

Ru-catalyzed hydrogenation of aromatic diamines: The effect of alkali metal salts

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Abstract

The influences of added alkali metal nitrates and nitrites on the performances of ruthenium catalysts in the liquid phase ring hydrogenation of 4,4'-methylenedianiline (MDA) and 1,4-phenylenediamine (PDA) have been examined. Sodium nitrate and sodium nitrite were shown to be the most effective promoters in enhancing the catalytic activity and in suppressing the formation of by-products. The effects of various solvents and the added water on the hydrogenation activity have also been investigated. The promoting effects of sodium nitrate and sodium nitrite were considerably enhanced in the presence of small amounts of water. XRD patterns of the Ru/Al₂O₃ catalyst sample obtained from the reaction performed in the presence of NaNO₃ or NaNO₂ revealed that the sodium aluminate (NaAlO₂) phase appears indicating that the cations of metal salts are interacting with the supporting material. An active species, NaOCH(CH₃)₂, was isolated and identified by spectroscopic and elemental analyses. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic hydrogenation of aromatic diamine to alicyclic diamines has been a topic of great interest. Alicyclic diamines and their derivatives, diisocyanates are very useful substances which are suitable for forming light stable urethane coatings and lacquers due to their high flexibilities [1,2]. Platinum group metals, ruthenium and palladium are commonly

used as the active catalysts for the hydrogenation of aromatic diamine, but palladium is found to be easily deactivated by the strong inhibitory action of ammonia produced along with the secondary amines [3]. It was previously shown that the addition of ammonia not only suppresses the formation of by-product but also poisons the catalyst [4]. Unlike ammonia, the addition of alkali hydroxide, especially lithium hydroxide, is found to suppress the formation of hydrogenolysis by-product without poisoning the catalyst [5]. Recently, it was also reported in the patent literature that alkali metal nitrates and

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sulfates, especially those of lithium, are very effective promoters in the selective ring hydrogenation of aromatic diamines [6]. In the course of studying the Ru-catalyzed ring hydrogenation of aromatic diamines with the presence of various types of metal salt promoters, we have found that alkali metal nitrites, especially sodium nitrite is also effective promoters in enhancing the catalytic activity and in preventing the catalyst poisoning. Furthermore, the catalytic activity of ruthenium was found to increase significantly when small amounts of water and sodium nitrite or sodium nitrate are co-present. The main objectives of this work are to develop the highly active catalyst system for the ring hydrogenation of aromatic diamines and to attain a better understanding of the promoting effects of metal nitrates, metal nitrites and water by characterizing the structure of catalysts by using X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FT-IR).

2. Experimental

2.1. Chemicals

The aromatic diamines, metal nitrates, metal nitrites and metal sulfates were purchased from Aldrich Chemical Co. and used without further purification. All solvents were obtained from J.T. Baker and distilled just before use according to the literature methods [7]. 5% Ru/C, 5% Ru/Al₂O₃, and 5% Ru/SiO₂ were purchased from Engelhard Co. and vacuum dried at 120°C to remove traces of water present. All chemicals were stored under N₂ to avoid contact with atmospheric water. Unsupported ruthenium catalyst was prepared according to the literature method described by Struijck et al. [8]. NaOCH₃ and NaOCH(CH₃)₂ were prepared by reacting metallic sodium with the corresponding alcohol. The NaNO₃-doped Ru/C catalyst was prepared by adding 1 g of 5% Ru/C into the aqueous solution containing 5 mmol NaNO₃ and subsequent drying at 120°C overnight.

2.2. Hydrogenation reaction

All hydrogenation reactions were conducted in a Parr 100 ml stainless steel bomb with a magnet drive stirrer and an electrical heater. The catalyst, substrate, solvent, and metal salt, if necessary, were put into the bomb. NaNO₃ and other metal salts were added in a fine powder. Reactions were carried out at 1000 rpm stirring rates to minimize hydrogen mass transfer as a limitation to the reaction rates. The reactor was purged with nitrogen followed with hydrogen and then pressurized to about 600 psig with hydrogen. The bomb was then heated with agitation to a specified reaction temperature with addition of hydrogen from a reservoir tank (ballast tank) to maintain a specified pressure. The drop in pressure in the ballast tank was recorded by means of a pressure transducer and a recorder and provided a convenient method for observing the progress of the reaction. The reaction was considered complete when hydrogen consumption stopped. After reaction, the bomb was cooled to room temperature, vented and the product mixture removed. After removing the catalyst by filtration, product mixture was analyzed by GC and GC-Mass and HPLC.

2.3. Catalyst characterization

The infrared spectra of the catalyst samples were recorded on a Mattson Infinity FT-IR spectrometer equipped with MCT detector. ¹H-NMR spectra were measured on a Varian Unity Plus 300 spectrometer in CD₃OD. Shimadzu (XRD 6000) diffractometer with a nickel-filtered CuK α excitation source was employed to obtain XRD patterns for all the catalyst samples. The X-ray source was operated at 30 kV and 40 mA with scanning rate 2° min⁻¹. Compound identification was accomplished by the comparison of measured spectra of the samples with those of reference samples or JCPDS powder diffraction file data.

The surface areas were determined by the modified BET methods from the adsorption

isotherms of nitrogen temperature with the help of the Area-Meter II.

3. Results and discussion

3.1. Effect of support

Catalytic ring hydrogenation reactions of 1,4-phenylenediamine (PDA) and 4,4'-methylene dianiline (MDA) were carried out at 140°C over supported and unsupported Ru catalysts. The effect of support was examined and the results are listed in Table 1. The catalytic activities were found in the order of Ru/C > Ru > Ru/AlF₃ > Ru/Al₂O₃ > Ru/SiO₂. The highest activity of Ru/C is probably ascribed to the fact that active carbon support has much larger surface area, consequently higher dispersion of active ingredient in comparison with other supports. However, the higher activities of Ru/AlF₃ ($S = 53 \text{ m}^2 \text{ g}^{-1}$) and unsupported Ru ($S = 42 \text{ m}^2 \text{ g}^{-1}$) compared with those of Ru/Al₂O₃ ($S = 198 \text{ m}^2 \text{ g}^{-1}$) and Ru/SiO₂ ($S = 220 \text{ m}^2 \text{ g}^{-1}$) cannot be explained in terms of surface area only. It is likely that there should be some other factors to govern the activity of ruthenium such as metal-support interaction and acidity of support. As will be discussed in the later section, oxygen containing support might share the

oxygen atom with Ru(0) and makes the Ru(0) to an partially oxidized, inactive form.

3.2. Effects of temperature and pressure

Effects of temperature and pressure on the hydrogenation reactions of PDA and MDA were investigated and the results are shown in Table 2. The increase of reaction temperature results in the enhanced rate of reaction along with the increased formation of side products such as cyclohexyl amine and *N*-alkylcyclohexyl amine, indicating that deamination reaction and *N*-alkylation reaction of amine with alcohol are facilitated at higher reaction temperatures. The pressure does not seem to have a significant effect on the hydrogenation as long as the reaction pressure is maintained above 800 psig. Below 800 psig, the rate of the reaction becomes slower, but the decrease in the rate is much less pronounced than in the case of temperature.

3.3. Effect of solvent

Various solvents were tested for their effects on the hydrogenation reactions and the results are listed in Table 3. No reaction was observed either in benzene or in *n*-hexane. The reaction occurred most rapidly in methanol or ethanol,

Table 1
Effect of supports on the hydrogenation of aromatic diamines^a

Entry	Diamine	Catalyst ^b	Time (min)	Conv. (%)	Product composition (%)			
					A	B	C	D
1	MDA	Ru	60	94.0	62.1	28.8	0.7	2.4
2	MDA	5% Ru/C	20	99.9	78.0	14.5	1.3	6.1
3	MDA	5% Ru/Al ₂ O ₃	60	43.4	3.3	37.8	0.5	1.8
4	MDA	5% Ru/AlF ₃	60	56.8	18.0	35.8	0.4	2.6
5	MDA	5% Ru/SiO ₂	60	19.0	0.6	14.7	0.3	3.4
6	PDA	5% Ru/C	20	80.5	—	61.9	10.1	8.5
7	PDA	5% Ru/Al ₂ O ₃	60	13.3	—	5.4	4.3	3.6

(A) Both rings hydrogenated, di(4-aminocyclohexyl)methane. (B) One ring hydrogenated, 4-aminocyclohexyl-4-aminophenylmethane or 1,4-cyclohexyl diamine. (C) Deaminated. (D) *N*-alkylated and high boiler.

^aAromatic diamines (25 mmol) were hydrogenated in isopropanol (25 ml) at 140°C under the hydrogen pressure of 1200 psig.

^bMolar ratio of diamine/Ru: 50 for MDA, 100 for PDA.

Table 2
Effect of temperature and pressure on the hydrogenation of aromatic diamines^a

Entry	Diamine	Temp. (°C)	Pressure (psig)	Conv. (%)	Product composition (%)			
					A	B	C	D
1	MDA	100	1200	31.3	2.2	28.0	tr.	1.1
2	MDA	120	1200	80.2	14.4	61.4	0.4	4.0
3	MDA	140	1200	99.9	78.0	14.5	1.3	6.1
4	MDA	160	1200	98.6	65.3	—	5.1	28.2
5	MDA	140	800	69.8	14.1	53.3	0.6	1.8
6	MDA	140	1000	91.4	57.4	28.9	0.8	4.3
7	MDA	140	1400	100	82.2	13.5	0.8	3.5
8	PDA	100	1200	14.1	—	11.6	1.1	1.4
9	PDA	120	1200	68.4	—	53.7	7.4	7.3
10	PDA	140	1200	80.5	—	61.9	10.1	8.5
11	PDA	160	1200	100	—	52.8	18.4	28.8
12	PDA	140	800	70.3	—	52.9	7.8	9.6
13	PDA	140	1000	72.5	—	56.6	6.9	9.8
14	PDA	140	1400	85.5	—	66.8	9.1	9.6

(A) Both rings hydrogenated, di(4-aminocyclohexyl)methane. (B) One ring hydrogenated, 4-aminocyclohexyl-4-aminophenylmethane or 1,4-cyclohexyl diamine. (C) Deaminated. (D) *N*-alkylated and high boiler.

^aAromatic diamines (25 mmol) were hydrogenated with 5% Ru/C in isopropanol (25 ml) for 20 min. Molar ratio of diamine/Ru: 50 for MDA, 100 for PDA.

but the formation of undesirable *N*-alkylated side products were predominant, these are believed to be formed from the reaction of amine with alcohol. Unlike in methanol and ethanol, the reaction in isopropanol yielded ring hydrogenated product with high yield and selectivity,

producing only a negligible amounts of *N*-alkylated compounds. The use of *t*-butyl alcohol solvent significantly retarded the rate of reaction, strongly indicating that a steric factor is governing the reactivity. In other words, *N*-alkylation rather than ring hydrogenation takes

Table 3
Effect of solvents on the hydrogenation of aromatic diamines^a

Entry	Diamine	Solvent	Conv. (%)	Product composition (%)				
				A	B	C	D	E
1	MDA	Methanol	99.7	69.2	8.1	6.8	7.3	8.2
2	MDA	Isopropanol	99.9	78.0	14.5	1.3	2.1	4.0
3	MDA	<i>t</i> -Butanol	57.2	4.7	48.6	1.5	tr.	1.8
4	PDA	Methanol	92.6	—	57.7	15.2	10.0	9.7
5	PDA	Ethanol	84.4	—	57.5	12.1	7.6	7.2
6	PDA	Isopropanol	80.5	—	61.9	10.1	1.9	6.6
7	PDA	<i>t</i> -Butanol	45.4	—	29.1	8.5	tr.	7.8
8	PDA	<i>t</i> -Amyl alcohol	42.6	—	27.6	8.6	—	6.4
9	PDA	THF	40.1	—	26.1	7.9	—	6.1
10	PDA	DMF	19.6	—	11.8	2.5	—	5.3
11	PDA	DMSO	N.R.	—	—	—	—	—
12	PDA	Hexane	N.R.	—	—	—	—	—
13	PDA	Benzene	N.R.	—	—	—	—	—

(A) Both rings hydrogenated, di(4-aminocyclohexyl)methane. (B) One ring hydrogenated, 4-aminocyclohexyl-4-aminophenylmethane or 1,4-cyclohexyl diamine. (C) Deaminated. (D) *N*-alkylated. (E) High boiler.

^aAromatic diamines (25 mmol) were hydrogenated with 5% Ru/C in various solvents (25 ml) at 140°C under the hydrogen pressure of 1200 psig for 20 min. Molar ratio of diamine/Ru: 50 for MDA, 100 for PDA.

place dominantly with a less sterically hindered alcohol as in the case of methanol and ethanol, and the rate of reaction becomes much slower with a bulky, hindered alcohol such as *t*-butanol and *t*-amyl alcohol. Therefore, a moderately hindered alcohol solvent such as isopropanol should be used for the hydrogenation to proceed at a reasonable rate. It is also conceivable that transfer hydrogenation from alcohol to amine is participating and this may explain why isopropanol yields ring hydrogenated products more selectively. The hydrogenation reactions are also conducted in coordinating solvents such as THF, DMF and DMSO. The reactions in THF and DMF were found to proceed much slower compared with those in isopropanol and yielded large amounts of unidentified high boiling side products. In DMSO, surprisingly, no reaction was observed implying that DMSO may act as a strong poison.

3.4. Effect of added metal salt

The Ru-catalyzed reactions were performed in the presence of various types of alkali metal salts. Tables 4 and 5 show that addition of NaNO_3 , LiNO_3 or NaNO_2 is more effective in

Table 5

Effect of added metal salts on the hydrogenation of MDA^a

Entry	Metal salt	Conv. (%)	Product composition (%)			
			A	B	C	D
1	NaCl	94.0	29.7	56.4	2.8	5.1
2	NaBr	91.6	26.0	57.7	3.0	4.9
3	NaI	25.1	0.3	16.2	0.9	7.7
4	KI	25.0	0.3	16.8	0.9	7.0
5	Na_2SO_4	97.0	39.0	48.9	2.9	6.2
6	Na_2CO_3	87.1	24.1	53.0	2.9	7.1
7	ZnSO_4	73.2	13.4	50.2	2.6	7.0
8	NaOCH_3	44.0	3.1	37.0	0.3	3.6
9	$\text{NaOCH}(\text{CH}_3)_2$	99.9	91.4	3.0	1.8	3.7

A: Both rings hydrogenated, di(4-aminocyclohexyl)methane.

B: One ring hydrogenated, 4-aminocyclohexyl-4-aminophenylmethane or 1,4-cyclohexyl diamine.

C: Deaminated.

D: *N*-alkylated and high boiler.

^aMDA (25 mmol) was hydrogenated with 5% Ru/C (1 g) in isopropanol (25 ml) in the presence of various metal salt (5 mmol) at 140°C under the hydrogen pressure of 1200 psig for 20 min.

enhancing the catalytic activity and in suppressing the formation of side products compared to other metal salts. It is interesting to note that the catalytic activity is not affected by addition of KNO_3 or KNO_2 and is greatly suppressed by the presence of CsNO_3 and RbNO_3 . Concerning the anion of sodium salts, NO_3^- and NO_2^- show

Table 4

Effect of added metal nitrates and nitrites on the hydrogenation of aromatic diamines^a

Entry	Diamine	Metal Salt	Conv. (%)	Product composition (%)			
				A	B	C	D
1	MDA	NaNO_3	99.9	97.3	0.4	tr.	2.2
2	MDA	NaNO_2	99.8	98.2	tr.	tr.	1.6
3	PDA	LiNO_3	96.0		95.0	1.0	tr.
4	PDA	NaNO_3	98.6		97.8	0.8	—
5	PDA	NaNO_2	99.8		99.8	tr.	tr.
6	PDA	KNO_3	76.6		64.6	5.3	6.7
7	PDA	KNO_2	75.3		64.7	4.4	6.2
8	PDA	CsNO_3	19.9		16.3	1.2	2.4
9	PDA	RbNO_3	N.R.				
10	PDA	NH_4NO_3	N.R.				
11	PDA	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	N.R.				
12	PDA	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	N.R.				

(A) Both rings hydrogenated, di(4-aminocyclohexyl)methane. (B) One ring hydrogenated, 4-aminocyclohexyl-4-aminophenylmethane or 1,4-cyclohexyl diamine. (C) Deaminated. (D) *N*-alkylated and high boiler.

^aAromatic diamines (25 mmol) were hydrogenated with 5% Ru/C in isopropanol (25 ml) in the presence of various metal nitrate and nitrite (5 mmol) at 140°C under the hydrogen pressure of 1200 psig for 20 min. Molar ratio of diamine/Ru: 50 for MDA, 100 for PDA.

a promoting effect, whereas SO_4^{2-} and CO_3^{2-} act as a mild poison. The promoting effect of NaNO_3 and NaNO_2 may be attributed to the fact that NaNO_3 and NaNO_2 are more easily chemisorbed by ruthenium and makes the ruthenium more hydrophilic, as a result of which the adsorption of hydrophilic substrate, amine can be facilitated. Another possible explanation for the promoting effect of NaNO_3 and NaNO_2 is likely that NaNO_3 and NaNO_2 act as a source to produce ammonia by the reaction with H_2 and the resulting ammonia plays a role in promoting hydrogenation of aromatic amine. Details on the role of NaNO_3 and NaNO_2 will be discussed in Section 3.5. The effect of halide ion, however, is rather surprising. The catalytic activity of ruthenium decreases to a great extent by the addition of NaX ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) as going from Cl^- to I^- . The striking effect of I^- seems to be rationalized by the fact that NaI is more easily dissociated into Na^+ and I^- , and the I^- ions, in turn, strongly and irreversibly adsorb onto the active sites of ruthenium resulting in a severe poisoning of the catalyst. Dramatic change in the catalytic activity was observed by the addition of sodium alkoxide, i.e., the addition of NaOCH_3 makes the catalyst inactive while the presence of $\text{NaOCH}(\text{CH}_3)_2$ considerably enhances the performances of the catalyst. Further details on the influences of the added alkoxide will be discussed later. Even though we did not make an elaborate study of the influence of the type of anion and cation on the performances of the catalyst, it appears, from the above results, that both cation and anion of the metal salts are playing important roles in determining whether a certain metal salt acts as a promoter or a poison. Besides the adsorption of alkali metal salts onto the ruthenium, it is also conceivable that intermediate species formed from the interaction of the metal salt with ruthenium catalyst are responsible for the catalytic activity. It still remains under question how a certain cation or anion can act as a promoter or poison, and various factors such as ionic size, ionization potential of cation and

anion of the metal salt need to be considered to elucidate this phenomenon more clearly.

3.5. Spectroscopic analysis

3.5.1. FT-IR

It is interesting to note that the addition of NaNO_2 , NaNO_3 , LiNO_3 promote the ring hydrogenation in addition to suppressing the formation of by-products. Various FT-IR experiments were performed to elucidate the role of above salts in the ring hydrogenation of aromatic diamine. The catalyst mixture was isolated after hydrogenation at 140°C performed with Ru , Ru/C or $\text{Ru/Al}_2\text{O}_3$ catalyst in the presence of NaNO_2 , NaNO_3 or LiNO_3 in isopropanol. As shown in Fig. 1, the FT-IR spectrum of the catalyst mixture shows strong absorption peak at around 1450 cm^{-1} , quite different from the characteristic peaks of the metal nitrates and nitrites used. The absorption peak at around 1450 cm^{-1} was also observed when Ru ,

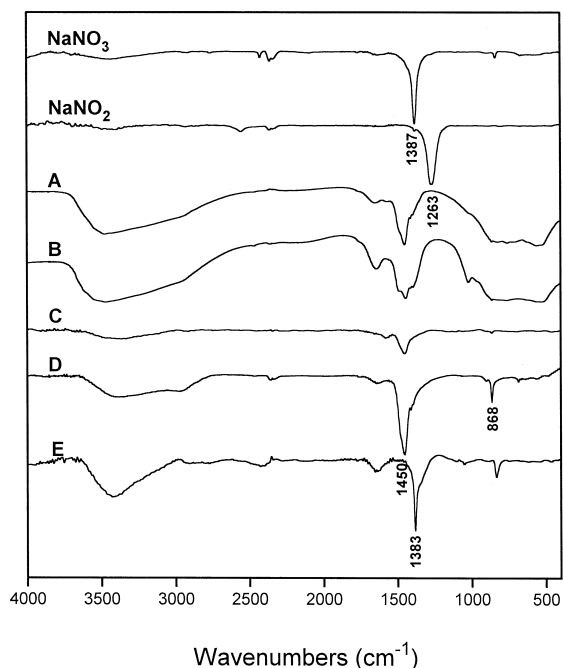
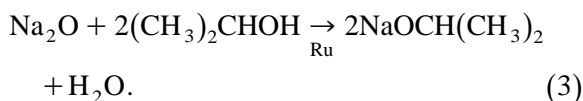
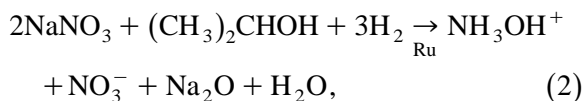
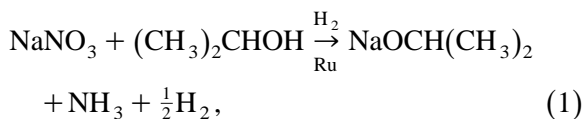


Fig. 1. IR spectra of various catalysts, after reaction. (A) $\text{Ru/Al}_2\text{O}_3 + \text{NaNO}_3$; (B) $\text{Ru/Al}_2\text{O}_3 + \text{NaNO}_2$; (C) $\text{Ru/C} + \text{NaNO}_3$; (D) $\text{Ru(O)} + \text{NaNO}_3$; (E) $\text{Ru(O)} + \text{RbNO}_3$.

Ru/C or Ru/Al₂O₃ was reacted with NaNO₃ or NaNO₂ in isopropanol at 140°C without the presence of H₂ or in hexane under high pressure of H₂. The observation of the same peak at around 1450 cm⁻¹ from NaNO₃ and NaNO₂ may suggest that at least one of N–O bond in NaNO₃ was lost by the interaction with H₂ or hydrogen atom in isopropanol. However, only absorption peaks corresponding to individual nitrates were observed in the IR spectra of catalyst mixtures obtained from the reactions with other metal nitrate, KNO₃, CsNO₃, RbNO₃, Zn(NO₃)₂ · 6H₂O, Al(NO₃)₃ · 9H₂O, etc. These results may imply that the cation of metal nitrates or nitrites is playing important role in promoting or in depressing catalytic activity of Ru, and the presence of absorption peak at around 1450 cm⁻¹ is required for the metal nitrate and nitrite to become an effective promoter. Even though, at the moment, it is hard to conclude the role of cation of metal nitrates and metal nitrites in the catalytic activity of ruthenium, it is quite possible that cation other than Li⁺ and Na⁺ may interact with Ru and form catalytically inactive bimetallic species. Miller and Wilkinson reported that the spectra of ionic nitrates such as NaNO₃ and Co(NO₃)₂ · 6H₂O show strong absorption band in the range 1350–1390 cm⁻¹ (NO₂ asymmetric stretching) and in the range 836–815 cm⁻¹ (NO₂ deformation) [9]. In complexes where the nitrate and nitrite group is covalently bound through one oxygen atom, the symmetry is lowered and thus the NO₂ asymmetric stretching frequencies increase in going from an ionically to a covalently bound nitrite or nitrate group [9–11]. From the FT-IR absorption peak at around 1450 cm⁻¹, it is initially assumed that covalently bound NO₂ or NO₃ species of ruthenium ([Ru–NO₂] or [Ru–NO₃]) are formed from the interaction of Ru with metal nitrates or metal nitrites, which could, in turn, react with hydrogen to form [Ru–NH₂] or [Ru–NH₃] because NO₃⁻ is known to react with H₂ to give NH₃OH⁺ in the presence of Pd catalyst [12,13]. The possibility of the formation of [Ru–NH₃] or [Ru–NH₂] species also can be

excluded by the observation of the peak at around 1450 cm⁻¹ in the absence of H₂. However, it is still conceivable that [Ru–NH₂] or [Ru–NH₃] might be formed by the hydrogen transfer reaction of isopropanol to [Ru–NO₂] or [Ru–NO₃] because no absorption peak at around 1450 cm⁻¹ was observed when ruthenium catalyst was treated with sodium nitrate in *n*-hexane solvent under a nitrogen pressure. In a separate experiment, Ru (40 mg) was reacted with NaNO₃ (200 mg) in isopropanol (40 ml) at 140°C for 2 h under 1000 psig H₂ pressure. After the reaction, the reactor was cooled to a room temperature and the reaction mixture was filtered to separate the insoluble ruthenium catalyst mixture. The resulting clear solution was evaporated to dryness to give a white compound. FT-IR spectra of the white soluble compound and of the insoluble catalyst mixture show the same strong absorption peak at around 1450 cm⁻¹. The white compound was identified as NaOCH(CH₃)₂ by elemental analysis [Calculated: C, 43.9%; H, 8.6%; Na, 28.0%. Found: C, 42.8%; H, 8.7%; Na, 28.2%] and ¹H NMR results [nmr δH in CD₃OD: 1.2 (d), 3.9 (m), 5.5 (s)]. It is, therefore, believed that the strong absorption peak at around 1450 cm⁻¹ in the IR spectrum of the catalyst mixture originated from the presence of small amounts of NaOCH(CH₃)₂. Ru-catalyzed hydrogenation reaction of MDA was conducted in the presence of NaOCH(CH₃)₂ separately prepared by reacting sodium metal with isopropanol in order to see whether the in-situ formation of NaOCH(CH₃)₂ from NaNO₃ or NaNO₂ is responsible for the activity enhancement (see Table 5). As expected, the addition of NaOCH(CH₃)₂ gives the similar catalytic activity to that obtained when the Ru-catalyzed hydrogenation reaction was performed in the presence of NaNO₃ or NaNO₂. It seems obvious that ruthenium is assisting or catalyzing the reaction between NaNO₃ and isopropanol, but the mechanism for the formation of NaOCH(CH₃)₂ and the role of ruthenium are still not clear. Plausible pathways to the forma-

tion of $\text{NaOCH}(\text{CH}_3)_2$ are also postulated as Eqs. (1)–(3) even though none of the equations is verified.



3.5.2. XRD

Fig. 2 shows XRD patterns of catalyst samples obtained after hydrogenation reactions with metallic Ru, 5% Ru/C and Ru/Al₂O₃. Intense peaks of Ru(0) are shown in the metallic ruthenium while peaks corresponding to Ru(0) are not observed in both Ru/C and Ru/Al₂O₃

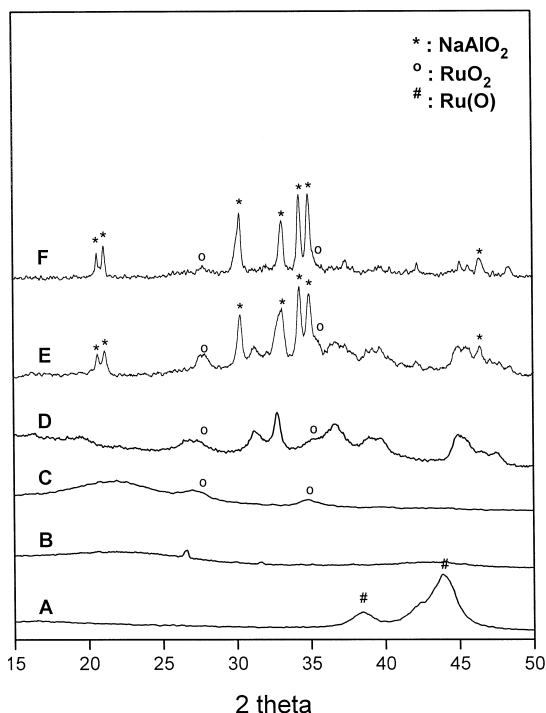


Fig. 2. XRD patterns of various catalysts, after reaction. (A) Ru(O); (B) Ru/C; (C) Ru/SiO₂; (D) Ru/Al₂O₃; (E) Ru/Al₂O₃ + NaNO₃; (F) Ru/Al₂O₃ + NaNO₂.

catalyst samples. Additional broad peaks corresponding to RuO₂ are shown in Ru/Al₂O₃ and Ru/SiO₂ catalyst samples obtained after reaction, indicating that oxygen transfer from alumina to Ru(0) occurred during the reaction. Furthermore, the XRD patterns of the Ru/Al₂O₃ catalyst sample obtained from the reaction performed in the presence of a promoter, NaNO₃ or NaNO₂ reveal that sodium aluminate (NaAlO₂) phase appears. The formation of NaAlO₂ strongly indicates that the cations of promoters are also interacting with the supporting material. Such an interaction may give a new compound as in case of NaAlO₂ or at least provide chemical or physical change in the supporting material as in carbon support. The chemical or physical change in the supporting material, in turn, should affect the hydrogenation activity of catalyst. Interestingly, IR spectrum of NaAlO₂ also shows the similar strong absorption band at around 1450 cm⁻¹ to that of NaOCH(CH₃)₂. From these results, it is tentatively concluded that in the Ru/Al₂O₃ catalyzed hydrogenation reaction of aromatic diamines, the interactions of added NaNO₃ or NaNO₂ with the supporting material, Al₂O₃ and isopropanol are taking place in a competitive fashion even though we are not able to figure out what percentage of the intensity of the IR absorption band at around 1450 cm⁻¹ is due to the presence of NaOCH(CH₃)₂ in the case of Ru/Al₂O₃.

3.6. Effect of water

Accidentally, we found that the promoting effects of NaNO₃ and NaNO₂ in the hydrogenation of MDA and PDA are greatly enhanced by the presence of small amounts of water. Experimental results are summarized in Table 6. Both Ru/C and Ru/Al₂O₃ behave similarly showing higher activities when water is co-present with NaNO₃ or NaNO₂. In the absence of NaNO₃ or NaNO₂, the effect of water on the reaction rate was almost negligible within the range of water

Table 6
Effect of water on the hydrogenation of MDA^a

Entry	Water (ml)	Metal salt	Conv. (%)	Product composition (%)			
				A	B	C	D
1	—	none	80.2	14.4	61.4	0.4	4.0
2	0.1	none	81.5	13.7	59.4	1.7	6.7
3	0.4	none	82.0	14.2	58.0	2.7	7.1
4	0.8	none	80.8	14.7	54.9	3.5	7.7
5	—	NaNO ₃	98.1	61.3	34.8	tr.	2.0
6	0.05	NaNO ₃	99.6	78.1	18.9	0.7	1.9
7	0.1	NaNO ₃	100	85.4	10.8	1.1	2.7
8	0.2	NaNO ₃	99.1	91.8	3.0	1.5	2.8
9	0.4	NaNO ₃	100	93.9	1.9	1.6	2.6
10	0.8	NaNO ₃	99.8	87.1	4.3	3.2	5.2
11	0.4	NaNO ₂	99.3	93.1	2.2	1.9	2.1
12 ^b	—	NaNO ₃	97.6	80.6	12.1	1.8	3.1

A: Both rings hydrogenated, di(4-aminocyclohexyl)methane.

B: One ring hydrogenated, 4-aminocyclohexyl-4-aminophenylmethane or 1,4-cyclohexyl diamine.

C: Deaminated.

D: N-alkylated and high boiler.

^aMDA (25 mmol) was hydrogenated with 5% Ru/C (1 g) in isopropanol (25 ml) in the presence of water and NaNO₃ (5 mmol) at 120°C under the hydrogen pressure of 1200 psig for 20 in.

^b5% Ru/C (1 g) was added to the aqueous solution containing NaNO₃ (5 mmol) and dried at 120°C overnight.

content from 0.01 ml up to 0.8 ml of water in 25 ml isopropanol. Beyond 0.8 ml water content, however, water shows an adverse effect, i.e., decreased the rate of hydrogenation and increased by-products formation. Separate experiments were performed to elucidate the role of water in enhancing the promoting effect of NaNO₃ and NaNO₂ and the results are shown in Table 6. It is anticipated that addition of water increases the solubility of the metal salt consequently resulting in a more effective interaction of metal salt with ruthenium catalyst. NaNO₃-Ru/C was prepared ex-situ by an impregnation method with a hope that the catalyst with a highly dispersed NaNO₃ would give higher catalytic activity even in the absence of water. Contrary to our expectation, the activity of the catalyst prepared by an impregnation method did not give the highest activity implying that the function of water is rather complicated. In fact, the highest catalytic activity was obtained when 0.4 ml of water was added into 25 ml isopropanol containing Ru/C and NaNO₃. The IR spectra of the catalyst mixtures sepa-

rated from the hydrogenation reaction with Ru/Al₂O₃ and NaNO₃ in the presence of water show a more intense absorption peak at around 1450 cm⁻¹ compared to that of the catalyst mixture isolated from the reaction in the absence of water. This result indicates that water may also play a certain role in facilitating the transformation of ionic NO₃ bond into covalent NO₃ bond as well as in increasing the solubility of NaNO₃. Water is also known to eliminate the catalyst toxicity of amine or ammonia, an important side product in the hydrogenation of aromatic amine, by converting it to the nontoxic ammonium cation [14,15]. Therefore, it is anticipated that the use of aqueous ammonia with the ruthenium catalyst should promote the hydrogenation reaction. However, the addition of 1 ml aqueous ammonia into 25 ml isopropanol was found to depress the reaction rate by about 30%. In view of this, the role of the added water seems to be rather complicated besides the simple detoxification of ammonia which can be produced from the hydrogenation of NaNO₃, NaNO₂ or amine.[11]

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