Review

How To Get Isocyanate?
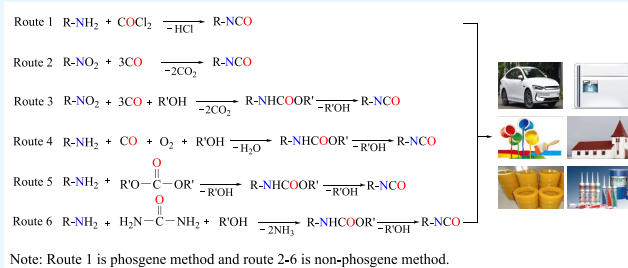
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ABSTRACT: Isocyanate, a pivotal chemical intermediate to synthesize polyurethane with widespread applications in household appliances, automobiles, and construction, is predominantly produced via the phosgene process, which currently holds a paramount status in industrial isocyanate production. Nonetheless, concerns arise from the toxicity of phosgene and the corrosiveness of hydrogen chloride, posing safety hazards. The synthesis of isocyanate using nonphosgene methods represents a promising avenue for future development. This article primarily focuses on the nonphosgene approach, which involves the formation of carbamate through the reaction of nitro-amino compounds with carbon monoxide, dimethyl carbonate, and urea, among other reagents, subsequently leading to the thermal decomposition of carbamate to get isocyanate. This paper emphasizes the progress in catalyst development during the carbamate decomposition process. Single-component metal catalysts, particularly zinc, exhibit advantages such as high activity, cost-effectiveness, and compatibility with a wide range of substrates. Composite catalysts enhance isocyanate yield by introducing a second component to adjust the active metal composition. The central research direction aims to optimize catalyst adaptation to reaction conditions, including temperature, pressure, time, and solvent, to achieve high raw material conversion and product yield.

Route 1: $R\text{-}NH_2 + COCl_2 \xrightarrow{-HCl} R\text{-}NCO$

Route 2: $R\text{-}NO_2 + 3CO \xrightarrow{-2CO_2} R\text{-}NCO$

Route 3: $R\text{-}NO_2 + 3CO + R'OH \xrightarrow{-2CO_2} R\text{-}NHCOOR' \xrightarrow{-R'OH} R\text{-}NCO$

Route 4: $R\text{-}NH_2 + CO + O_2 + R'OH \xrightarrow{-H_2O} R\text{-}NHCOOR' \xrightarrow{-R'OH} R\text{-}NCO$

Route 5: $R\text{-}NH_2 + R'O\!-\!\overset{\overset{O}{\|}}{C}\!-\!OR' \xrightarrow{-R'OH} R\text{-}NHCOOR' \xrightarrow{-R'OH} R\text{-}NCO$

Route 6: $R\text{-}NH_2 + H_2N\!-\!\overset{\overset{O}{\|}}{C}\!-\!NH_2 + R'OH \xrightarrow{-2NH_3} R\text{-}NHCOOR' \xrightarrow{-R'OH} R\text{-}NCO$

Note: Route 1 is phosgene method and route 2-6 is non-phosgene method.

1. INTRODUCTION

Isocyanates, compounds featuring the isocyanate group (−NCO), are extensively used in the production of polyurethane foam, coatings, and adhesives, holding substantial market potential.[1] They can be categorized into aromatic and aliphatic isocyanates based on structural differences. Currently, aromatic isocyanates, such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), dominate industrial usage. Aliphatic isocyanates (ADIs), including hexamethylene-diisocyanate (HDI) and isophorone diisocyanate (IPDI), primarily serve in nonyellow polyurethane materials.[2]

Isocyanate consumption is steadily increasing, but volatile raw material prices and availability present significant constraints. The phosgene process is the current industrial method for isocyanate production. However, phosgene, a highly toxic gas, poses environmental and health risks.[3−5] Consequently, substantial research endeavors are dedicated to devising new isocyanate production methods. This review discusses isocyanate preparation techniques, including the phosgene and nonphosgene methods. The phosgene method comprises liquid and gas phase approaches, whereas the nonphosgene method includes reduction carbonylation, oxidation carbonylation, dimethyl carbonate, and urea methods. Additionally, the paper examines the advancements in catalysts for thermal carbamate decomposition within the nonphosgene method, along with future prospects.

2. PRODUCTION PROCESS OF ISOCYANATE

Isocyanate production methods are categorized into the phosgene and nonphosgene routes, as delineated in Figure 1. These methods can be summarized into six reaction pathways.
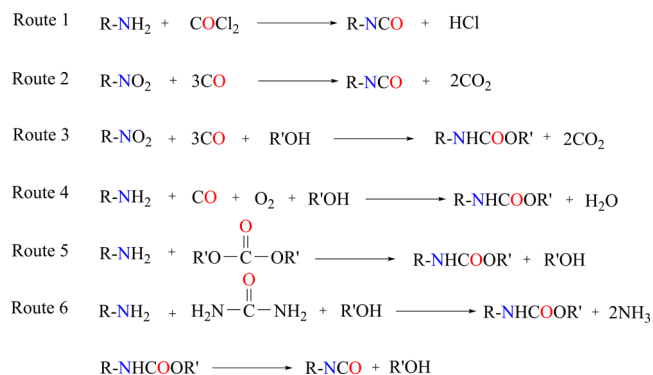
Route 1: $R\text{-}NH_2 + COCl_2 \longrightarrow R\text{-}NCO + HCl$

Route 2: $R\text{-}NO_2 + 3CO \longrightarrow R\text{-}NCO + 2CO_2$

Route 3: $R\text{-}NO_2 + 3CO + R'OH \longrightarrow R\text{-}NHCOOR' + 2CO_2$

Route 4: $R\text{-}NH_2 + CO + O_2 + R'OH \longrightarrow R\text{-}NHCOOR' + H_2O$

Route 5: $R\text{-}NH_2 + R'O\!-\!\overset{\overset{O}{\|}}{C}\!-\!OR' \longrightarrow R\text{-}NHCOOR' + R'OH$

Route 6: $R\text{-}NH_2 + H_2N\!-\!\overset{\overset{O}{\|}}{C}\!-\!NH_2 + R'OH \longrightarrow R\text{-}NHCOOR' + 2NH_3$

$R\text{-}NHCOOR' \longrightarrow R\text{-}NCO + R'OH$

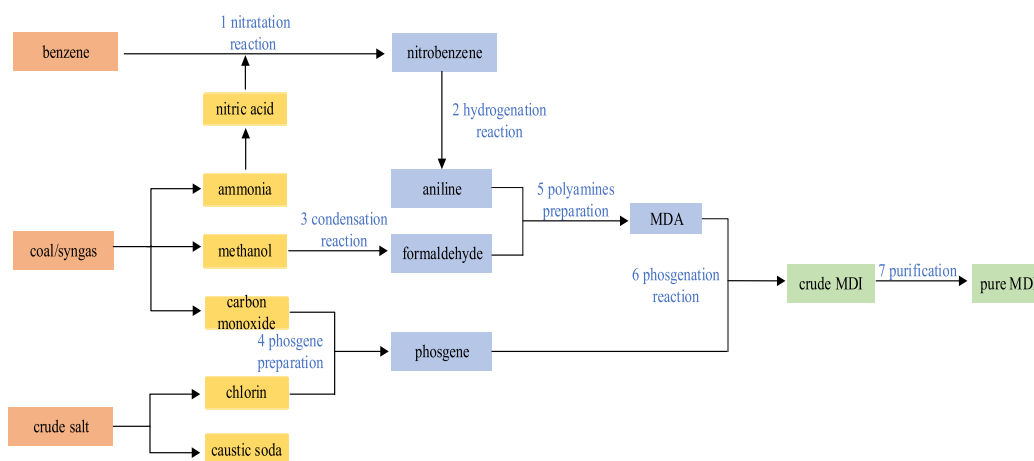**Figure 1.** Isocyanate process production route.
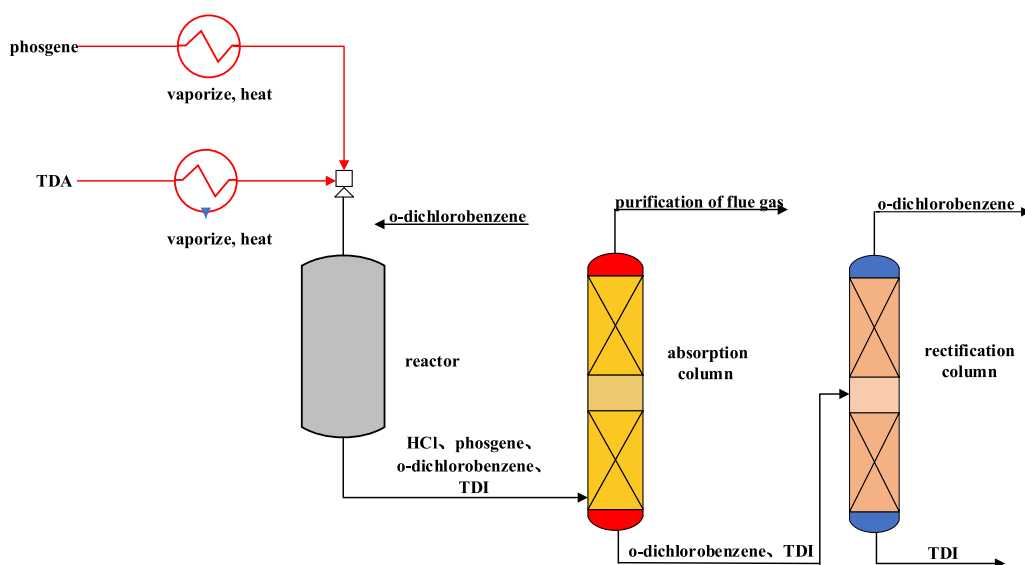
Figure 2. Wanhua MDI production process.

Figure 3. Production of TDI by the gas phase phosgene method socyanate process production route.

Route 1: Traditional phosgene method involving nitro compound hydrogenation to amino and subsequent phosgene-induced isocyanate synthesis. Route 2: Direct method, which constitutes the most concise route for synthesizing isocyanate by directly reacting nitro compounds with carbon monoxide. Route 3: Nitro-reduction carbonylation method. Route 4: Amino oxidation carbonylation method. Route 5: Dimethyl carbonate method. Route 6: Urea method. It is noteworthy that reaction pathways 3, 4, 5, and 6 necessitate carbamate thermal decomposition to produce isocyanate.

2.1. Phosgene Method. The phosgene method is differentiated into liquid and gas phase techniques based on varying reaction conditions, specifically the phase of the organic amine.

2.1.1. Liquid Phase Phosgene Method. The liquid phase phosgene method can be further subdivided into salt phosgenation and direct phosgenation techniques. Salt phosgenation, predominantly employed in the production of aliphatic isocyanates in the last century, commences with amines forming hydrochloride or carbonate with HCl or CO_2 gas. Subsequently, the reaction with liquid phase phosgene generates isocyanates. This method enables isocyanate production under mild conditions, even at room temperature,

although it exhibits longer reaction times, higher solvent requirements, and the production of substantial byproducts.[6] Currently, the liquid phase salt-forming phosgene method is primarily utilized by Japanese manufacturers for aliphatic isocyanate production but is gradually being phased out.

The direct phosgene method entails the direct conversion of organic amines and phosgene into isocyanate. This method is suitable for the phosgenation of amine compounds with high boiling points, low vaporization propensity, and low reactivity, commonly applied in the production of substantial tonnage of isocyanates like MDI and TDI.[7,8] Various domestic and foreign enterprises, including Gansu Yinguang, Cangzhou Dahua, Yantai Juli, Wanhua Chemical, BASF, Covestro, and Huntsman, employ liquid gasification technology. For example, Wanhua's liquid phase MDI production relies on aniline, formaldehyde, and phosgene as raw materials. The process involves polyamine manufacturing, phosgenation, and separation and refinement, with a central focus on the condensation of aniline and formaldehyde in the presence of hydrochloric acid (or a catalyst) to produce diphenylmethanediamine and polyamine. This product subsequently reacts with phosgene and MDA to yield crude MDI,[9] as depicted in Figure 2.

Table 1. Different Catalysts Catalyze the Reaction of DMC and Aliphatic Amines to Synthesize Carbamate

| substrate | catalyst | reaction conditions | | | $Y_{carbamate}$/% | $S_{carbamate}$/% |
		time/h	temperature/°C	DMC:amine/mol:mol		
hexylamine[37]	FeCl$_3$	24	90	20:1	---	>99
ethylenediamine[38]	NaOCH$_3$	2	70	10:1	86.6	---
butylamine[39]	Fe/HY-mmm	1	120	4:1	95.0	---
hexamethylenediamin[40]	Mn(OAc)$_2$	10	80	4:1	86.1	---
hexamethylenediamine[41]	H$_4$[SiW$_{12}$O$_{40}$]	6	90	3:1	---	64.8
hexamethylenediamine[42]	Zn/SiO$_2$	6	80	2:1	68.5	---
hexamethylenediamine[43]	KATriz	10	30	3:1	---	~100
aniline[44]	[BuDBU]Ala IL	4	120	10:1	89.9	---
aniline[45]	ZrO$_2$/SiO$_2$	7	170	20:1	---	80.1
aniline[46]	ZIF-7 (Zn(BeIM)$_2$)	2	190	12:1	92.0	---
aniline[47]	Ce$_{0.98}$Zr$_{0.02}$O$_2$	7.5	140	30:1	88.0	---
toluene diamine[48]	Zr-MOF-808@MCM-41	3	160	12:1	95/0	---
toluene diamine[49]	CeO$_2$	7.5	140	30:1	90.0	---
toluene diamine[50]	Au-CeO$_2$	10	170	30:1	---	87.8

2.1.2. Gas Phase Phosgene Method. The gas phase phosgene process entails the vaporization of amine compounds at elevated temperatures (200~600 °C) and direct reaction with gaseous phosgene to produce isocyanate. Initially applied for aliphatic isocyanate preparation, it has evolved to accommodate the production of aromatic isocyanates through reactor enhancements.[10,11] The initial TDI production plant established by Bayer Materials (BMS) in Shanghai, Germany, represents a notable instance of gas phase phosgene application, as illustrated in Figure 3. This method superheats phosgene and TDA to over 300 °C under normal pressure before introducing them into the reactor through a uniquely designed nozzle. The process involves contact with inert solvent (o-dichlorobenzene) sprayed along the flow, concluding with the concentration and distillation of the TDI product. The approach's merits include short reaction residence times (less than 1 min), high space−time yields, and reduced byproducts. Compared to traditional devices with equivalent production capacities, equipment dimensions are significantly reduced, and investment costs are lowered. Preliminary pilot test data suggest that this process reduces solvent consumption by 80% and energy consumption by 60%. Moreover, for an annual output of 250,000 tons of TDI, carbon dioxide emissions can decrease by approximately 60,000 tons/year.[12−14]

The phosgene process presently stands as the most crucial technological approach for the industrial production of organic isocyanate. It offers the benefits of a well-established process, rapid reactions, high yields, and cost-effectiveness. However, phosgene, while serving as a reactant, is highly toxic and energy-intensive, and its presence within the system contradicts the principles of intrinsic safety and green chemistry. Additionally, when the byproduct, hydrogen chloride, comes into contact with water, it transforms into hydrochloric acid, which is exceptionally corrosive to metallic materials. This characteristic imposes stringent requirements on the water content in equipment and process materials throughout the entire plant. In China, as of the "14th Five-Year National Cleaner Production Implementation Plan" introduced by The State Council in 2021 and the "14th Five-Year Hazardous Chemical Safety Production Planning Plan" issued by the Ministry of Emergency Management in 2022, there is a proposition to impose strict limitations on new projects involving phosgene and phosgene distribution points. These

regulatory requirements introduce additional costs and challenges to the utilization of phosgene. Consequently, the feasibility of sustaining phosgene-based isocyanate production becomes increasingly challenging, and ultimately, it may face a phase-out.

2.2. Nonphosgene Method. The high toxicity and safety concerns associated with the phosgene process have driven the search for more environmentally friendly chemical pathways. Currently, the nonphosgene process for industrial isocyanate production entails two primary steps: the catalyzed synthesis of carbamate from nitro or amine compounds and CO, followed by the thermal decomposition of carbamate to yield the respective isocyanate. Notably, this method eliminates chloride involvement in the reaction, simplifying separation and purification operations thus enhancing product quality.

2.2.1. Direct Method. The United States Melamine Company introduced the direct method in the early 1960s, replacing phosgene with CO as the carbonylation reagent for the direct conversion of nitrohydrocarbons into isocyanates, releasing CO$_2$. This method exhibits a rational reaction pathway but entails stringent reaction conditions, necessitating high-quality equipment and precise process control. Additionally, most catalysts used are expensive Group VIII metal compounds, increasing production costs, rendering the method unapplied in industry to date.[15,16]

2.2.2. Reductive Carbonylation of Nitro Compounds. The reductive carbonylation of nitro compounds, employing a direct method, aims to create milder reaction conditions, enhance product stability, and facilitate storage and transportation. A two-step process has been proposed to convert nitro compounds into carbamates, which are subsequently heated to yield isocyanates.

This reaction primarily utilizes homogeneous transition metal catalysts such as Pt,[17] Rh,[18] Ru,[19] and Pd.[20−22] However, recycling of these catalysts proves challenging. To address the separation issue, heterogeneous catalysts, including Fe−Cu metal selenides supported by cerium and γ-Al$_2$O$_3$, as well as Rh, Ru, and Pd complexes,[23,24] have been suggested, and various forms of such catalysts have been developed.

2.2.3. Oxidative Carbonylation of Amine Compounds. The oxidative carbonylation of amines necessitates the presence of oxidants, such as molecular oxygen,[25−27] nitro compounds, iodine, quinone, its derivatives,[28] or unsaturated organic substances.[29,30] Among these, molecular oxygen serves

as the primary oxidant. This reaction entails a mixture of CO and O_2, which can be potentially explosive within a specific concentration range. Utilizing CO_2 as a sustainable carbon source, recent advancements have been made in the synthesis of carbamates, ureates, and other compounds via CO_2 and amines.[31−36] However, limitations persist, including the intrinsic high kinetic inertia and thermodynamic stability of CO_2, necessitating dehydrating agents, harsh reaction conditions, and low amine conversion rates.

2.2.4. Dimethyl Carbonate Method. Dimethyl carbonate (DMC) is an eco-friendly reagent due to its structural similarity to phosgene, making it a suitable substitute for carbonylation. It stands out for its lack of chloride ions, reduced corrosiveness, and minimal equipment material requirements. This process has garnered significant attention in the exploration of nonphosgene isocyanate synthesis. The reaction of aliphatic amines with DMC can be carried out under very mild conditions (<90 °C) to obtain 65−98% carbamate and aromatic amines (such as aniline, toluene, and diamine) due to the low nucleophilicity and basicity, making the reaction conditions more harsh, as shown in Table 1.

In industrial production, only fundamental raw materials, such as CO, O_2, and amine compounds, are consumed, avoiding the use of phosgene. Methanol can be recycled as a byproduct to synthesize dimethyl carbonate again, enhancing atomic efficiency and aligning with the clean production direction in the chemical industry. The cyclic process is depicted in Figure 4.
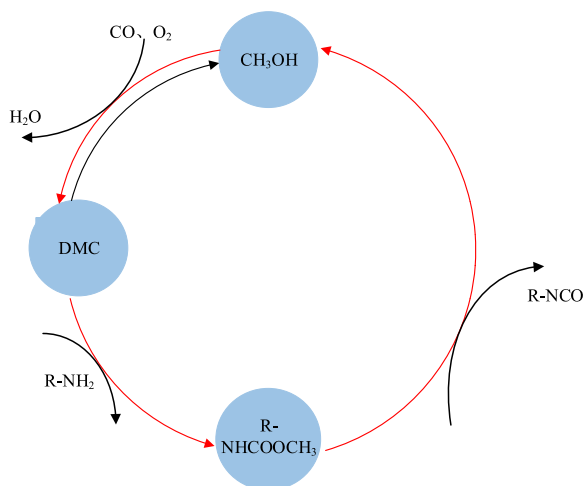

Figure 4. Methanol cycle diagram.

2.2.5. Urea Method. The urea process is centered on urea, alcohol, and amines as raw materials to synthesize the corresponding carbamates, which further decompose to produce isocyanates.[51−54] The byproducts of the urea method solely consist of alcohol and NH_3, with alcohol serving as the raw material for the initial step reaction and NH_3 being the raw material for urea synthesis. This process route achieves "zero emission" for isocyanate synthesis. It not only utilizes cost-effective urea as a raw material but also explores new applications for urea. This green synthesis pathway holds significant implications for the entire polyurethane industry. Though it remains in the experimental phase, there are still many issues that need to be solved, such as the development of

efficient catalysts and effective removal of ammonia, which are crucial for the smooth progress of the reaction.

In summary, the nonphosgene processes exhibit diversity based on different raw materials. Nonetheless, the ultimate step remains the acquisition of isocyanates through the thermal decomposition of carbamates. This thermal decomposition is a reversible endothermic reaction that requires heat input during the process and the timely removal of the product. The −NCO group exhibits strong reactivity, making it susceptible to side reactions, such as carbamate decarbonylation (resulting in amines), isocyanate−amine reactions leading to ureas, isocyanate−carbamate reactions producing urea formates, and isocyanate polymerization. Therefore, it is essential to select effective catalyst systems and appropriate reaction conditions to enhance product yield and selectivity.

This paper concentrates on the thermal decomposition and synthesis of 1,6-hexamethylenediamarboxylate (HDC) into HDI, research progress in catalysts employed in the thermal decomposition and synthesis of 2,4-toluene methyl dicarbamate (TDC) into TDI, diphenylmethane methyl diphenyl-methane dicarbamate (MDC), and diphenylmethane methyl diphenylcarbamate (MDPC) into MDI and methyl phenyl-carbamate (MPC) into phenylisocyanate (PI). These catalysts are categorized based on their composition, including single-component metal catalysts, composite metal catalysts, and other catalysts.

3. CATALYST FOR THE THERMAL DECOMPOSITION OF CARBAMATE

3.1. Single-Component Metal Catalyst. In recent years, multiphase catalysts comprising metal elements and their oxides have found wide application in the thermal decomposition of carbamates due to their stability, mild preparation conditions, reusability, and absence of significant weakening effects. The research findings are outlined in Table 2.

Zinc, owing to its electron-absorbing properties, proves to be an effective catalyst for cracking reactions across various substrates. Yin et al.[55] employed zinc powder as a catalyst, utilized dioctyl phthalate (DOP) as a heat carrier and solvent, and reacted at 240 °C for 30 min, resulting in an HDI yield of 35.3%. Hyun et al.[56] converted HDC to HDI using zinc oxide in an electron donor polyglycol dimethyl ether (PGDE) solvent. In this catalytic system, HDC was entirely transformed, and the HDI yield approached 97%. The catalytic reaction mechanism of ZnO was proposed through in situ infrared spectroscopy, where H atoms initially formed hydrogen bonds with the O site on the zinc oxide surface, leading to the removal of the N−H group (Figure 5). The O−C=O group coordinated with the zinc site, which exhibited electron absorption characteristics in a single-tooth mode; carbon, nitrogen, and oxygen form a conjugated system; and during the heating process, the single bond of C−O becomes weak and breaks, culminating in the generation of isocyanate. Additionally, the methoxy group connected to zinc reacted with hydrogen, releasing methanol. Zamani et al.[58] used the same catalyst, MPC, as a substrate and diphenyl ether as a solvent, yielding an MPC conversion rate of only 12.2%, with aniline and urea (DPU) as the primary byproducts. This indicates that different substrates exhibit significant variations in catalyst performance. While the results may not be ideal, the author conducted a comprehensive molar balance analysis of the products and established a stable and safe quantitative

Table 2. Decomposition Performance of Carbamate Catalyzed by a Single-Component Metal Catalyst

| substrate | catalyst | reaction condition | | | | | $Y_{isocyanate}$/% | $S_{isocyanate}$/% |
		time/min	temperature/°C	vacuum/kPa	cat:sub/wt:wt	solvent		
HDC[55]	Zn	30	240	11.33	2%	DOP	35.3	---
HDC[56]	ZnO	150	180	---	6%	PGDE	97.0	---
HDC[57]	Co_2O_3	180	230	680	5%	Chlorobenzene	83.0	---
MPC[58]	ZnO	60	200	---	60%	Diphenyl ethers	0.8	---
MPC[59]	Bi_2O_3	60	176−178	---	5%	ODCB	78.5	---
MDC[60]	ZnO	20	260	---	60%	DPB	63.3	---
MDC[61]	Cu	120	250	350	5%	ODCB	95.8	---
TDC[62]	ZnO	90	240	7.33	23%	DOP	99.9	---
TDC[63]	Fe_2O_3	90	230	7.33	---	DOP	80.3	---
MDPC[64]	Cu_2O	12	220	0.6	0.06%	---	---	86.2
MDPC[65]	Sb_2O_3	12	220	0.67	1%	---	---	84.4
MDPC[66]	MOF-5-NO_2	15	210	0.6	0.5%	---	81.6	---
MPC[67]	ZnO	180	200	13	1%	---	---	91.1
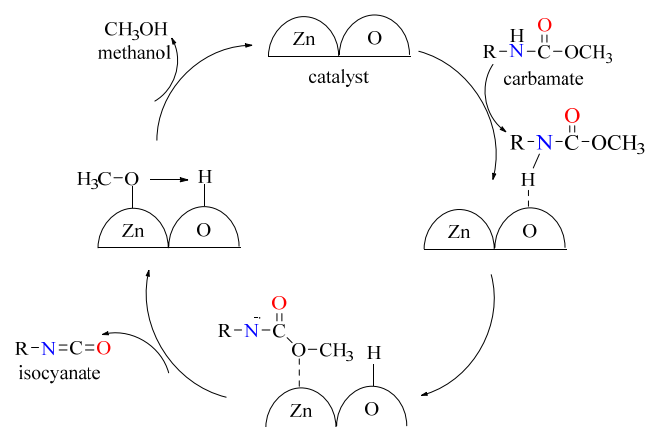
Figure 5. Reaction mechanism of carbamate decomposition catalyzed by ZnO. Adapted with permission from Hyun, M.J.; Shin, M.; Kim, Y.J.; Suh, Y.-W. Phosgene-free decomposition of dimethylhexane-1,6-dicarbamate over ZnO. Res. Chem. Intermediat. **2016**, 42 (1), 57−70. 10.1007/s11164-015-2224-x.[56] Copyright 2016. Springer Link.

Figure 6. Green synthetic TDI process.

analysis method for isocyanates, which holds higher research value in comparison to chromatography.

The research findings of this research group have unveiled an intrinsically secure green synthesis process for TDI. This process entails the synthesis of toluene diamine (2,4-TDA) and dimethyl carbonate (DMC) to produce TDI, which is then catalyzed for decomposition. The reaction process can be delineated as follows: Our research group has ascertained that zinc acetate serves as a highly efficient catalyst for the synthesis of TDC from 2,4-TDA and DMC.[62,68,69] Under the conditions of $nTDA/nDMC = 1/30$ and $mTDA/mZn(OAC)_2 = 1/0.16$, the yields of TDC and ZnO reach 98.9% and 90.1%, respectively, at 160 °C over a duration of 7 h. As the reaction progresses, zinc acetate undergoes gradual transformation into nanometer-sized zinc oxide, which can be employed for catalytic decomposition of TDC. The overall yield of isocyanate attains 99.9% through reaction with DOP at 240 °C and 7.33 kPa for 1.5 h. This continuous reaction comprises various isomers and reaction pathways (Figure 6), with 2,4-TDA initially converting to monocarbamate and subsequently forming dicarbamate, driving the reaction. Throughout the entire reaction process, methanol is the sole byproduct, which can be recycled for DMC synthesis, thereby enhancing atomic
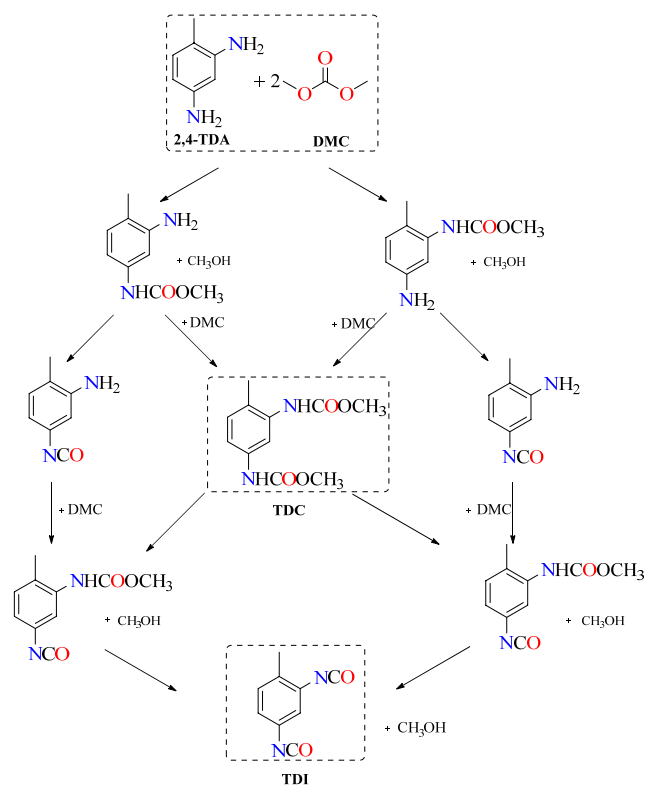
efficiency, aligning with the direction of clean production in the chemical industry and paving the way for industrialization.

Concerning the synthesis of isocyanate via carbamate, most of the existing studies have primarily focused on methyl carbamate (Me), although there have been investigations into propyl carbamate (Pr), butyl carbamate (Bu), and phenyl ester (Ph) as well. In the context of TDC materials, our research group has observed that Fe_2O_3 exhibits universal catalytic cracking capabilities for the aforementioned carbamates.[63] Under identical reaction conditions, carbamate decomposition is more susceptible as the number of carbon atoms in the alcohol (phenol) oxygen group increases. Hence, the order of Fe_2O_3-catalyzed TDC decomposition, from easiest to most challenging, is as follows: TDC(Ph), TDC(Bu), TDC(Pr), and TDC(Me). An in-depth examination of TDC(Me) catalytic

decomposition by Fe_2O_3 has revealed that the catalyst's acidity, pore size, and morphology directly impact its catalytic activity. Commercial Fe_2O_3 has demonstrated superior catalytic efficacy relative to homemade Fe_2O_3 due to its larger pore size and inclusion of SiO_2 components.

Dai et al.[59] conducted an inquiry into the catalytic performance of diverse metal oxides in the decomposition reaction of MPC. In comparison to acidic oxides (Nb_2O_5, MoO_3) and basic oxides (MgO, CaO), amphoteric oxides (Bi_2O_3, PbO) prove more favorable for MPC decomposition. The utilization of a PbO catalyst resulted in a MPC conversion rate of 93.6%, whereas acidic and alkaline oxides led to a 47% MPC conversion rate, accompanied by numerous byproducts and the generation of PI (Figure 7). These findings elucidate
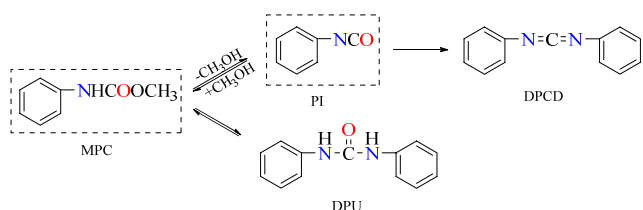

Figure 7. MPC reaction system.

that the outermost orbitals of Bi^{3+} and Pb^{2+} with $5s^2$ and $6s^2$ electron distributions, respectively, exhibit a high cation conversion rate. This facilitates hydrogen extraction from N—H groups and enhances the catalytic activity of metal oxides.

The inclusion of an appropriate solvent in the liquid-phase cracking reaction can dilute active groups, effectively suppressing polymerization reactions, and enhance isocyanate selectivity. However, the substantial addition of high-boiling solvents in the reaction process can lead to reduced product concentration and intricate subsequent separation and purification procedures. Therefore, Wang et al. conducted the decomposition reaction of MDPC without the use of a solvent. Investigations into the impact of nano-Cu_2O preparation conditions,[64] Sb_2O_3 crystal structure,[65] and reaction conditions on MDPC decomposition were undertaken. The outcomes revealed that Cu_2O prepared through the hydrolysis method and cubic-phase Sb_2O_3 exhibited the most effective catalytic performance, achieving MDI selectivity exceeding 84% at 220 °C over 12 min. In the subsequent

year, the research group explored the catalytic activity of metal—organic framework (MOF) nanomaterials in carbamate decomposition. MOFs have garnered attention due to their substantial specific surface area, high porosity, and unsaturated sites. The authors used MOF-5 with a Zn_4O metal cluster center as a ligand to modify the catalytic performance by substituents.[66] They found that through modification with nitro it was determined that the electron distribution in MOF-5-NO_2 shifted from the Zn_4O metal cluster center to the organic ligand, enhancing Lewis acidity and accelerating MDPC decomposition. This approach, compared to the solvent method, yields higher target product concentrations, reduces energy consumption and pollution during separation and purification, and charts a new path for isocyanate synthesis via a nonphosgene method.

While carbamate thermal decomposition reactions can also occur in the gas phase,[70] the requisite reaction temperatures generally range from 350 to 550 °C. These high temperatures accelerate raw material decomposition, resulting in elevated equipment costs, increased energy consumption, and greater byproduct formation, which diminish isocyanate selectivity. In contrast, liquid phase pyrolysis can be conducted at relatively lower temperatures (180−300 °C). The addition of inert solvents serves to dilute reactants, lower active group concentrations, hinder side reactions, and promote the progression of the reaction. Consequently, in the industrial production of isocyanate, liquid phase cracking reactions offer more promising development prospects.

As depicted in Table 2, single-component metal catalysts, exemplified by ZnO, facilitate carbamate catalytic decomposition. These catalysts offer advantages such as high catalytic activity, cost-effectiveness, and broad applicability across substrates. However, challenges, including elevated reaction temperatures, lower product concentrations, and intricate catalyst preparation processes, persist. Current research underscores the importance of investigating methods to reduce reaction temperatures, decrease polymerization occurrences, and achieve product selectivity and catalyst stability over extended durations.

3.2. Composite Metal Catalyst. To enhance reactivity and optimize reaction conditions, the study delved into composite metal catalysts, involving the modification of active components and the optimization of active metal composition. This was achieved by introducing a second component to the

Table 3. Decomposition Performance of Carbamate Catalyzed by a Composite Metal Catalyst

substrate	catalyst	reaction condition					$Y_{isocyanate}$/%	$S_{isocyanate}$/%
		time/min	temperature/°C	vacuum/kPa	cat:sub/wt:wt	solvent		
HDC[71]	ZnO/Al_2O_3	---	240	9	---	DOP	86.10	---
HDC[72]	ZnO/Zn	120	220−240	3.33−11.33	4%	DOP	92.50	---
HDC[73]	CuO/ZnO	120	230	---	6%	----	83.80	---
HDC[74]	$ZnAlPO_4$	---	350	11.33	---	DOP	89.40	---
HDC[75]	ZnO/Zn	15	250	7.33	---	NO	81.24	---
HDC[76]	Zn-2Co/ZSM-5	150	230	680	1.28%	Chlorobenzene	---	91.20
HDC[77]	Zn-Co/ZSM-5	60	250	---	1.5%	DOS	83.80	---
MHDC[78]	$Bi_2O_3/Fe_2O_3/HTixOy$	120	210	---	1%	BMMIMBF4	---	---
MPC[79]	Bi/Zn	60	175	---	5%	ODCB	---	91.70
MDC[80]	ZnO/Zn	80	250	---	64%	DBP	67.30	---
MDC[81]	ZnO/SBA-15	50	275	20	20%	DMP	85.60	---
TDC[82]	Bi_2O_3/Fe_3O_4	120	190	6.5	0.5%	[EMMIm]NTf2	91.00	---
TDC[83]	Fe_2O_3/SiO_2	90	240	7.33	36%	DOP	92.30	---

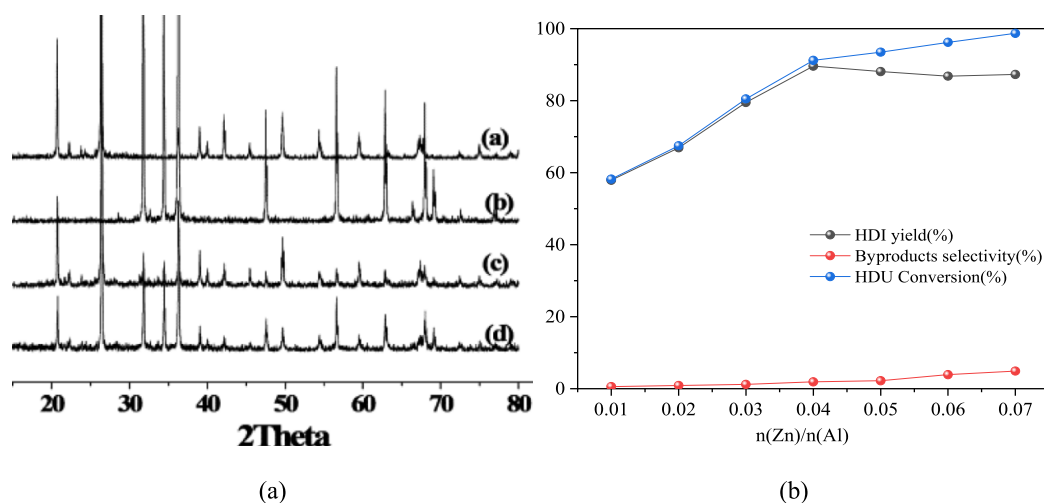(a)   (b)

Figure 8. (a) XRD patterns of ZnAlPO$_4$ catalysts: (a) ZnAlPO$_4$ (0.04); (b) ZnO; (c) ZnAlPO$_4$ (0.05); and (d) ZnAlPO$_4$ (0.15). (b)Effects of n(Zn)/n(Al) on HDI yield, byproduct selectivity, and HDC conversion. Adapted with permission from Sun, D.L.; Luo, J.Y.; Wen, R.Y.; Deng, J.R.; Chao, Z.S. Phosgene-free synthesis of hexamethylene-1,6-diisocyanate by the catalytic decomposition of dimethylhexane-1,6-dicarbamate over zinc-incorporated berlinite (ZnAlPO$_4$). *J. Hazard. Mater.* **2014**, *266*, 167−173. 10.1016/j.jhazmat.2013.12.022.[74] Copyright 2014. Elsevier.

single-component metal catalyst, aiming to elevate the conversion rate of carbamate and increase isocyanate yield. The research findings are summarized in Table 3.

The HDI was produced through the decomposition of HDC catalyzed by a ZnO-Al$_2$O$_3$ composite catalyst, with the highest HDI yield reaching 86.1% under optimal reaction conditions.[71] Zhang et al.[72] observed that the Zn-ZnO catalyst exhibited robust catalytic activity in the HDC decomposition reaction, suggesting that HDI selectivity is closely linked to the active metal types. Moreover, the selectivity of products is also affected by the different catalyst preparation methods. Kim et al.[73] prepared CuO-ZnO catalysts for HDC pyrolysis through coprecipitation (CP), sequential precipitation (SP), and initial wet impregnation (IW). The results indicated that the catalyst derived from the sequential precipitation method retained the properties of CuO and ZnO, possessing a relatively larger surface area, which led to higher HDI yields compared to the other two methods.

Sun et al.[74] reported the utilization of a composite zinc−beryllium structured catalyst (ZnAlPO$_4$) for catalytic HDC cracking. The incorporation of Zn(II) into the aluminum phosphate framework generated adjacent oxygen vacancies, enhancing electron absorption capacity compared to zinc oxide. The catalyst's performance could be adjusted by altering the Zn/Al molar ratio. XRD characterization revealed that a Zn/Al molar ratio exceeding 0.04 resulted in the appearance of zinc oxide phases in the catalyst, diminishing HDI yields. The molar ratio providing optimal catalytic effects was 0.04, as both excessively high or low ratios increased byproduct selectivity and reduced raw material conversion (Figure 8). The research was conducted in a custom-designed continuous flow fixed-bed reactor, where the feedstock entered as a liquid into a quartz tube. Adjusting the cooling temperature of the condensate tube enabled the separation of HDI and CH$_3$OH, achieving up to 89.4% HDI yields under optimized reaction conditions. Additionally, the catalyst demonstrated stability, with no significant decrease in catalytic activity after five cycles, making it suitable for HDC decomposition after regeneration. The research group established an environmentally friendly production route from HDA and DMC to HDI using the same catalyst,[84] with methanol remaining as the sole

byproduct. By integrating the HDI production process of DMC with the DMC production process of CH$_3$OH, a green zero-emission approach could be realized, with significant industrial applicability.

Fan et al.[75] explored the HDC decomposition reaction, catalyzed by a two-component catalyst comprising various metal oxides (Sb$_2$O$_3$, SiO$_2$, ZnO, Al$_2$O$_3$, etc.) and zinc. The study revealed that when Zn/ZnO served as the catalyst and naphthene oil acted as an inert high-boiling solvent HDC could be decomposed to yield an 81.24% HDI output after 15 min at 250 °C and 0.094 MPa. Dai et al.[79] corroborated that the properties of the second component significantly influenced the catalyst's catalytic performance. The author combined Bi with various metals (Al, Sn, Mo, Zn, La, Ce, etc.) for MPC catalytic decomposition. It was discovered that the addition of a second component generated some inactive phases, altering the catalyst's acidity and basicity, thereby diminishing catalyst performance and increasing PI selectivity. Only the addition of Mo and Zn in the d region enhanced the activity of the bismuth-based catalyst, although the former produced more byproducts, and PI selectivity reached only 34.5%. With a Bi/Zn molar ratio of 2, the MPC conversion rate was 86.0%, and PI selectivity reached 91.7%, slightly exceeding that of Bi$_2$O$_3$. The bimetal's excellent catalytic activity could be attributed to the positive synergistic effect of the bimetals. Therefore, studying the synergistic catalytic effect of different metals to enhance the performance of a single-component catalytic system holds significant promise.

Supported catalysts refer to catalysts composed of transition metals with active sites supported on the surface of another material. These catalysts exhibit higher catalytic activity compared to unsupported bulk phase catalysts due to better dispersion and larger specific surface areas. Molecular sieves, known for their unique pore structure, are suitable choices as catalyst carriers. Ammar et al.[76] utilized chlorobenzene as a solvent, employing a Zn−Co bimetal-supported ZSM-5 catalyst for HDC decomposition. This approach introduced zinc−cobalt species to the monometallic support, significantly increasing the number of strong acidic sites on the catalyst. The result was an improvement in raw material conversion and isocyanate selectivity. Different Zn−Co mass fractions in

zeolites led to varying catalytic activities. Higher Co content facilitated HDC decomposition into HDI, as cobalt promoted the formation of new strong acid sites, and the synergy between Zn and Co led to the formation of weak, medium, and strong acid sites in the bimetal-supported ZSM-5 catalyst. This effectively influenced the catalyst's acid site distribution (Figure 9). Among all catalysts, the Zn-2Co/ZSM-5 catalyst
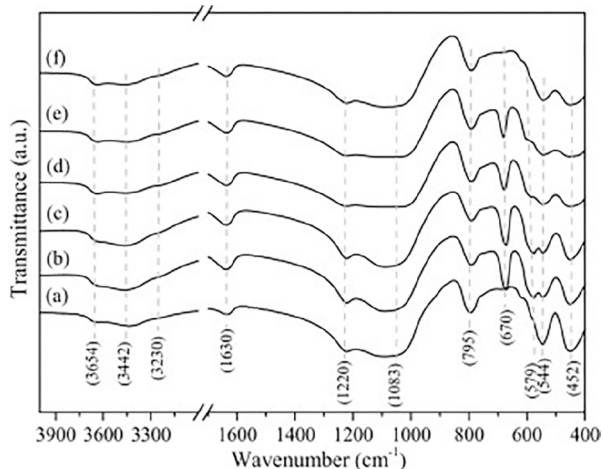

Figure 9. NH$_3$-TPD profiles of bare ZSM-5 (a), 2Co/ZSM-5 (b), Zn-2Co/ZSM-5 (c), Zn−Co/ZSM-5 (d), 2Zn−Co/ZSM-5 (e), and 2Zn/ZSM-5 (f) catalysts. Adapted with permission from Ammar, M.; Cao, Y.; He, P.; Wang, L.G.; Chen, J.Q.; Li, H.Q. Zn−Co bimetallic supported ZSM-5 catalyst for phosgene-free synthesis of hexamethylene-1,6-diisocyanate by thermal decomposition of hexamethylene-1,6-dicarbamate. *Chin. Chem. Lett.* **2017**, *28* (7), 1583−1589. 10.1016/j.cclet.2017.03.015.[76] Copyright 2017. Elsevier.

displayed exceptional performance, with an HDI selectivity of 91.2% and byproduct selectivity of 1.3%. Cao et al.[77] examined the effect of Zn−Co/ZSM-5 on HDC catalytic decomposition under different solvents, reaction temperatures, and reaction times. Ultimately, the use of dioctyl sebacate as a solvent at 250 °C for 1 h resulted in an 83.8% HDI yield. The catalytic mechanism is shown in Figure 10. The H atom of the amide group forms a hydrogen bond with lattice oxygen on the surface of the catalyst, and the oxygen atom in the methoxy group forms a covalent bond with Zn−Co bimetal coordination. Then the hydrogen atom and oxygen atom are split, respectively, to produce isocyanate, and the hydrogen atom is attacked by an oxygen atom, resulting in the coordination bond breaking to form CH$_3$OH and catalyst regeneration. Additionally, the research group explored different metal oxides, such as CuO, ZnO, and MgO, loaded onto ZSM-5 for HDC pyrolysis, with HDI yields exceeding 80%.[85] Guo et al.[81] prepared a ZnO/SBA-15 composite nanocatalyst that exhibited high catalytic activity for the thermal decomposition of MDC. The catalyst particles were evenly distributed, offering good dispersion. MDC was entirely converted at 275 °C over 50 min, resulting in an 85.6% MDI yield.

In the process of carbamate decomposition, the solvent plays a crucial role as a heat transfer medium. However, organic solvents with high boiling points impose significant limitations. Ionic liquids (ILs), recognized as environmentally friendly solvents and functional materials, have attracted substantial attention in various scientific domains, including chemistry, biology, physics, and engineering. ILs serve diverse functions,
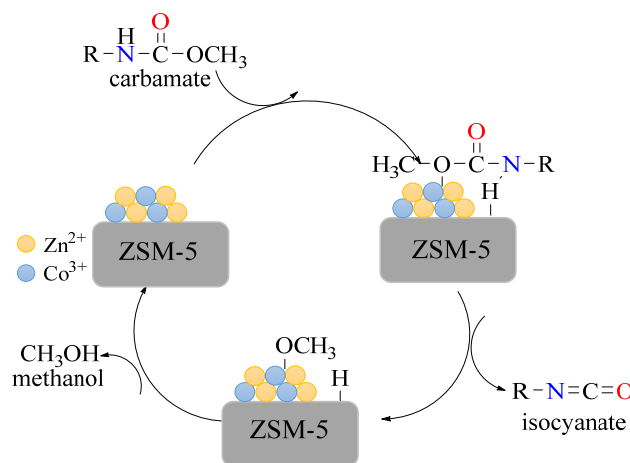

Figure 10. Possible reaction mechanism for the thermal decomposition of HDC to HDI over the Zn−Co/ZSM-5 catalyst. Adapted with permission from Cao, Y.; Chi, Y.; Muhammad, A.; He, P.; Wang, l.; Li, H. Nonphosgene synthesis of hexamethylene-1,6-diisocyanate from thermal decomposition of hexamethylene-1,6-dicarbamate over Zn−Co bimetallic supported ZSM-5 catalyst. *Chin. J. Chem. Eng.* **2019**, *27* (3), 549−555. 10.1016/j.cjche.2018.05.001.[77] Copyright 2019. Elsevier.

such as catalysts, solvents, and catalyst carriers, and many catalytic reactions can be efficiently carried out in ionic liquid systems.[86−89] Because of their high thermal stability, lack of volatility, reusability, and low vapor pressure, ILs offer substantial advantages for the liquid-phase catalytic synthesis of isocyanates. Han et al.[78] conducted a thermal analysis to explore the changes in mass within the ionic liquid and organic solvent during the heating process while investigating the thermal decomposition of methyl 1,6-adipic carbamic acid (MHDC) in various ionic liquid media using Bi$_2$O$_3$/Fe$_2$O$_3$ as a catalyst, as illustrated in Figure 11. The results revealed that there was no mass loss in the ionic liquid during the reaction. Additionally, both the anions and cations exerted varying degrees of influence on the catalytic system's activity. The catalyst's formation mechanism is modulated by altering the ionic liquid's structure, thereby adjusting its catalytic performance. Deng et al.[82] observed that ultrafine powder metal oxides and ionic liquid combinations have universal applicability in catalyzing the decomposition of alkyl or aryl carbamates. Employing thermal analysis, they achieved a TDI yield of 91.00% at 190 °C for 2 h using TDC as the substrate and Bi$_2$O$_3$/Fe$_3$O$_4$ as the catalyst. Owing to the substantial disparity in the boiling points between the ionic liquid−metal oxide catalytic system, it facilitates the improved separation of isocyanates from the alcohol produced during the reaction, thereby enhancing its industrial utility.

In their research, this group utilized a Fe$_2$O$_3$/SiO$_2$ catalyst, TDC as the substrate, and DOP as the solvent, conducting the reaction at 240 °C under 7.33 kPa pressure for 1.5 h.[83] This approach resulted in a total yield of TDI and TMI reaching 99.6%. The catalytic effect of a two-component catalyst, obtained through physical or chemical mixing, exceeded that of the single-component Fe$_2$O$_3$ (which yielded 89% of isocyanate). Both components cooperatively facilitated the reaction. The authors contend that the coordination of Fe^{3+} and Si^{4+} with the carbonyl oxygen in TDC represents a pivotal step in its decomposition. The simultaneous presence of Fe^{3+} and Si^{4+} alters the electron cloud distribution of the catalyst,
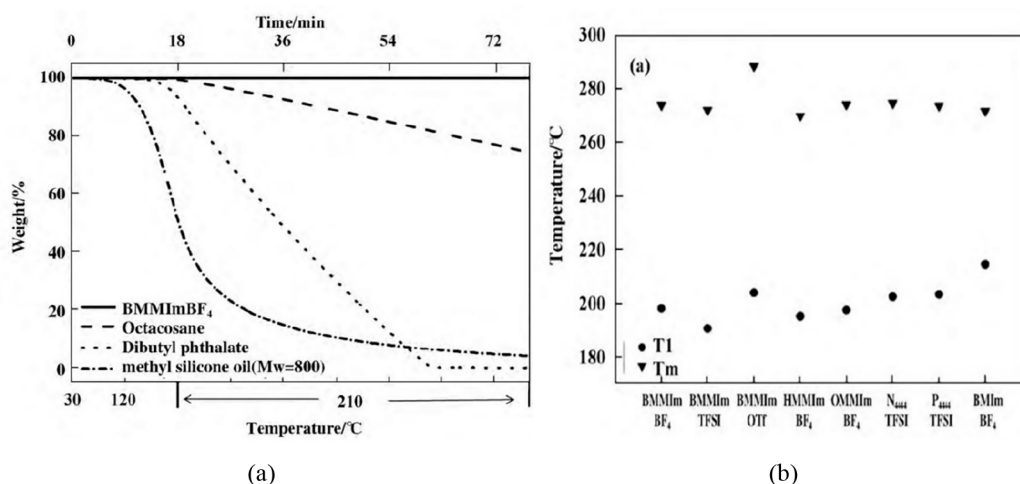
(a)   (b)

Figure 11. (a) Thermogravimetric curves of different solvents. (b) Effects of ionic liquids on MHDC decomposition. Adapted with permission from Han, Y.; Liu, S.; Wang, P.; Deng, Y. Synthesis of isocyanate by thermal decomposition of carbamate in ionic liquid catalytic system. *J. Mol. Catal. (China)* **2016**, 30 (4), 297–306. 10.16084/j.cnki.issn1001-3555.2016.04.001.[78] Copyright 2016. Cnki.

Table 4. Other Catalysts Catalyze the Decomposition Performance of Carbamate

substrate	catalyst	reaction condition					$Y_{isocyanate}$/%
		time/min	temperature/°C	vacuum/kPa	cat:sub/wt:wt	solvent	
HDU[90]	chromium picolinate	0.3	260	7.33	1%	NO	86.16
MDM[91]	*N,N*-dimethylaniline	24	195	---	1.43%	*N,N*-dimethylaniline	46.00
MDU[92]	dibutyltin dilaurate	---	270	4	---	sulfolane	90.00
MDC[93]	MMK-10	24	190	---	25%	decaline	68.00
TDC[94]	Mo(CO)$_6$	2	250	superatmospheric pressure	---	*N*-hexadecane	82.00

promoting the cleavage of C═O double bonds and N−H bonds, simplifying the formation of −NCO groups.

Presently, composite metal catalysts have been effective in enhancing isocyanate yields. Nonetheless, most studies have primarily focused on catalyst preparation and the influence of reaction conditions on carbamate catalytic performance. Few studies have delved into the discussion of catalytic mechanisms, the selection of metal components or carriers, or the stability of real process conditions. Substantial opportunities for advancing composite catalyst systems persist.

3.3. Other Catalysts. Catalysts comprising metal complexes or organotin compounds initially found application in carbamate decomposition, and the research status is detailed in Table 4.

Zhang[90] established that chromium picolinate exhibited an effective catalytic role in carbamate decomposition, resulting in an HDI yield of 86.12% after a 20 min reaction at 260 °C and 7.3 kPa, using HDU as the substrate. The inclusion of chromium picolinate enhanced compatibility with high boiling point solvents, improved dispersion, and significantly reduced the required dosage to only 1% of the raw material (Wt). Nonetheless, the high reaction temperature and the presence of chromium(III) compounds limited their use, as they are associated with Class 3 carcinogens.

Henson et al.[91] decomposed MDC to produce MDI at 195 °C, with *N,N*-dimethylaniline serving as both a solvent and catalyst. After 24 h of reaction, they achieved only a 46% MDI yield, primarily due to the prolonged reaction time, the mixing of *N,N*-dimethylaniline with reactants, and the difficulty in separating these components postreaction. Thus, these catalysts were not widely adopted. Rosenthal[95] employed *n*-hexadecane as the reaction solvent and Mo(CO)$_6$ as the

catalyst. Under reaction conditions of 250 °C, superatmospheric pressure, and an N$_2$ flow rate of 8.3 mL/min for 2 h, they achieved a 100% conversion rate of TDC and an 82% yield of TDI.

Organotin compounds also represent common catalysts for carbamate catalytic cracking. Spohn et al.[92] utilized Bu$_2$Sn-(OMe)$_2$ as a catalyst for the catalytic cracking of MPC, employing 1,2-dichloroethane as a solvent during a 1.25 h reaction at 88 °C, resulting in a 17.1% PI yield. The PI yield increased to 33% following a 40 min reaction with toluene. Guenter et al.[94] utilized dibutyltin dilaurate as a catalyst to process sulfolane solvent containing MDU in a thin-layer evaporator, operating at a flow rate of 100 g/h, a reaction temperature of 270 °C, and a reaction pressure of 4 kPa. Secondary condensation divided the gas phase mixture into two components: component I comprised a mixture of solvent and ethanol, while component II contained a mixture of solvent, MDI, MDU, and MIU. Component II yielded 54.1% and 90% following four extractions with cyclohexane.

In the process of carbamate decomposition to obtain isocyanates, there has been limited research on the utilization of silicon-based materials, such as kaolin, montmorillonite, and bentonite. Pedro et al.[93] investigated the use of montmorillonite K-10 as a catalyst for evaluating the decomposition of various carbamates. They observed that montmorillonite K-10 exhibited effective catalytic activity for monoisocyanates with electron-withdrawing groups, achieving nearly complete conversion to isocyanates at 183 °C for 5 h. However, for diisocyanates like MDI and TDI, longer reaction times were required. The reaction mechanism is that the hydroxyl group on the catalyst loses a hydrogen proton under the action of solvent, combines with carbamate to form an ionic compound,

and transfers the amino hydrogen to form isocyanate under the interaction. The alcohol obtained by decomposition is easily adsorbed to the catalyst, enabling effective separation of isocyanates from alcohol and thereby preventing reverse reactions. The specific mechanism is illustrated in Figure 12. Additionally, these catalysts are cost-effective and exhibit good reusability.
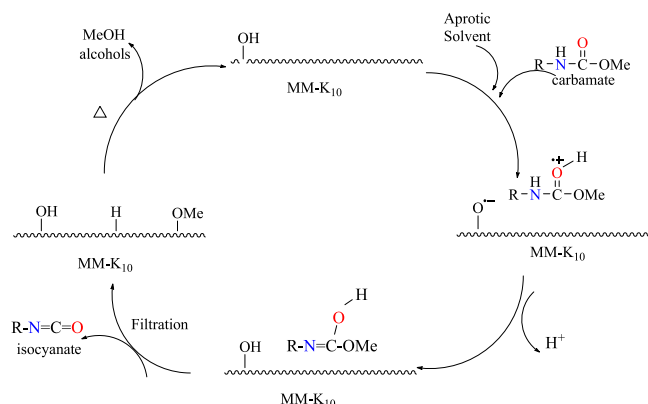

Figure 12. Carbamate decomposition reaction catalyzed by montmorillonite K-10. Adapted with permission from Pedro, U.; Marc, S.; Pilar, S.; Sergio, C.; Carmen, C.; Elena, F. A new and efficient catalytic method for synthesizing isocyanates from carbamates. *Tetrahedron Lett.* **2002**, *43* (9), 1673−1676. 10.1016/S0040-4039(02)00094-1.[93] Copyright 2002. Elsevier.

In contrast, the utilization of organic catalysts in this context dates back to an earlier period. These catalysts are associated with issues such as extended reaction times and reduced efficiency. Moreover, the reaction system is typically homogeneous, making it challenging to recycle the catalyst, limiting its further development.

Because the isocyanate is more active and easy to polymerize, the carbamate catalytic decomposition reaction needs a highly active and highly selective catalyst to accelerate the decomposition reaction speed and match the reaction conditions such as reaction temperature, time, and pressure to remove the main product from the reaction system in time. Therefore, researchers should focus on the development of efficient catalysts. Previous studies have shown that zinc-containing catalysts have high catalytic activity in the thermal decomposition reaction of carbamate due to the electron-absorbing properties of Zn, and the addition of second metals or carriers provides a variety of types of ligand systems for cations. The physical and chemical properties such as the surface content of the second component and the total acid content of the catalyst provide greater advantages for the decomposition reaction and may show higher potential than metal oxides. At the same time, optimizing the reaction conditions, making the reaction rate match the product removal rate, improving the yield, reducing the outflow of solvent or heat carrier, and reducing the subsequent separation are also a direction of research.

4. CONCLUSIONS AND PERSPECTIVES

Isocyanate is the key raw material for the production of polyurethane. Due to the extreme toxicity of phosgene, the synthesis method of isocyanate is gradually changing from phosgene to nonphosgene. This paper provides an overview of the synthesis processes for isocyanates, particularly focusing on nonphosgene methods, including reductive carbonylation, oxidative carbonylation, dimethyl carbonate, and urea, all of which necessitate carbamate thermal decomposition to yield isocyanates. When compared to the phosgene method, carbamate thermal decomposition is technically feasible, environmentally friendly, and safe. The key challenge lies in the development of an efficient catalyst system. Existing studies have primarily identified Zn as the active metal component in the catalyst. However, the reaction temperatures in these studies often exceed 200 °C, leading to increased production of byproducts and reduced isocyanate selectivity. Therefore, further research is needed to explore efficient catalyst systems, and especially the active metal loading on some macroporous carriers can be considered, so that the catalyst is easy to separate and reusable. It is also necessary to further optimize the process conditions, so that the reaction rate matches the product removal rate and reduces the outflow of solvents or heat carriers, with the goal of conducting the reaction under more moderate conditions. Additionally, elucidating the catalytic reaction mechanism and intrinsic reaction dynamics is essential to provide theoretical guidance for industrial applications.

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Notes

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