



Article

DBU-Intercalated α -Zirconium Phosphates as Latent Thermal Catalysts in the Reaction of Hexamethylene Diisocyanate and Phenol

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Abstract: The catalytic activity of 1,8-diazabicyclo [5,4,0]undec-7-ene-intercalated α -zirconium phosphates (α -ZrP·DBU) as thermal latent catalysts in the reaction of hexamethylene diisocyanate (HDI) and phenol was investigated. α -ZrP intercalation compounds with varying amounts of DBU (α -ZrP·xDBU, where x = 0.58, 0.44, 0.22, and 0.10) were prepared. The reaction of HDI and phenol with α -ZrP·DBU was carried out at varying temperatures for 30 min periods. The α -ZrP·DBU showed high catalytic activity in the reaction of HDI-phenol under heating conditions. The α -ZrP·DBU extended the pot lifetimes at 25 °C.

Keywords: α -zirconium phosphate; intercalation; latent thermal catalyst; urethane; pot life



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1. Introduction

DBU (1,8-diazabicyclo [5,4,0]undec-7-ene) has been widely used as a catalyst for preparation of polyurethanes [1,2]. Generally, multifunctional alcohols and isocyanates are used to synthesize polyurethanes. In the preparation of polyurethane using DBU, an organic strong base catalyst, it is difficult to control the molding time due to the rapid reaction. Thus, it is very important to perform uniform mixing and molding of polyurethane to extend the pot lifetime. To resolve this problem, blocked isocyanates have been used to avoid unexpected reactions [3–6]. However, when using blocked reagents, low molecular weight deblocked compounds remain, which might affect the mechanical and thermal properties of the resulting polyurethane. Using castor oil as an alcohol component and toluene diisocyanate (TDI) as an isocyanate component, DBU-acetylacetone was added as a catalyst [7]. By adjusting the mixing ratio of DBU-acetylacetone for the suppression of DBU activity, the pot lifetime was extended and the components reacted at low temperature. However, the pot lifetime was 6 min without the addition of acetylacetone and 9–12 min with the addition of acetylacetone, which are too short for their use as latent thermosetting catalysts. Zivic et al. reported DBU derivatives of thioxanthone as photobase catalysts to promote the preparation of polyurethane [8]. Alsarraf reported that cyclic guanidine compounds reacted with two equivalents of isocyanates as latent catalysts [9]. In the preparation of polyurethane with these guanidine-isocyanate derivatives, the guanidine-isocyanate derivatives were first dissolved in THF. We hoped to avoid using organic solvents in the polymerization reaction. Recently, we reported that DBU-intercalated α -zirconium phosphate (α -ZrP·DBU) served as a latent thermal catalyst in the reaction of epoxy resins. The α -ZrP·DBU catalyst can be obtained simply by mixing DBU and α -ZrP in methanol at ambient temperature [10]. The intercalated compound of α -ZrP·DBU is expected to possess different reactivity with organic compounds and organic salts. We examined herein the catalytic activity of α -ZrP·DBU in the reaction of hexamethylene diisocyanate (HDI) and phenol as a model reaction in polyurethane synthesis.

2. Results and Discussion

In the preparation of polyurethane using a base catalyst, the reaction is very rapid and it is difficult to maintain the pot life to obtain uniform resins. Hence, we studied how to extend the time for uniform mixing and molding by using DBU-intercalated α -zirconium phosphate as a thermal latent catalyst for polyurethane synthesis. We previously reported that DBU-intercalated α -ZrP (α -ZrP·DBU) showed high stability at 40 °C and high reactivity at 120 °C in the reaction of glycidyl phenyl ether (GPE) and hexahydro-4-methylphthalic anhydride (MHHPA) [11]. To prepare α -ZrP intercalation compounds with various DBU contents, DBU and α -ZrP were simply mixed in methanol. The compositions were estimated by elemental analyses as shown in Table 1. The charge molar ratio of α -ZrP to DBU (DBU/ZrP) was 1.0, 0.5, 0.25, or 0.10. The DBU content of the intercalation compounds was determined by elemental analyses and were found to be $\text{Zr}(\text{HPO}_4)_2 \cdot 0.58\text{DBU} \cdot 2.2\text{H}_2\text{O}$, $\text{Zr}(\text{HPO}_4)_2 \cdot 0.44\text{DBU} \cdot 1.7\text{H}_2\text{O}$, $\text{Zr}(\text{HPO}_4)_2 \cdot 0.22\text{DBU} \cdot 1.8\text{H}_2\text{O}$, and $\text{Zr}(\text{HPO}_4)_2 \cdot 0.10\text{DBU} \cdot 1.6\text{H}_2\text{O}$, respectively. These compounds are abbreviated as, e.g., α -ZrP·0.58DBU. Basal distances of 14.0 Å ($2\theta = 6.3^\circ$) for α -ZrP·0.58DBU, 13.4 Å ($2\theta = 6.6^\circ$) and 12.3 Å ($2\theta = 7.2^\circ$) for α -ZrP·0.44DBU, 12.1 Å ($2\theta = 7.3^\circ$) for α -ZrP·0.25DBU, and 12.1 Å ($2\theta = 7.3^\circ$) for α -ZrP·0.10DBU were estimated from XRD patterns as shown in Figure 1. The basal distances for all intercalated α -ZrP·DBU compounds were expanded from pristine α -ZrP (7.6 Å, $2\theta = 11.7^\circ$).

Table 1. Composition determined by elemental analysis and basal distance

Catalyst	C (%)	H (%)	N (%)	<i>d</i> (Å)	Composition
α -ZrP·0.58DBU	14.99	3.84	3.96	14.0	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.58\text{DBU} \cdot 2.2\text{H}_2\text{O}$
α -ZrP·0.44DBU	11.78	3.30	3.24	13.4, 12.3	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.44\text{DBU} \cdot 1.7\text{H}_2\text{O}$
α -ZrP·0.22DBU	6.38	2.63	1.75	12.1	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.22\text{DBU} \cdot 1.8\text{H}_2\text{O}$
α -ZrP·0.10DBU	3.12	2.10	0.84	12.1	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.10\text{DBU} \cdot 1.6\text{H}_2\text{O}$

The ^{31}P MAS NMR spectra of the α -ZrP·DBU compounds are shown in Figure 2. The ^{31}P MAS NMR spectra showed multiple peaks for α -ZrP·0.58DBU (−21.0, −23.0, −24.0), α -ZrP·0.44DBU (−19.0, −22.4), α -ZrP·0.22DBU (−15.4, −16.8, −17.5, −22.0, −23.9), and α -ZrP·0.10DBU (−21.9, −23.2). A single peak for pristine α -ZrP was observed at δ −20.1 [12]. The multiple peaks for the α -ZrP·DBU compounds due to the interactions of the different positions of DBU and H_2O into the layers of α -ZrP.

To determine the activity of the α -ZrP·DBU compounds, the reaction of HDI–phenol with α -ZrP·DBU compounds was evaluated as shown in Scheme 1. The conversion of phenols with α -ZrP·DBU as a function of temperature was estimated by ^1H -NMR analyses as shown in Supplementary Materials. A signal due to protons at the *o*-position of the starting phenol was observed at δ 6.83. In the reaction product of urethane, a signal due to protons at the *m*-position was observed at δ 7.35. The conversions were determined by the ratio of these two peak areas.

For the reaction of HDI–phenol with α -ZrP·DBU compounds, Figure 3 shows the conversion of phenols after 30 min as a function of temperature during the reaction with SA-102 (■), α -ZrP·0.58DBU (□), α -ZrP·0.44DBU (◇), α -ZrP·0.22DBU (△), and α -ZrP·0.10DBU (○). For U-cat SA-102 (DBU salt of 2-ethylhexanoate abbreviated as SA-102), a commercial DBU salt catalyst, the conversion was 98% at 25 °C for 30 min. The conversion with α -ZrP·0.58DBU was 86% at 25 °C for 30 min. For α -ZrP·0.44DBU, α -ZrP·0.22DBU, and α -ZrP·0.10DBU catalysts, the conversions were all lower at ca. 10% at 25 °C for 30 min. However, the conversions with α -ZrP·0.44DBU, α -ZrP·0.22DBU, and α -ZrP·0.10DBU were about 90% at 60 °C for 30 min. Thus, these α -ZrP·0.44DBU, α -ZrP·0.22DBU, and α -ZrP·0.10DBU catalysts showed very low conversions of the reaction of phenols at 25 °C but the reaction proceeded smoothly at 60 °C.

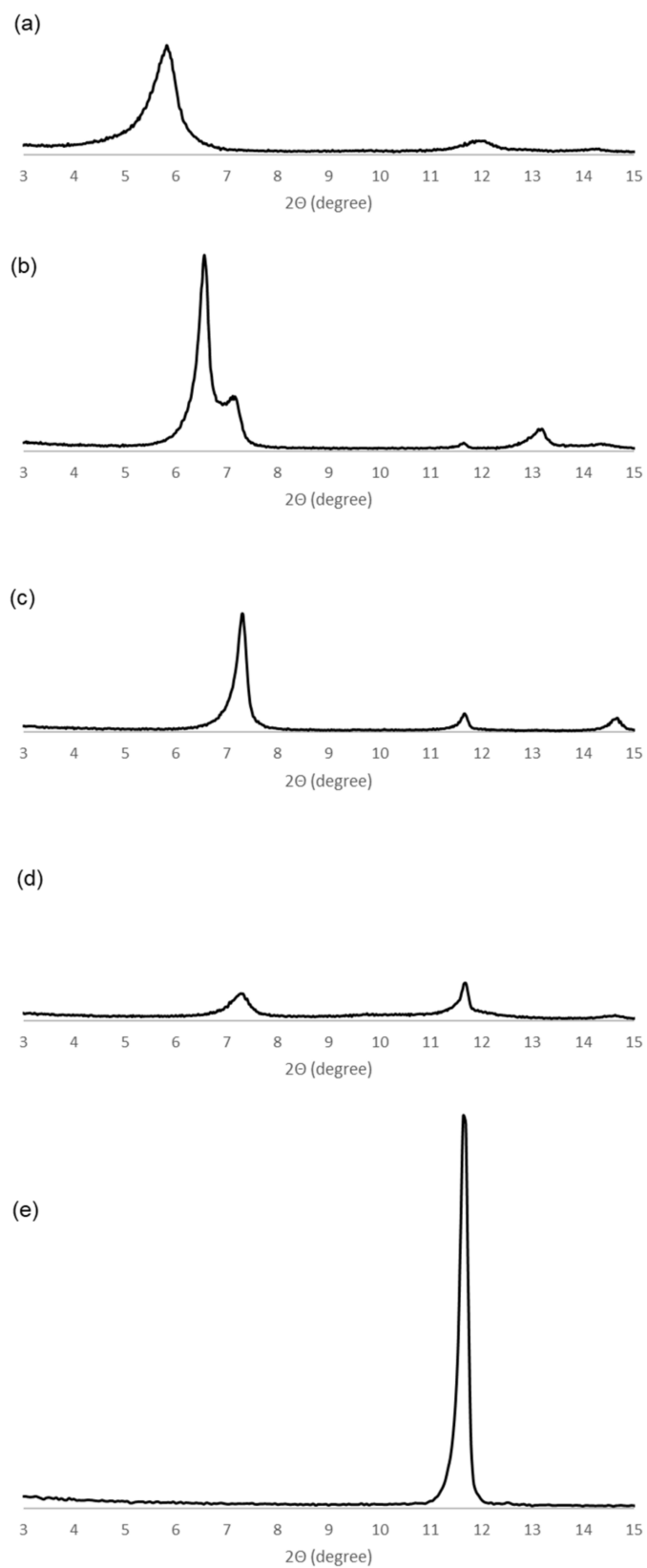


Figure 1. XRD patterns for (a) α -ZrP·0.58DBU, (b) α -ZrP·0.44DBU, (c) α -ZrP·0.22DBU, (d) α -ZrP·0.10DBU, and (e) pristine α -ZrP.

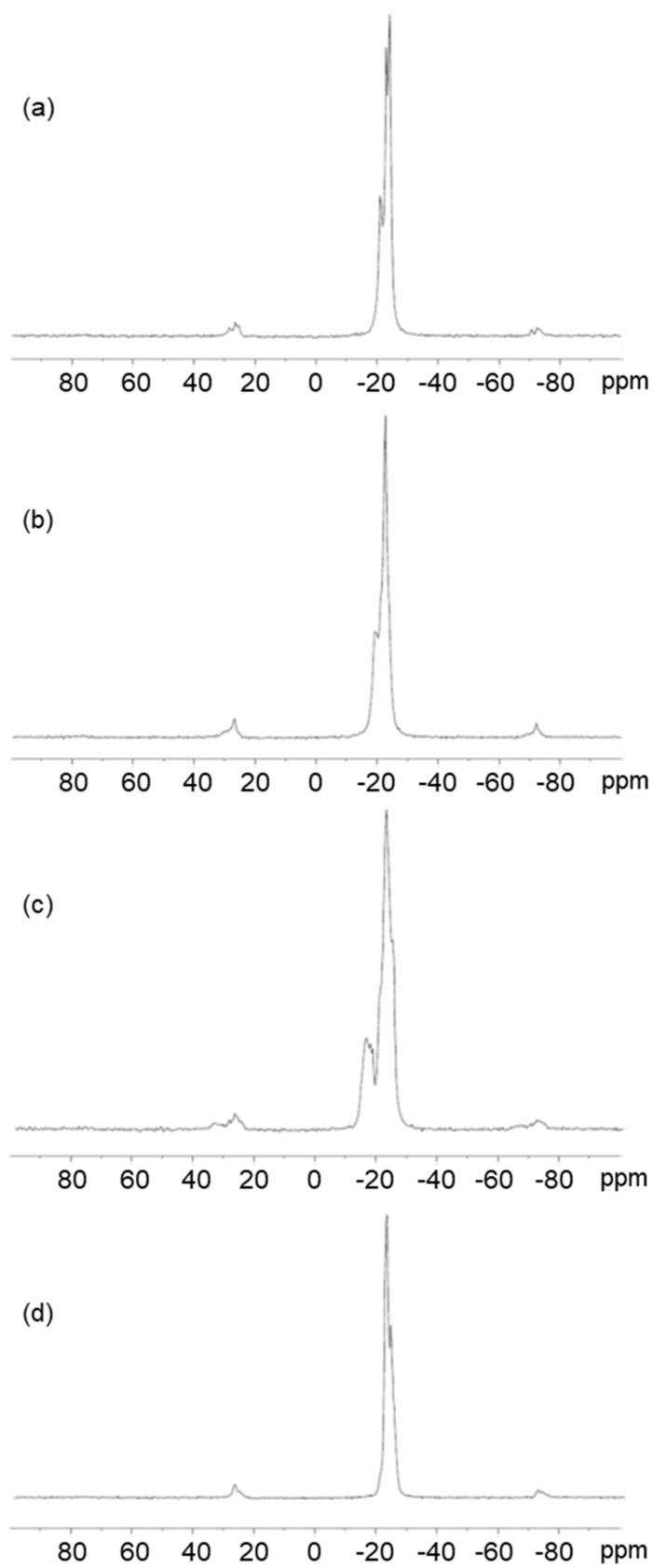


Figure 2. ^{31}P NMR spectra of (a) $\alpha\text{-ZrP}\cdot 0.58\text{DBU}$, (b) $\alpha\text{-ZrP}\cdot 0.44\text{DBU}$, (c) $\alpha\text{-ZrP}\cdot 0.22\text{DBU}$, and (d) $\alpha\text{-ZrP}\cdot 0.10\text{DBU}$.



Scheme 1. Reaction of HDI and phenol with α -ZrP DBUs.

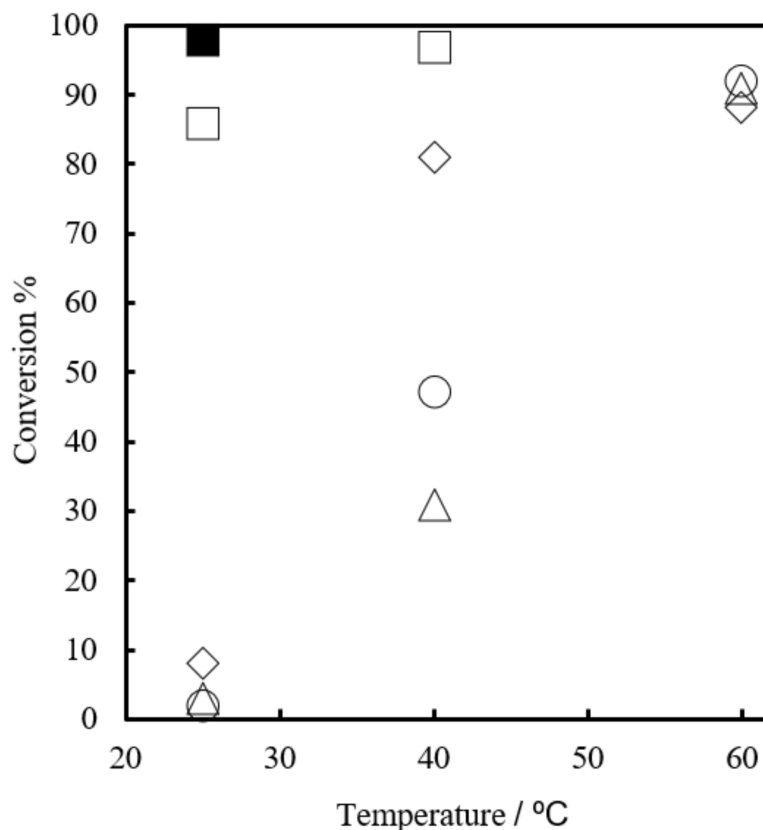


Figure 3. The conversion of phenol after 30 min as a function of temperature during reaction with SA-102 (■), α -ZrP·0.58DBU (□), α -ZrP·0.44DBU (◇), α -ZrP·0.22DBU (△), and α -ZrP·0.10DBU (○).

The pot lifetimes for the α -ZrP·DBU compounds were evaluated at 25 °C as shown in Figure 4. The pot lifetimes at 25 °C for the SA-102 and α -ZrP·0.58DBU catalysts were not determined. The conversion was 24% with α -ZrP·0.44DBU at 25 °C for 1 h. The conversions with α -ZrP·0.22DBU and α -ZrP·0.10DBU were 22% and 18% at 25 °C for 2 h. These catalysts could extend the pot lifetime at 25 °C. The conversion with α -ZrP·0.44DBU for 1.5 h was 36% and with α -ZrP·0.22DBU and α -ZrP·0.10DBU were 55% and 35% for 4 h. The pot life for 30% conversion was over 1.5 h for α -ZrP·0.44DBU and 4 h for α -ZrP·0.22DBU and α -ZrP·0.10DBU. The correlations of time-conversion with α -ZrP·0.22DBU and α -ZrP·0.10DBU showed good linear approximation, and the formulas were $C (\%) = 8.5 T (h)$ and $C (\%) = 12.8 T (h)$ (%Conversion = coefficient \times hour time) for α -ZrP·0.22DBU and α -ZrP·0.10DBU respectively.

The reaction behavior suggested that the salt type catalyst SA-102 was rapidly dissociated and reacted to produce urethane in high conversion at 25 °C. The pot lifetime for the α -ZrP·DBU catalysts depended on the DBU content in α -ZrP and the catalysts showed high activity at 60 °C. The difference in the activities of SA-102 and α -ZrP·DBU compounds might be caused by the protection of DBU in the interlayer of α -ZrP.

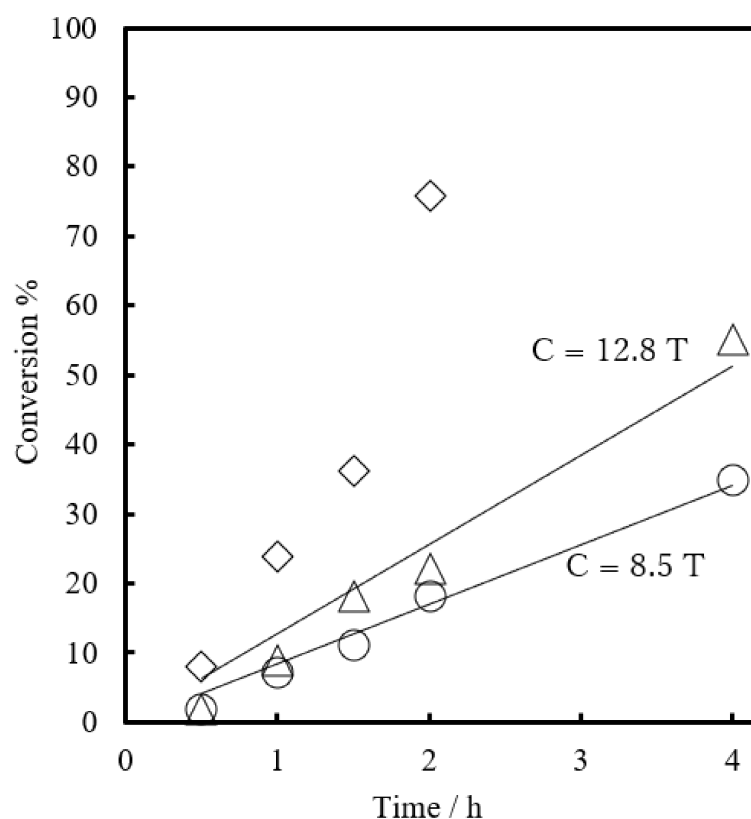


Figure 4. Conversion of phenol as a function of time during reaction with α -ZrP-0.44DBU (\diamond), α -ZrP-0.22DBU (\triangle), and α -ZrP-0.10DBU (\circ) at 25 °C.

3. Experimental Section

3.1. Materials

Zr(HPO₄)₂·H₂O (CZP-100) was purchased from Daiichi Kigenso Kagaku Kogyo Co., Ltd. Hexamethylene diisocyanate (HDI), and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Phenol was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Solvents were used as received without further purification. U-CAT SA102 was purchased from San-Apro, Ltd., (Kyoto, Japan).

3.2. Measurements

X-ray diffraction (XRD) patterns were obtained using a RIGAKU RINT2200 with CuK α radiation over a scan range of 3–15° at a rate of 2° min⁻¹. NMR spectra in solution were recorded on a Varian Unity-300 (300 MHz) spectrometer (Palo Alto, CA, USA) and a JEOL JNM-ECZS (400 MHz) spectrometer (Tokyo, Japan) using tetramethylsilane (TMS) as an internal standard. The contents of alkylamine and water in the intercalation compounds of α -ZrP were measured using a Perkin Elmer CHN microanalyzer. ³¹P MAS NMR spectra were recorded on a BRUKER AVANCEIII600WB NMR spectrometer equipped with 4.0 mm MAS probe head.

3.3. Preparation of DBU-Intercalated α -ZrP (α -ZrP-0.10DBU)

The intercalation of DBU into the layers of α -Zr(HPO₄)₂·H₂O (α -ZrP) was carried out by slightly modifying a previously reported method [10]. Approximately 5.0 g of α -ZrP was added to 33 mL of a DBU 0.256 g (1.68 mmol) methanol solution. The reaction mixture was then allowed to stand at ambient temperature for 24 h, following which the product was collected by centrifugation at 5000 rpm for 15 min and washed with methanol five times. The resulting residue was dried under vacuum. The preparation of α -ZrP-0.58DBU,

α -ZrP·0.44DBU, and α -ZrP·0.22DBU was carried out by varying the molar ratio of DBU/Zr to 1, 0.5, and 0.25, respectively.

3.4. Typical Model Reaction Procedure of HDI and Phenol

A mixture of phenol (944 mg, 10.0 mmol) and α -ZrP·0.44DBU (4.2 mg, DBU content: 4.9 μ mol, 0.1 mol% for HDI) was stirred. After 5 min, HDI (862 mg, 5.1 mmol) was added to the mixture, which was then heated at 40 °C. After 30 min, a small aliquot of the reaction mixture was dissolved in CDCl₃ and its ¹H-NMR spectrum was acquired to determine the extent of conversion. For the reactions of HDI and phenol with the α -ZrP·0.58DBU, α -ZrP·0.22DBU, and α -ZrP·0.10DBU catalysts, the DBU equivalents were unified to 0.1 mol% for HDI.

4. Conclusions

We prepared various DBU-intercalated compounds of α -ZrP with DBU/Zr molar ratios of 0.58, 0.44, 0.22, and 0.10. The catalytic activity of α -ZrP·DBU compounds in the reaction of HDI and phenol was investigated. The α -ZrP·0.58DBU catalyst did not have an appreciable pot lifetime at 25 °C for 30 min. The α -ZrP·0.44DBU catalyst showed a 24% pot lifetime in the conversion at 25 °C for 1 h. The α -ZrP·0.22DBU and α -ZrP·0.20DBU had 22% and 18% pot lifetimes at 25 °C for 2 h. These catalysts showed high reactivity at 60 °C for 30 min. These catalysts can be applied for the syntheses of polyurethanes. The polymerization of diols and diisocyanates with α -ZrP·DBU would be studied further.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11050614/s1>, Figure S1: The ¹H-NMR spectra after the reaction of HDI and phenol with a) α -ZrP·0.10DBU at 25 °C and b) α -ZrP·0.58DBU at 40 °C for 30 min.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Abbreviation	Compound Name
α -ZrP	α -zirconium phosphate
DBU	1,8-diazabicyclo[5,4,0]undec-7-ene
HDI	hexamethylene diisocyanate
SA-102	DBU salt of 2-ethylhexanoate

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