Supporting Information

Supported $ZnBr_2$ and carbon nitride bifunctional complex catalysts for the efficient cycloaddition of CO_2 with diglycidyl ethers

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The determination of the conversion of BDODGE and the selectivity by ^1H NMR analysis:

In ^1H NMR analysis, a certain amount of sample (m_{BDODGE} or $m_{product}$) and a fixed amount of toluene (5.5 mg) were added to the solvent $CDCl_3$ for test. From the obtained NMR spectra of BDODGE, the peaks of a and b (2.72-3.09 ppm and 3.22 ppm) of BDODGE (Fig.4S A) and the peak of $–CH_3$ (2.29 ppm) of toluene were integrated. The integration of the $–CH_3$ peak of toluene (I_{CH3}) was determined to 100. Then, the epoxy value of BDODGE can be calculated according to the following equation.

$$X_{epoxy}(BDODGE) = \frac{100}{epoxy\ equivalent\ weight} = \frac{n_{function\ epoxy}}{m_{BDODGE}} = \frac{n_{toluene} \times (I_a + I_b)}{I_{CH3} \times m_{BDODGE}} \qquad (1)$$

In Eq. (1), m_{BDODGE} was the mass of BDODGE brought for the test; $n_{function\ epoxy}$ and $n_{toluene}$ signified the mole amount of function epoxy in BDODGE and of toluene introduced in this NMR test, respectively; I_a, I_b, and I_{CH3} were separately the integrations of peaks of a and b of epoxy groups (Fig.4S A) and the peak of $–CH_3$ of toluene.

$$X_{carbonate}(product) = \frac{100}{carbonate\ equivalent\ weight} = \frac{n_{function\ carbonate}}{m_{product}} = \frac{n_{toluene} \times (I_{a'} + I_{b'})}{I_{CH3} \times m_{productE}}$$

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(2)

$$\mathrm{X}_{\text{epoxy}}(product) = \frac{100}{epoxy\ equivalent\ weight} = \frac{n_{function\ epoxy}}{m_{product}}$$

$$= \frac{n_{toluene} \times (I_a + I_b)}{I_{CH3} \times m_{product}}$$

(3)

Likewise, the carbonate value and epoxy value of the product were calculated. The Eq. (2) and Eq. (3) were determined with the same method as above. However, m_{product} was the mass of product introduced for the test; $n_{\text{function carbonate}}$ represented the mole amount of function carbonate in the product, $I_{a'}$, $I_{b'}$ were the integrations of characteristic peaks of cyclic carbonate as labeled in Fig.4S B. It should be noted that I_a, I_b in Eq. (3) meant the integrations of the same peaks of remained epoxide in the product as those marked in Fig.4S A.

According to the above calculations, the conversion of BDODGE and the selectivity to the corresponding cyclic carbonate could be evaluated as below:

$$\text{Conversion (\%)} = \frac{\mathrm{X}_{\text{epoxy}}(\text{BDODGE}) - \mathrm{X}_{\text{epoxy}}(\text{product})}{\mathrm{X}_{\text{epoxy}}(BDODGE)}$$

$$\text{Selectivity (\%)} = \frac{\mathrm{X}_{\text{carbonate}}(\text{product})}{\mathrm{X}_{\text{epoxy}}(\text{BDODGE}) - \mathrm{X}_{\text{epoxy}}(\text{product})}$$

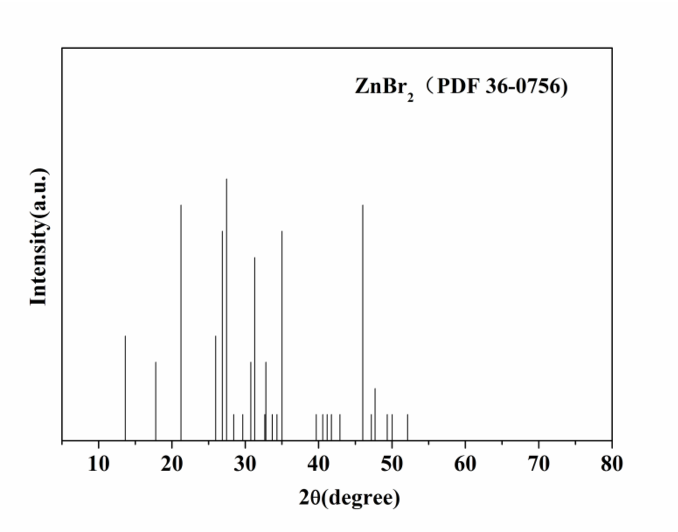
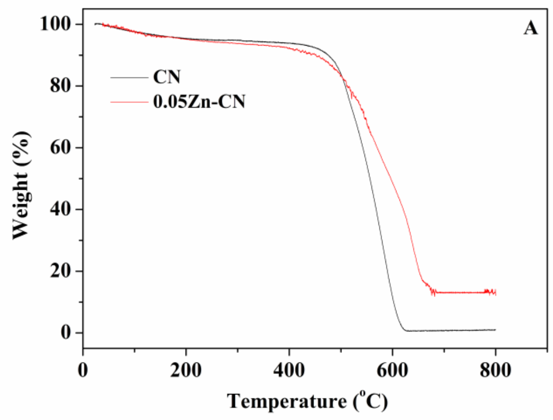


Fig.1S. Standard XRD pattern of $ZnBr_2$ (PDF 36-0756).



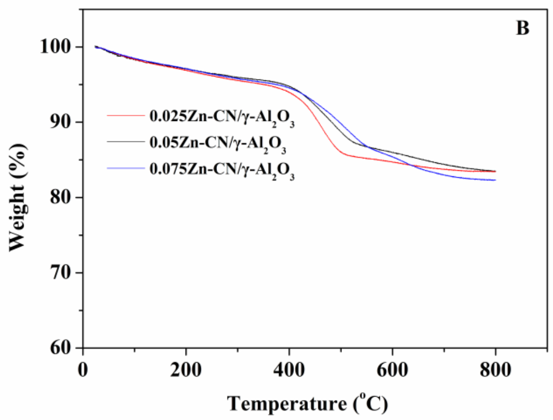


Fig.2S. TG analysis of CN, Zn-CN and Zn-CN/γ-Al_2O_3 samples.

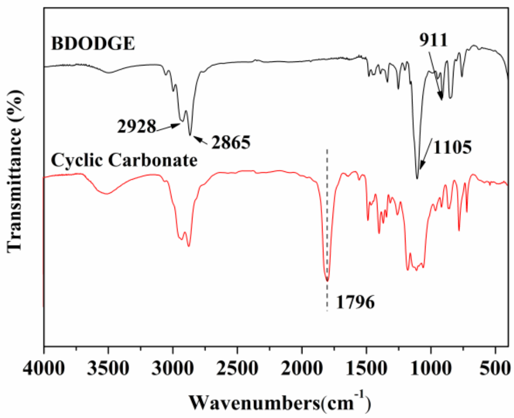


Fig.3S. FT-IR spectra of 1, 4-butanediol diglycidyl ether (BDODGE) and the corresponding cyclic carbonate

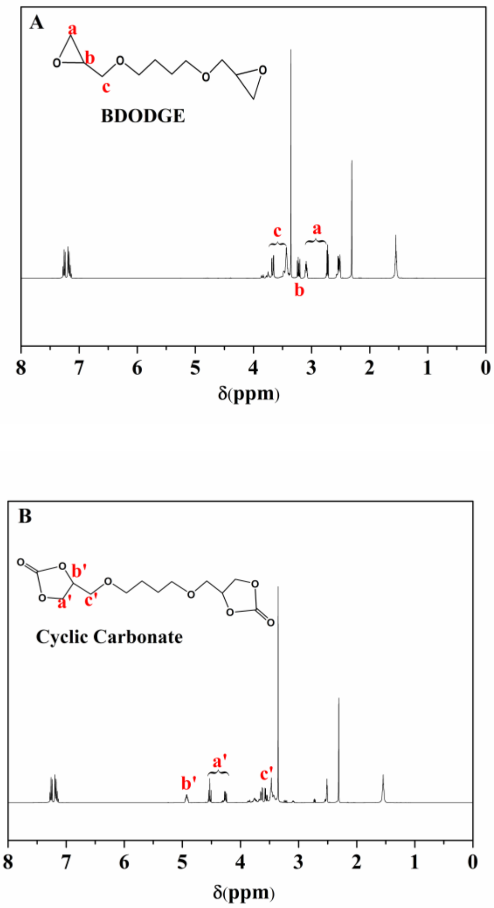


Fig.4S. [1]H NMR spectra of 1, 4-butanediol diglycidyl ether (BDODGE) (A) and the corresponding cyclic carbonate (B).

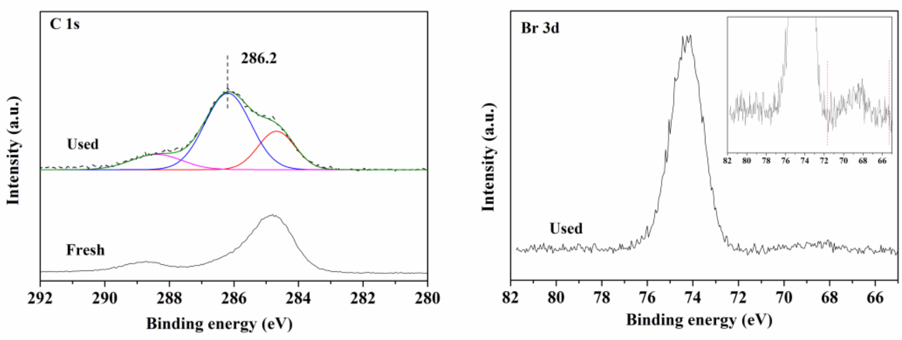


Fig.5S. XPS spectra of fresh and reused 0.05Zn-CN/γ-Al_2O_3.

Table 1S. Zn element detection of the Zn-CN/γ-Al_2O_3 catalysts.

Entry	**Catalyst**	**Zn element content (%)**
1	0.025Zn-CN/γ-Al_2O_3	1.22
2	0.05Zn-CN/γ-Al_2O_3	2.18
3	0.075Zn-CN/γ-Al_2O_3	3.28

Table 2S. Catalytic activities of varied metal modified CN supported γ-Al_2O_3 materials for the cycloadditon of CO_2 to BDODGE [a] .

Entry	**Doped salt** [b]	**Conversion (%)**	**Selectivity (%)**
1	$ZnCl_2$	35.4	97.9
2	$MgCl_2$	32.8	98.1
3	$FeCl_3$	38.8	98.2
4	$CoCl_2$	29.3	98.2
5	$AlCl_3$	38.5	99.1
6	$ZnBr_2$	91.4	98.9

[a] Reaction conditions: W(BDODGE)=30 g, W(catalyst)=2.27 g , p(CO_2)=1.0 MPa, 140 °C, t=20 h;

[b] The doped salt was added with the same mole amount of metal.

Table 3S. Zn element detection of the fresh and used 0.05Zn-CN/γ-Al_2O_3 catalyst.

Entry	**Catalyst**	**Zn element content(%)**	
		Before use	**After use**
1	0.05Zn-CN/γ-Al_2O_3	2.18	1.77