.05$ g h mol^{-1}; molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.3 : 9.3 : 1.1; Pd content, 2.0 wt%.

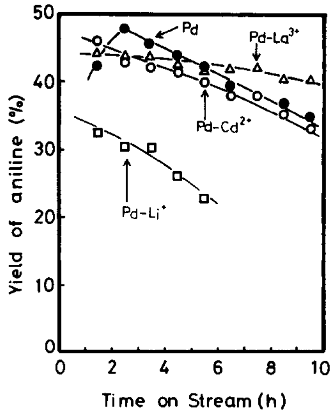


FIG. 11. Effect of addition of cations on the catalytic properties of palladium supported on alumina. Reaction conditions: 250°C; $W/F = 2.98$ g h mol^{-1}; molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 7.5 : 7.5 : 1.1: except for Pd–Li for which W/F and the ratio are 3.06 g h mol^{-1} and 1 : 9.7 : 9.7 : 1.1.

again supports that the hydrogenation of phenol into cyclohexanone is the rate-determining step for the amination of phenol.

Effect of Alloying

The nature of supported metals often changes greatly by the existence of other metal components, even if they do not form miscible alloys (*13*). To improve the catalytic properties of palladium by alloying, gold or copper was supported simultaneously with palladium. Figure 8 shows the effect of alloying. Here, Pd (2 wt%)–Al_2O_3 was prepared from palladium chloride in hydrochloric acid (second method). The catalyst showed slightly higher activity than Pd (2 wt%)–Al_2O_3 prepared from palladium–ammine complex. As seen in Fig. 8, Pd–Au–Al_2O_3 catalyst shows higher activity than Pd–Al_2O_3, and the former has much more stability than the latter. On the other hand, Pd–Cu–Al_2O_3 shows less activity than Pd–Al_2O_3, though the catalyst stability seems to be increased. In Fig. 9 is shown the dependence of the catalytic properties on the gold content. The catalytic activity increases slightly by alloying, though the selectivity to aniline does not change. The addition of copper is more drastic as shown in Fig. 10. By adding a small amount of copper, catalytic activity is diminished greatly, and is completely depressed at Cu/Pd = 1.

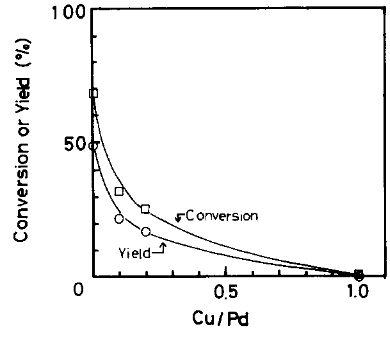


FIG. 10. Effect of addition of copper on the catalytic properties of palladium supported on alumina. Reaction conditions: 250°C; $W/F = 6.10$ g h mol^{-1}; molar feed ratio, phenol : ammonia : hydrogen : water = 1 : 9.3 : 9.3 : 1.1; Pd content = 1.0 wt%.

Effect of Metal Cations

Furuoya *et al.* (*14, 15*) reported that the deactivation of supported palladium catalyst can be inhibited by supporting trivalent metal cations such as La^{3+} or Al^{3+} together with palladium, while monovalent or divalent cations have no effect. Here, we have

TABLE 2

Dispersion of Palladium Supported on Alumina

Catalyst	Metal surface area (m^2/g-catalyst)	m^2/g-Pd	Dispersion (%)
Pd (2 wt%)	6.0	300	45
Pd(2 wt%)–Li (0.2 wt%)	3.6	180	27
Pd(2 wt%)–Al^{3+} (0.2 wt%)	6.9	350	52
Pd (2 wt%)–Au (0.2 wt%)	7.8	390	59

examined the effect of cations on the catalytic properties of Pd–Al_2O_3 for amination of phenol. The results are shown in Fig. 11. Pd–Li^+–Al_2O_3 catalyst has much less activity than Pd–Al_2O_3, the catalytic properties of Pd–Ca^{2+}–Al_2O_3 catalyst being almost the same as those of Pd–Al_2O_3 catalyst. In the case of Pd–La^{3+}–Al_2O_3 catalyst, the deactivation of the catalyst was greatly suppressed, though the initial activity was almost the same as that of Pd–Al_2O_3 catalyst. The similar effect was observed also with Pd–Al^{3+}–Al_2O_3.

To learn the effect of alloying or metal cations on the dispersion of palladium metal, the amount of adsorbed carbon monoxide was determined at 20°C. Before adsorption, catalysts were heated under vacuum at 400°C for 3 h. Since the adsorption isotherm was approximated by the Langmuir equation, the maximum amount of adsorbed carbon monoxide expected from the Langmuir equation was used to calculate the palladium surface area. In Table 2, the metal surface area and the dispersion for several catalysts are listed. Thus, the dispersion of palladium is better in the cases of Pd–Au–Al_2O_3 and Pd–Al^{3+}–Al_2O_3, and worse in the case of Pd–Li^+–Al_2O_3 than in the case of Pd–Al_2O_3. This suggests that the sintering of supported palladium can be inhibited by making an alloy or by the presence of large cations.

ACKNOWLEDGMENT

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