January, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 55—60 (1987)

Vapor-Phase Amination of Cyclohexanol over Silica-Supported Platinum Group Metal Catalysts

Hideaki Hamada,* Yasushi Kuwahara, Takahiro Sato,† and Katsuhiko Wakabayashi
National Chemical Laboratory for Industry, Higashi, Yatabe, Tsukuba-gun, Ibaraki 305
†Science University of Tokyo, Noda, Chiba 278
(Received June 24, 1986)

Vapor-phase amination of cyclohexanol with ammonia over silica-supported platinum and other platinum group metal (Ru, Rh, Pd, Ir) catalysts has been studied. Cyclohexylamine and aniline are the main products. Platinum is the most active metal, although there is not much difference in the activity between platinum and other metals. The reaction is suggested to proceed as follows. The first step, which is rate-determining, is the dehydrogenation of cyclohexanol to cyclohexanone intermediate, from which cyclohexylamine and aniline are formed in the parallel process via cyclohexylideneamine. From reaction-rate measurements on Pt/SiO_2 catalysts with different Pt particle size, the amination reaction has been found to be structure-insensitive. The catalytic activity decreases with time on stream probably because of the deposit of carbonacious or polymeric materials on the catalyst surface.

The amination of cyclohexanol to cyclohexylamine with ammonia has been carried out over various acidic catalysts such as ThO_2[1] and Al_2O_3.[2] In addition, supported or unsupported metal catalysts are also effective for this reaction. For example, Raney Ni, Co, Cu,[3,4] and Cu–Zn oxide catalysts[5] were used for the vapor-phase amination, and reduced Ni catalysts[6] for the liquid-phase amination.

Recently, it has been found that the reaction of cyclohexanol and ammonia over platinum group metal catalysts gives aniline by simultaneous amination and dehydrogenation. Baker[7] obtained aniline in high selectivity by vapor-phase reaction of cyclohexanol/NH_3/H_2 over Pt/C catalysts. Carrubba and Golden[8] used Pt/SiO_2 for the same reaction. Moreover, modified Pd/Al_2O_3 catalysts are also useful for aniline formation according to an European patent.[9] Richardson and Lu[10] studied dehydrogenation and amination of cyclohexanol over a commercial Pt/SiO_2 catalyst by changing contact time and reaction time and speculated a possible reaction pathway. However, no study has been made on the basic nature of cyclohexanol amination over platinum group metal catalysts, which is useful information to develop high-performance catalysts.

In this paper, the catalytic activity and selectivity of silica-supported platinum group metals for the vapor-phase cyclohexanol amination is first investigated. Then, the reaction mechanism is examined by changing reaction conditions or performing related reactions. Structure sensitivity of the reaction is also studied by changing metal particle size. Finally, catalyst deactivation is discussed.

Experimental

Preparation of Catalysts. All the catalyst samples used in this study were prepared by impregnation of silica (Davison #57) with an aqueous solution of metal chloride salts ($RuCl_3 \cdot H_2O$, $RhCl_3 \cdot 3H_2O$, $PdCl_2$, $IrCl_4 \cdot H_2O$, $H_2PtCl_6 \cdot 6H_2O$). The samples were then dried with a rotary evaporator (353 K 1 h, 383 K 1 h) and finally reduced in flowing hydrogen (773 K 3 h).

Characterization of Catalysts. In order to know the percentage metal exposed or dispersion (for fresh catalysts), hydrogen chemisorption measurements were performed at room temperature in the pressure range of 5—30 kPa with a conventional volumetric adsorption system. Catalyst samples reduced at 723 K were outgassed for 1 h at the same temperature before the measurements. The chemisorption values were determined by extrapolating the linear portion of adsorption isotherms to zero pressure except for Pd/SiO_2. In the case of Pd/SiO_2, the chemisorption value was taken as the difference between the first adsorption value and the backsorption value measured after evacuation at room temperature for 10 min, in order to eliminate the contribution of hydride formation.[11] Percentage metal exposed or dispersion was calculated from the chemisorption value on the assumption that one hydrogen atom is chemisorbed on each metal atom at the surface. Then, metal particle size was calculated by using the following equation, assuming a spherical shape.[12]

$$d = 6V/AD \qquad (1)$$

where d is the metal particle size, D is the dispersion, V is the volume occupied by a metal atom in the bulk, and A is the effective average area occupied by a metal atom in the surface.

Reaction Procedures. The amination reactions were carried out with a continuous flow reactor at atmospheric pressure. Cyclohexanol was pumped by a motor-driven syringe to the preheating zone of the reactor. Ammonia from a cylinder was dried through a potassium hydroxide column and mixed with hydrogen before entering the reactor. The reactant gas flow was 24 mmol h^{-1} of cyclohexanol, 98 mmol h^{-1} of ammonia, and 98 mmol h^{-1} of hydrogen. The reaction products were trapped by bubbling into a ice-cold trap containing 2-propanol as the solvent and *N,N*-dimethylaniline as the internal standard for analysis.

Catalysts placed in the reactor were first reduced in flowing hydrogen at 723 K for 30 min and the temperature was lowered to the reaction temperature. Then, ammonia and cyclohexanol were fed. The products were analyzed by a gas chromatograph with a 3-m column of Silicone DC-

Table 1. Activity of Silica-Supported Platinum Group Metal Catalysts[a)]

Metal	Catalyst				Conversion	Turnover rate $10^{-3}\,s^{-1}$ (Selectivity %)					
	$L^{b)}$ wt%	$L^{b)}$ mmol g^{-1}	$D^{c)}$ %	Weight g	%	Total	Cyclohexylamine	Aniline	Dicyclohexylamine	N-cyclohexylaniline	Cyclohexane +Benzene
Ru	0.51	0.050	17	1.01	7.9	63.62	61.17(96.1)	0.82(1.3)	1.36(2.1)	0.00(0.0)	0.28(0.4)
Rh	0.54	0.052	54	1.43	8.2	13.94	9.42(67.6)	2.51(18.0)	0.61(4.4)	0.33(2.4)	1.07(7.7)
Pd	0.50	0.047	35	1.45	6.7	19.01	11.44(60.2)	4.66(24.5)	0.82(4.3)	1.89(10.0)	0.20(1.0)
Ir	0.53	0.027	65	1.41	9.4	23.65	18.54(78.4)	1.13(4.8)	3.29(13.9)	0.19(0.8)	0.50(2.1)
Pt	0.50	0.026	64	0.25	7.3	114.87	77.23(67.2)	12.90(11.2)	1.89(1.6)	12.14(10.6)	10.72(9.3)

a) Reaction temperature: 493 K. b) *L* is the metal loading. c) *D* is the metal dispersion.

550 operating from 378 K to 468 K at a rate of 10 K min^{-1}. Product yield (*Y*), cyclohexanol conversion (*C*), product selectivity (*S*), and turnover rate of formation (*TOR*) were calculated on the cyclohexanol basis from the following equations.

$$Y/\% = \frac{\text{Product produced/mol}}{\text{Cyclohexanol fed/mol}} \times 100 \qquad (2)$$

$$C = \text{Total product yields} \qquad (3)$$

$$S/\% = \frac{\text{Product yield}}{\text{Cyclohexanol conversion}} \times 100 \qquad (4)$$

$$TOR/s^{-1} = \frac{\text{Product produced/mol s}^{-1}}{\text{Amount of Surface catalyst metal atoms/mol}} \qquad (5)$$

As carbon balance was fairly good, Eq. 3 is not a bad selection for the calculation of cyclohexanol conversion. The catalyst amount was controlled so that the conversion was less than 10% in most cases.

Results and Discussion

Catalytic Activity and Selectivity of Platinum Group Metals. Table 1 summarizes the reaction results on silica-supported platinum group metal catalysts. The loading of these metals was approximately fixed at 5 wt%. As catalyst deactivation was observed, initial activity values are taken in Table 1. The main products were cyclohexylamine and aniline. The by-products detected were cyclohexane, benzene, dicyclohexylamine, and *N*-cyclohexylaniline. As will be discussed later, the last two products are considered as the condensation products of two cyclohexylamine molecules, and one aniline and one cyclohexylamine molecule, respectively.

The most active catalyst is Pt/SiO_2 because the conversion per unit weight was the largest. It also gave the largest total turnover rate. However, the difference between Pt and Rh, the least active metal, is within one order of magnitude. With respect to selectivity, aniline was barely formed on Ru or Ir, showing that these two metals have little activity for dehydrogenation to aniline. On the other hand, aniline formation was observed on Rh, Pd, and Pt, among which Pd showed the highest selectivity to aniline. This nature of catalyst metals agrees very much with the work by Ono and Ishida on phenol amination,[13)] where aniline was formed in high selectivity on Pd, Pt, and Ph/Al_2O_3 while aniline was not detected on Ru/Al_2O_3. Another point to be noted is that the elimination of amino or hydroxyl group was observed on Rh and Pt, resulting in the formation of cyclohexane and benzene.

Taking high activity into consideration, all the following studies were done with Pt/SiO_2.

Effect of Reaction Conditions. The effect of reaction temperature on cyclohexanol amination was examined in the temperature range of 478—539 K and is shown in Fig. 1. Both cyclohexylamine and aniline yield increased with temperature. But the selectivity shifts to aniline at high temperatures. Therefore, high temperature is desirable for aniline formation. In fact, Richardson et al.[10] obtained aniline in high selectivity at 573 K.

In Fig. 2 is shown the effect of contact time on the conversion and yield. The yield of each product increased almost proportionally with contact time within the range to 3.5 g h mol^{-1}. The selectivity change with contact time is plotted in Fig. 3, which shows that the selectivity to dicyclohexylamine increases and that to cyclohexylamine decreases. This suggests that the former originates by condensation reaction of two molecules of the latter. Similarly, *N*-cyclohexylaniline is thought to be formed by condensation of cyclohexylamine and aniline, although this conclution is not so clear as in the case of dicyclohexylamine.

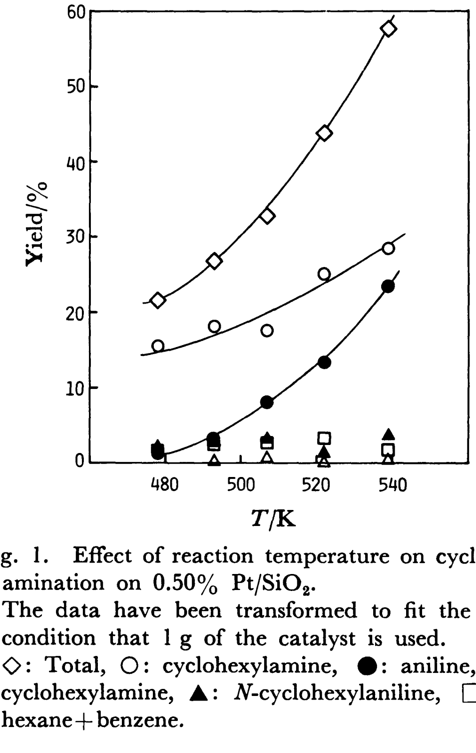

Fig. 1. Effect of reaction temperature on cyclohexanol amination on 0.50% Pt/SiO$_2$.
The data have been transformed to fit the reaction condition that 1 g of the catalyst is used.
◇: Total, ○: cyclohexylamine, ●: aniline, △: dicyclohexylamine, ▲: *N*-cyclohexylaniline, □: cyclohexane+benzene.

When the yield of these dimers is divided and added to their component compounds (cyclohexylamine and aniline), the selectivity does not change much within the whole range of the experiment. This result indicates that cyclohexylamine and aniline are formed from cyclohexanol not in the consecutive process but in the parallel process.

Reaction Mechanism. In order to elucidate the reaction mechanism, several related reactions were performed. The results are summerized in Table 2. First, when cyclohexanol and hydrogen were passed over Pt/SiO$_2$ with inert N$_2$ instead of NH$_3$, cyclohexanone was formed as the only product, the cyclohexanol conversion being almost the same. Next, cyclohexanone was fed instead of cyclohexanol in the amination reaction. In this case, the conversion was much larger, but the product distribution was almost the same except for the ratio of monomers to dimers. Therefore, it is inferred that amination of cyclohexanone is a facile reaction, producing the same products in the same selectivity as the amination of cyclohexanol. In order to examine the formation pathway of cyclohexylamine or aniline, cyclohexylamine or aniline was passed at 493 K over Pt/SiO$_2$ in an atmosphere of ammonia and hydrogen. It was found that cyclohexylamine is not formed from aniline and the reverse reaction occurs to only a little extent. This means that conversion from cyclohexylamine to aniline is a difficult reaction under these

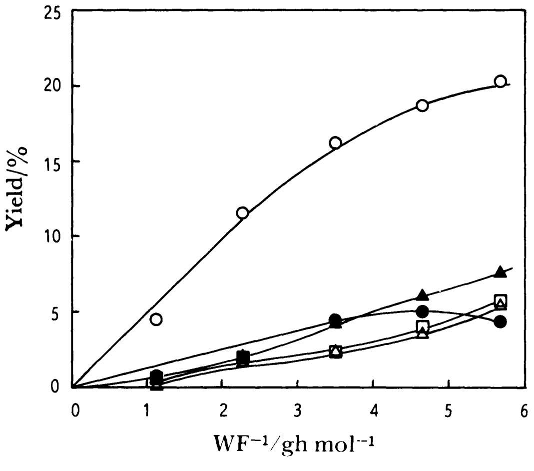

Fig. 2. Effect of contact time on the product yield in cyclohexanol amination at 493 K on 0.50% Pt/SiO$_2$. ○: Cyclohexylamine, ●: aniline, △: dicyclohexylamine, ▲: *N*-cyclohexylaniline, □: cyclohexane+benzene.

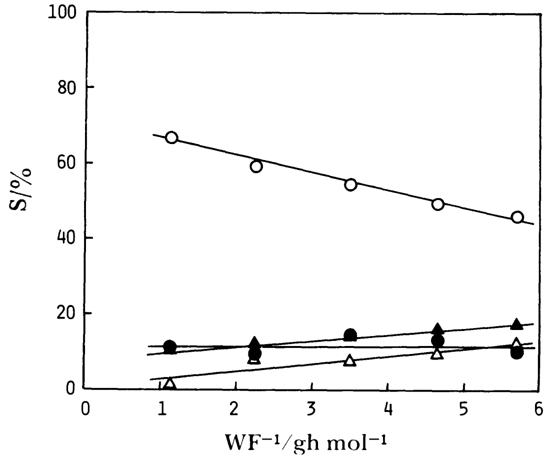

Fig. 3. Effect of contact time on the product selectivity in cyclohexanol amination at 493 K on 0.50% Pt SiO$_2$. ○: Cyclohexylamine, ●: aniline, △: dicyclohexylamine, ▲: *N*-cyclohexylaniline.

Table 2. Results of Related Reactions[a)]

Reactant	Yield/%						
	Cyclohexanol	Cyclohexylamine	Aniline	Dicyclohexylamine	*N*-cyclohexylaniline	Cyclohexane +Benzene	Cyclohexanone
Cyclohexanol/NH_3/H_2	—	1.52	0.26	0.069	0.119	0.099	0
Cyclohexanol/N_2/H_2	—	0	0	0	0	0	1.51
Cyclohexanone/NH_3/H_2	1.30	13.63	1.58	21.85	4.42	0.45	0
Cyclohexylamine/NH_3/H_2	0	—	1.33	4.31	2.21	0.57	0
Aniline/NH_3/H_2	0	0	—	0	0.33	0.72	0

a) Catalyst: 0.99 wt% Pt/SiO_2 0.07 g. Reaction temperature: 493 K. Reactant gas flow rate: 49/98/98 mmol h^{-1}.

reaction conditions or vice versa. Therefore, these two compounds are considered to originate not in the consecutive process but in the parallel process. It is unlikely that cyclohexylamine and aniline are in equilibrium. Ono and Ishida[13)] pointed out that cyclohexylamine and aniline are formed in equilibrium in the case of phenol amination at 523 K. The difference may be attributed to different catalysts and reaction conditions.

From these results, a reaction scheme represented by Fig. 4 can be given. The first step, which is rate-determining, is the dehydrogenation of cyclohexanol to cyclohexanone intermediate. Then, cyclohexylamine and aniline are formed simultaneously via cyclohexylideneamine by amination of cyclohexanone. The presence of cyclohexylideneamine intermediate has been proposed and proved in studies on amination reactions[13,14)] or hydrogenation of aniline.[15)]

Structure Sensitivity. Catalytic reactions on metal catalysts can be classified into two groups, one is structure-sensitive and the other structure-insensitive, depending on the manner how the catalytic activity is influenced by metal particle size or crystallographic plane.[16)] To investigate structure sensitivity of this amination reaction, six Pt/SiO_2 catalysts with different Pt particle size were prepared by changing Pt loading from about 0.30 to 6.5 wt%. With decreasing Pt loading, Pt dispersion increased from 16 to 73% and Pt particle size decreased consequently from 7.2 to 1.6 nm. The reaction results are shown in Table 3. It was found that catalytic activity per surface metal atom and product selectivity do not change much with Pt particle size. Therefore, it can be concluded that cyclohexanol amination on Pt/SiO_2 is a structure-insensitive reaction. This conclusion is also supported by the result of Table 1 that the catalytic activity is not so sensitive to the nature of the catalyst metal.[17)] Most of hydrogenation and dehydrogenation reactions have been found to be structure-insensitive. Therefore, this amination reaction can be expected to be structure-insensitive because the rate-determining step is the dehydrogenation of cyclohexanol to cyclohexanone. Thus, improving metal dispersion has no more effect than making metal surface area larger.

Strictly speaking, however, the product distribution seems to be affected by Pt particle size, because the selectivity to aniline decreased and the selectivity to

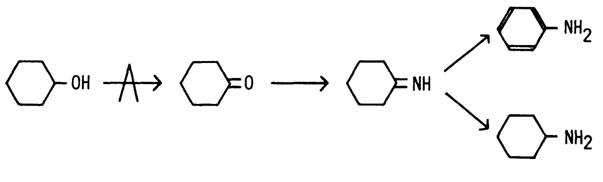

Fig. 4. Reaction scheme of cyclohexanol amination.

Table 3. Effect of Pt Particle Size[a)]

Catalyst				Conversion	Turnover rate / 10^{-3} s^{-1} (Selectivity / %)					
L[b)] wt%	D[c)] %	d[d)] nm	Weight g	%	Total	Cyclohexylamine	Aniline	Dicyclohexylamine	N-cyclohexylaniline	Cyclohexane +Benzene
0.30	73	1.6	0.354	6.72	106.02	67.13(63.3)	12.66(11.9)	2.77(2.6)	14.27(13.5)	9.19(8.7)
0.50	64	1.8	0.248	7.28	114.87	77.23(67.2)	12.90(11.2)	1.89(1.6)	12.14(10.6)	10.72(9.3)
0.99	49	2.3	0.188	6.69	83.22	53.24(64.0)	9.37(11.3)	4.27(5.1)	6.09(7.3)	10.25(12.3)
2.9	22	5.2	0.132	4.50	58.49	41.24(70.5)	4.49(7.7)	3.18(5.4)	1.65(2.8)	7.93(13.6)
6.5	16	7.2	0.071	5.39	90.23	50.94(56.5)	6.49(7.2)	5.06(5.6)	2.27(2.5)	25.48(28.2)

a) Reaction temperature: 493 K. b) L is the Pt loading. c) D is the Pt dispersion. d) d is the Pt particle size.

cyclohexane plus benzene increased with Pt particle size, as can be seen from Table 3. Especilally on 6.5% Pt/SiO2, considerable elimination of amino or hydroxyl group was observed, resulting in 28% selectivity to cyclohexane plus benzene. Hence, highly dispersed Pt/SiO2 is favorable for obtaining aniline in higher selectivity.

Deactivation of Catalysts. Figure 5 shows a typical change of the product yield with time on stream. The yield of each product dropped with time especially at the beginning of the reaction. It should be noted, however, that the product selectivity remains unchanged. Considering that this reaction is structure-insensitive, it is suggested that the number of surface Pt atoms decreases as the catalyst deactivation proceeds. In fact, Table 4 indicates that the catalyst deactivation is closely related to the decrease of

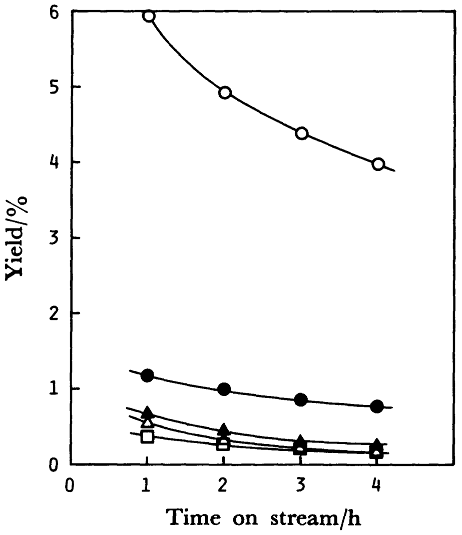

Fig. 5. Change in the product yield with time on stream in cyclohexanol amination at 493 K on 0.50% Pt/SiO$_2$. ○: Cyclohexylamine, ●: aniline, △: dicyclohexylamine, ▲: N-cyclohexylaniline, □: cyclohexane+benzene.

Table 4. Change in Percentage Pt Exposed by Reaction[a)]

L[b)]/%	D[c)]/%	
	Fresh	Used
0.30	73	36
0.50	63	35
0.99	49	35
2.9	22	19
6.5	16	14

a) Catalyst amount: 1.8 g. Reactions conditions: 523 K, 5 h. b) L is the Pt loading. c) D is the percentage Pt exposed, which is equal to Pt dispersion for fresh catalysts.

percentage Pt exposed, and that the extent of decrease is larger as the Pt loading is smaller.

Deactivation may be caused by sintering or surface fouling by carbonaceous or polymeric materials. In the case of this reaction, surface fouling is more likely because the catalyst weight increased by 10% after performing amination reaction. This conclution agrees with the work by Richardson and Lu.[10] However, regeneration of the deactivated catalysts by calcination with air and/or hydrogen has been unsuccessful so far.

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