1 Appearance of metal-ammonia complex aqueous solutions

The reaction of 30 wt% ammonia aqueous solution with copper and zinc acetate gave Cu(Am) and Zn(Am) aqueous solutions, respectively. The solutions were clear and had low viscosity as shown in Figure S1.

2 Dimensional stability of RPUR/Cu(Am)-1:1 and RPUR/Zn(Am)-1:1

Dimensional stability of RPUR/Cu(Am)-1:1 and RPUR/Zn(Am)-1:1 was investigated at 70°C and -25°C for 1, 7 and 14 days following ASTM D 2126-04 and ISO 2796-1986. After testing period, no visually distorted foam was observed (Figure S2). Both RPUR/Cu(Am)-1:1 and RPUR/Zn(Am)-1:1 showed desirable dimensional stability. The maximum % linear dimension changes after 14 days for -25°C and 70°C of RPUR/Cu(Am)-1:1 were -0.19% and -0.46%, respectively, while those of RPUR/Zn(Am)-1:1 were -0.45% and -1.01%, respectively (Figure S3). These values are in the range of industrial standard, BS4370: Part I: 1988 (1). The maximum % volume change (Figure S4) and % mass change (Figure S5) for both -25°C and 70°C of RPUR/Cu(Am)-1:1 were less than those of RPUR/Zn(Am)-1:1. These results indicated that RPUR/Cu(Am)-1:1 had better dimensional stability than RPUR/Zn(Am)-1:1. The slight shrinkage and mass decrease of the foams were observed after the testing period due to the fact that diffusion rate of air into the foams is about an order of magnitude slower than that of CO₂ out of the foams, especially at high temperature (2).

3 Morphology of PIR-PUR foams

The cell morphology of PIR-PUR foams catalyzed by Zn(Am)+KOct and DMCHA+KOct was compared to that of their reference RPUR foams (Figure S6).

4 Investigation of flame retardancy of PIR-PUR foams using horizontal burning test

5 The result for investigation of thermal stability of PIR-PUR foams
Figure S1: Aqueous solutions of synthesized metal-ammonia complex; (a) Cu(Am) and (b) Zn(Am).

Figure S2: RPUR foam appearance after 14 days of dimensional stability test.
Figure S3: % Linear change of RPUR/Cu(Am)-1:1 and RPUR/Zn(Am)-1:1 at (a) -25°C and (b) 70°C.
As previously mentioned, \([\text{Cu(NH}_3\text{)}_4\text{(H}_2\text{O)}_2]^2+\) and \([\text{Zn(NH}_3\text{)}_4\text{(H}_2\text{O)}_2]^2+\) could easily lose two \(\text{H}_2\text{O}\) molecules to give \([\text{Cu(NH}_3\text{)}_4]^2+\) and \([\text{Zn(NH}_3\text{)}_4]^2+\), respectively, which could catalyze the reaction between NCO and OH groups in gelling reaction to give urethane formation. Copper or zinc could act as the Lewis acid and induce more electrophilicity of NCO groups, while nitrogens of ammonia ligand could act as the Lewis base and induce more nucleophilicity of OH groups. In the case of isocyanurate formation accelerated by KOct, there has been the proposed catalytic mechanism of this commercial trimerization catalyst. Octoate anions seem to be the reactive species inducing the cyclization of NCO groups, whereas potassium cations appear not to have an important role in catalysis (3).

### 7 Reaction times of RPUR and PIR-PUR foams

**Figure S4:** % Volume change of RPUR/Cu(Am)-1:1 and RPUR/Zn(Am)-1:1 at -25°C and 70°C.

**Figure S5:** % Mass change of RPUR/Cu(Am)-1:1 and RPUR/Zn(Am)-1:1 at -25°C and 70°C.
Figure S6: SEM images of reference RPUR and PIR-PUR foams.
Figure S7: Digital images of burnt RPUR and PIR-PUR foams after horizontal burning test.
References


Table S1: Description of foam appearances used in recording the reaction times.

<table>
<thead>
<tr>
<th>Terminology</th>
<th>Description</th>
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<tbody>
<tr>
<td>Start time</td>
<td>The time that was recorded when CO$_2$ bubbles began to emerge on the surface of liquid foam mixture.</td>
</tr>
<tr>
<td>Gelation time</td>
<td>The time that was recorded when liquid foam mixture became gel.</td>
</tr>
<tr>
<td>Tack-free time</td>
<td>The time that was recorded when the outer surface of foam dried and lost stickiness with other materials.</td>
</tr>
<tr>
<td>Expansion time</td>
<td>The time that was recorded when rising process stopped.</td>
</tr>
</tbody>
</table>

Figure S8: Horowitz-Metzger plots for calculating activation energy ($E_a$) of thermal degradation of the foams; (a) the first and (b) the second thermal degradation stages.

Scheme S1: Possible catalytic mechanism of urethane formation.