

Effect of Alkali Metal Nitrates on the Ru/C-catalyzed Ring Hydrogenation of *m*-Xylylenediamine to 1,3-Cyclohexanebis(methylamine)

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Ru/C-catalyzed hydrogenation of *m*-xylylene diamine into 1,3-cyclohexanebis(methylamine) was greatly accelerated by the presence of LiNO₃, NaNO₂, or NaNO₃. It was found that the effect of the nitrate salt was significantly affected by the size of cation. The promoting effect of the nitrate salt increased with the decrease of the cation size: LiNO₃ ~ NaNO₃ > KNO₃ > CsNO₃ >> [1-butyl-3-methylimidazolium]NO₃. XRD analysis of the recovered catalysts after the hydrogenation reactions showed that LiNO₃ and NaNO₃ were completely transformed into LiOH and NaOH, respectively, along with the evolution of NH₃, while KNO₃ and CsNO₃ remained unchanged.

Key Words : Hydrogenation, *m*-Xylylenediamine, Ru/C, Alkali metal nitrate

Introduction

Alicyclic diamines have received recent interest as valuable feedstocks for manufacturing light stable polyurethane resins and coatings due to their high flexibilities.^{1,2} Alicyclic diamines have been prepared from the ring hydrogenation of aromatic diamines using Ru and Pd catalysts.³⁻⁵

One major drawback using those platinum group metal catalysts is that they tend to activate the C-N bond cleavage reactions, resulting in the formation NH₃ as well as various hydrogenolysis by-products.⁶ To prevent the hydrogenolysis side reactions, the hydrogenation was conducted in the presence of added NH₃. The addition of NH₃ was highly effective in reducing the hydrogenolysis side products, but NH₃ was also found to poison the catalysts.⁷⁻⁹

Unlike NH₃, the addition of alkali metal hydroxide, especially lithium hydroxide, was found to suppress the formation of hydrogenolysis by-product without poisoning the platinum metal catalysts.¹⁰ It has also been reported in a patent literature that alkali metal sulfates, especially those of lithium, are highly effective for promoting the ring hydrogenation of aromatic diamines.¹¹ We have also found that, in the Ru-catalyzed ring hydrogenation of phenylene diamines, alkali metal nitrates are effective additives in enhancing the catalytic activity and in preventing the catalyst deactivation.¹²

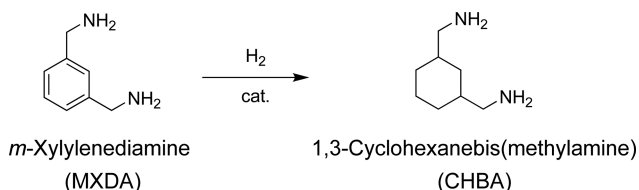
Herein, we report that the addition of alkali metal nitrate is highly effective for the Ru-catalyzed ring hydrogenation of *m*-xylylene diamine (MXDA) to produce 1,3-cyclohexanebis(methylamine) (CHBA), an important raw material for aliphatic polyurethanes.¹³

Experimental

Chemicals. *m*-Xylylenediamine, alkali metal salts, and solvents were purchased from Aldrich Chemical Co. and used without further purification. Ionic liquids were synthesized according to the previous literature.¹⁴ Ru/C, Ru/Al₂O₃, and Ru/SiO₂ were purchased from Aldrich Co. and dried under vacuum at 120 °C before use to remove trace of water present.

Hydrogenation Reaction. All the hydrogenation reactions were conducted in a 100 mL Parr reactor equipped with a magnet drive stirrer and an electrical heater. The reactor was charged with MXDA, solvent, an appropriate catalyst and a promoter, if necessary. The reactor was then purged with N₂ followed by H₂ and pressurized with H₂ up to about 2 MPa. Then, the reactor was heated with agitation to a reaction temperature with the addition of H₂ from a reservoir tank to maintain a specified pressure. To observe the progress of reaction with time, the drop in pressure in the reservoir tank was recorded by means of a pressure transducer and a recorder. The reaction was considered complete when H₂ consumption was stopped. At the end of the reaction, the reactor was cooled to room temperature, and the product mixture removed. After removing the catalyst by filtration, product mixture was analyzed by GC and GC-Mass.

Catalyst Characterization. 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



Scheme 1. Hydrogenation of MXDA to CHBA.

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scanning rate of 2 degree/min. Surface area was measured by the modified BET method from the adsorption isotherms of nitrogen temperature using a Area-Meter II.

Results and Discussion

Effect of Support. Catalytic ring hydrogenation reaction of MXDA was carried out in isopropanol at 120 °C using supported Ru catalysts. The effect of support was examined and the result was summarized in Table 1.

The highest activity of Ru/C could be ascribed to the larger surface area of the active carbon support than those of other supports. However, the higher activity of Ru/AlF₃ than those of Ru/SiO₂ cannot be explained by surface area only. The hydrogenation activity of Ru seems to be strongly correlated to the Ru-support interaction: the stronger the acidity of the support, the lower the hydrogenation activity of Ru.

Effect of Solvent. To find an optimal solvent for the ring hydrogenation of MXDA to CHBA, various solvents were tested at 120 °C using 5 wt % Ru/C catalyst. As can be seen in Table 2, the hydrogenation did not proceed at all in a non-polar solvent, cyclohexane. The MXDA conversions were higher in methanol and ethanol compared with those in isopropanol and butanol. In contrast, the selectivity to CHBA

Table 1. Effect of support on the hydrogenation of MXDA to CHBA^a

Entry	Catalyst ^b	SA (m ² /g)	Time (min)	Conversion (%)	Yield (%)	Selectivity (%)
1	Ru/C	550	20	58.5	43.2	73.8
2	Ru/C	550	60	78.5	59.2	75.4
3	Ru/Al ₂ O ₃	198	20	33.3	22.9	68.8
4	Ru/Al ₂ O ₃	198	60	48.3	32.9	68.1
5	Ru/AlF ₃	53	20	21.2	15.5	73.1
6	Ru/AlF ₃	53	60	51.2	36.5	71.3
7	Ru/SiO ₂	220	20	5.2	3.7	71.1

^aMXDA (2.72 g) was hydrogenated in IPA (25 mL) at 120 °C under H₂ pressure of 5.4 MPa. ^bMetal contents in supports and the weight ratio of MXDA/Ru were fixed at 5 wt % and 300, respectively.

Table 2. Effect of solvent on the hydrogenation of MXDA^a

Entry	Solvent	Conversion (%)	Yield (%)	Selectivity (%)
1	MeOH	67.6	37.8	55.9
2	EtOH	65.3	40.9	62.7
3	<i>n</i> -PrOH	62.7	41.0	66.4
4	IPA	58.5	43.2	73.8
5	<i>n</i> -BuOH	48.5	38.2	78.7
6	<i>t</i> -BuOH	33.3	27.0	81.1
7	THF	17.8	11.8	66.3
8	DMSO	n.r.	–	–
9	Cyclohexane	n.r.	–	–

^aMXDA (2.72 g) was hydrogenated with 5 wt % Ru/C in a solvent (25 mL) at 120 °C for 20 min under the H₂ pressure of 5.4 MPa. Weight ratio of MXDA/Ru was 300.

increased with the increase of the alkyl chain length of the alcohol. The formation of *N*-alkylated side products from the reaction of MXDA with alcohol seems to be more facilitated in lower alcohols. It is worth to note that the hydrogenation reaction of MXDA is more selective in moderately hindered isopropanol than in *n*-propanol, affording CHBA with higher yield and selectivity. The use of *t*-butyl alcohol solvent was found to significantly retard the hydrogenation, implying that the reactivity of Ru/C is strongly influenced by the steric factor around the hydroxyl group of alcohol solvents. From these results, it is likely that the hydroxyl group plays a vital role in activating the catalyst and also in stabilizing the active species. The availability of the hydroxyl group and the polarity of an alcohol would increase with the decrease of alkyl chain length and the steric hinderance around the hydroxyl group. However, as already mentioned, *N*-alkylation of MXDA is more facilitated in lower and less hindered alcohols, and thus an alcohol with moderate polarity and hinderance should be chosen to achieve higher CHBA selectivity and yield. In this context, isopropanol seems to be the best solvent for the selective hydrogenation of MXDA to CHBA. It is also conceivable that transfer hydrogenation from isopropanol to MXDA is participating and this may explain why isopropanol yields CHBA more selectively. The hydrogenation of MXDA was also performed in aprotic polar coordinating solvents such as THF, and DMSO. The hydrogenation of MXDA proceeded in THF, but much slowly compared with those in alcohol solvents along with the formation of large amounts of unidentified high boiling side products. In DMSO, surprisingly, the activity of Ru/C was completely quenched, suggesting that small amounts of sulfur compound or compounds were generated during the hydrogenation and poisoned the catalyst.

Effect of Temperature and Pressure. Effect of temperature and pressure on the hydrogenation reaction of MXDA was also investigated. As listed in Table 3, the conversion of MXDA increased with the temperature rise. However, the selectivity to CHBA decreased with the increasing reaction temperature due to the increased formation of side products such as 1-methyl-3-aminomethyl cyclohexane, 1,3-dimethyl

Table 3. Effects of temperature and pressure on the hydrogenation of MXDA^a

Entry	Temp. (°C)	Pressure (MPa)	Conv. (%)	Yield (%)	Selec. (%)
1	80	5.4	27.1	23.7	87.5
2	100	5.4	45.4	34.6	76.2
3	120	5.4	58.5	43.2	73.8
4	140	5.4	75.3	49.4	65.7
5	160	5.4	99.9	41.6	41.6
6	120	2.0	54.9	70.3	71.7
7	120	4.0	56.7	39.4	72.4
8	120	6.8	60.3	45.8	75.9
9	120	8.2	61.6	47.1	76.4

^aMXDA (2.72 g) was hydrogenated with 5 wt % Ru/C in IPA (25 mL) for 20 min. The weight ratio of MXDA/Ru was 300.

cyclohexane, and 3-aminomethyltoluene, implying that deamination reactions are facilitated at higher reaction temperature. On the contrary, the effect of H₂ pressure on the hydrogenation was much less pronounced.

Effect of Added Alkali Metal Nitrate and Nitrite. The Ru-catalyzed reactions were performed in the presence of various alkali metal nitrites and nitrates. Table 4 demonstrates that the catalytic activity of Ru/C is strongly affected by the cation of alkali metal nitrites and nitrates. Both the conversion of MXDA and the yield of CHBA were greatly increased by the addition of a Li and Na salt, LiNO₃, NaNO₃, or NaNO₂, whereas the effect of added KNO₃ and KNO₂ was almost negligible. Interestingly, the catalytic activity was drastically reduced by the presence of CsNO₃, suggesting that the size or the Lewis acidity of the alkali metal cation is extremely important. The poisoning effect of CsNO₃ and the promoting effects of LiNO₃, NaNO₃, and NaNO₂ are difficult to explain at the moment, but it is likely that cations and anions are functioning poisons and promoters, respectively. The poisoning effect seems to increase with the increase of the cation size. It is also conceivable that Ru interacts more strongly with the larger sized cation, thereby more rapidly facilitating the deactivation of the catalyst. To further investigate the effect of cation size, ionic liquids bearing a NO₃ or NO₂ anion were also tested. When 1-butyl-3-methylimidazolium nitrate ([BMIM]NO₃) or 1-butyl-3-methylimidazolium nitrite ([BMIM]NO₂) was added, the conversion of MXDA and the yield of CHBA were drastically reduced, supporting that larger sized cations function as poisons. In summary, it is obvious that the activity of a Ru catalyst is closely correlated to the physicochemical properties of a metal salt promoter such as the size, ionization potential, and Lewis acidity of the cation.

The effect of weight ratio of MXDA/metal nitrate was also investigated in the range of 3-20. As can be seen in Table 5, the yield of CHBA increased with the increase of the weight ratio up to 10, but remained almost constant on further increase of the molar ratio.

XRD Analysis. It is interesting to note that the addition of

Table 4. Effect of added metal nitrate and nitrite on the hydrogenation of MXDA^a

Entry	Metal salt	Conversion (%)	Yield (%)	Selectivity (%)
1	none	58.5	43.2	73.8
2	LiNO ₃	92.6	90.6	97.9
3	NaNO ₃	92.3	89.4	96.9
4	NaNO ₂	89.6	81.8	91.3
5	KNO ₃	63.8	55.7	87.3
6	KNO ₂	60.2	53.1	88.2
7	CsNO ₃	30.5	26.4	86.8
8	[BMIM]NO ₃	15.9	11.8	74.2
9	[BMIM]NO ₂	23.4	17.3	73.9

^aMXDA (2.72 g) was hydrogenated with 5 wt % Ru/C in IPA (25 mL) at 120 °C for 20 min under the H₂ pressure of 5.4 MPa. The weight ratio of MXDA/Ru and the molar ratio of MXDA/metal nitrate were fixed at 300 and 5, respectively.

Table 5. Effect of NaNO₃ loading on the hydrogenation of MXDA^a

Entry	Molar ratio (MXDA/NaNO ₃)	Conversion (%)	Yield (%)	Selectivity (%)
1	—	58.5	43.2	73.8
2	1	70.6	51.9	91.3
3	3	85.2	76.4	89.7
4	5	92.3	89.4	96.9
5	10	100	90.3	90.3
6	20	100	90.6	90.6

^aMXDA (2.72 g) was hydrogenated with 5 wt % Ru/C in IPA (25 mL) at 120 °C for 20 min under the H₂ pressure of 5.4 MPa. The weight ratio of MXDA/Ru was fixed at 300.

a metal salt such as NaNO₂, NaNO₃, and LiNO₃ promotes the ring hydrogenation while suppressing the formation of by-products. In order to have a clue on the role of the metal salt promoter in the ring hydrogenation of aromatic diamine, fresh and used catalyst mixtures were analyzed by XRD. The catalyst mixture was isolated after the hydrogenation performed at 120 °C in isopropanol in the presence of a Ru catalyst and an alkali metal nitrate.

As can be seen in Figure 1, any peak corresponding to Ru(0) was not observed in the XRD patterns of all the Ru/C catalyst samples irrespective of the presence of an alkali metal nitrate. It is interesting to note that the behaviors of LiNO₃ and NaNO₃ toward the hydrogenation are quite different from those of KNO₃ and CsNO₃. The XRD analysis of the fresh and the recovered Ru/C catalysts after the hydrogenation reactions in the presence of added LiNO₃ clearly indicates that all the added LiNO₃ was transformed into LiOH after the hydrogenation. NaNO₃ also showed the similar behavior to LiNO₃ toward the hydrogenation, generating NaOH. It has been reported that nitrate anion can be hydrogenated by noble metals like Pd and Pt, producing NH₃ and hydroxide anion as shown in Eq. (1).¹⁵⁻¹⁸

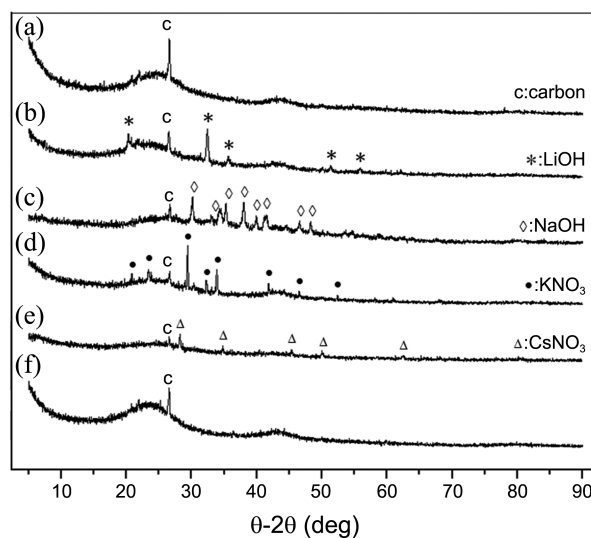
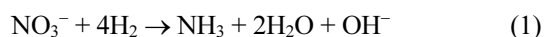


Figure 1. XRD patterns of (a) fresh Ru/C and isolated Ru/C after the reaction with (b) LiNO₃, (c) NaNO₃, (d) KNO₃, (e) CsNO₃, and (f) [BMIM]NO₃ addition.



Similar phenomenon is believed to occur on the surface of Ru. In contrast to LiNO₃ and NaNO₃, KNO₃, CsNO₃, and [BMIM]NO₃ were recovered unchanged at the end of the hydrogenation, suggesting that the activity of Ru to hydrogenate nitrate ion is strongly dependent on the cation size: the bigger the size, the lower the activity. From the combination of XRD analysis and the result of MXDA hydrogenation, it is likely that the promoting effects of LiNO₃ and NaNO₃ are originated from the formation of NH₃ and alkali metal hydroxides. Thus produced NH₃ and LiOH or NaOH are believed to make Ru more active and selective. As mentioned earlier, nitrate anion is likely to play a role as a promoter, while cation functions as a poison. In view of this, it is assumed that for LiNO₃ and NaNO₃, the poisoning effects of Li⁺ and Na⁺ are much smaller than the promoting effect of NO₃⁻. For KNO₃, the poisoning effect of K⁺ and the promoting effect of NO₃⁻ are almost balanced although KNO₃ is not converted into KOH. The significantly reduced activity of Ru by the addition of CsNO₃ and [BMIM]NO₃ could be ascribed to the stronger poisoning effects of the cations than the promoting effect of NO₃⁻.

Conclusions

The Ru/C-catalyzed hydrogenation of MXDA to CHBA proceeded more rapidly and selectively in the presence of added LiNO₃, NaNO₂, and NaNO₃. On the contrary, the activity of Ru/C was greatly suppressed when CsNO₃, [BMIM]NO₂, or [BMIM]NO₃ with a larger sized cation was used as an additive. XRD analysis showed the active promoters, LiNO₃ and NaNO₃ were transformed into LiOH and NaOH, respectively, after the hydrogenation, while KNO₃ and CsNO₃ were recovered unchanged. The promoting effects of LiNO₃ and NaNO₃ are assumed to be the forma-

tion of NH₃ and the corresponding hydroxide salts.

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