*Supplementary Materials*

# Direct Etherification Reaction of Glycerol Using Alkali Metal Cation ($Li^+$, $Na^+$ and $K^+$) Containing X-Type Zeolites as Heterogeneous Catalysts: Optimization of the Reaction Conditions

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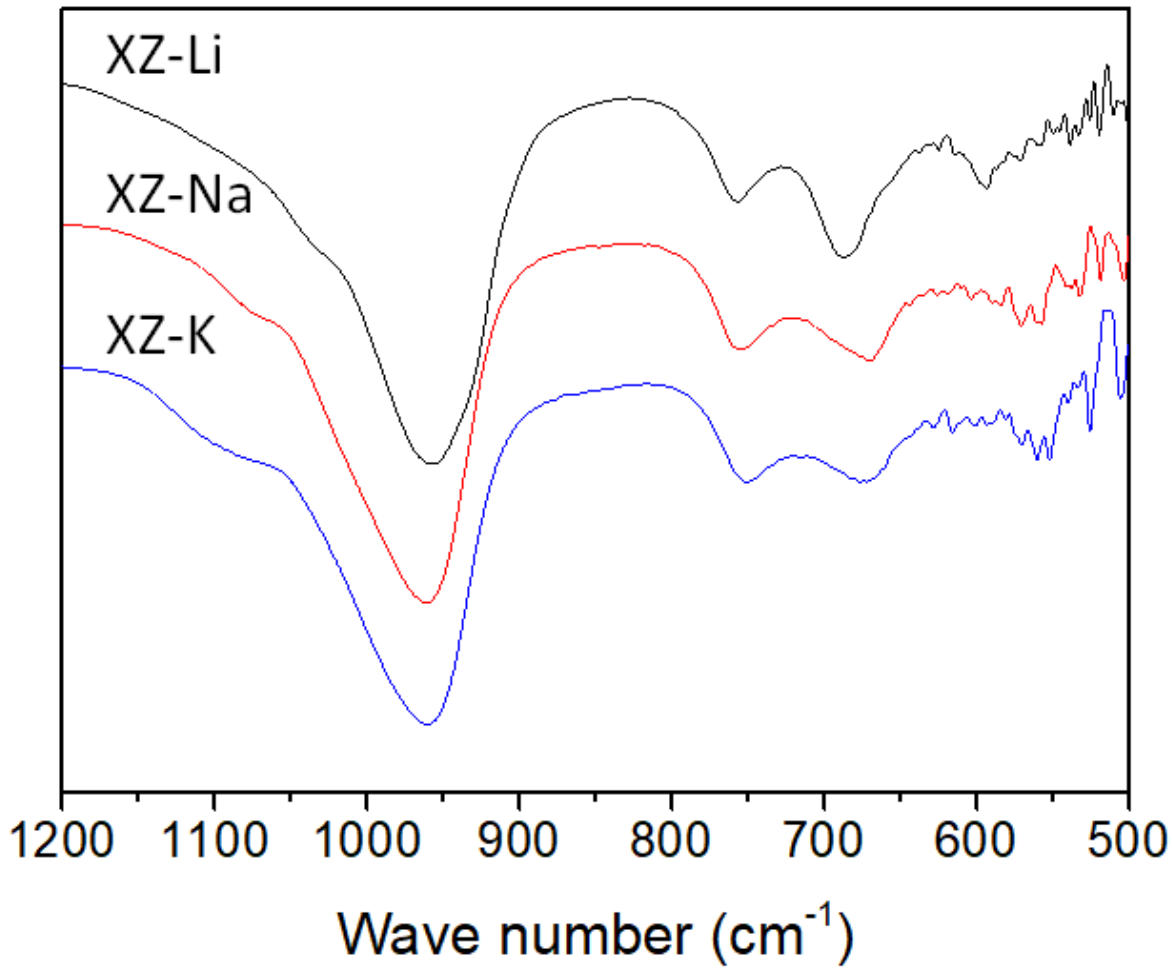


**Figure S1.** FT-IR spectra of zeolite XZ-M (M = Li, Na, and K).

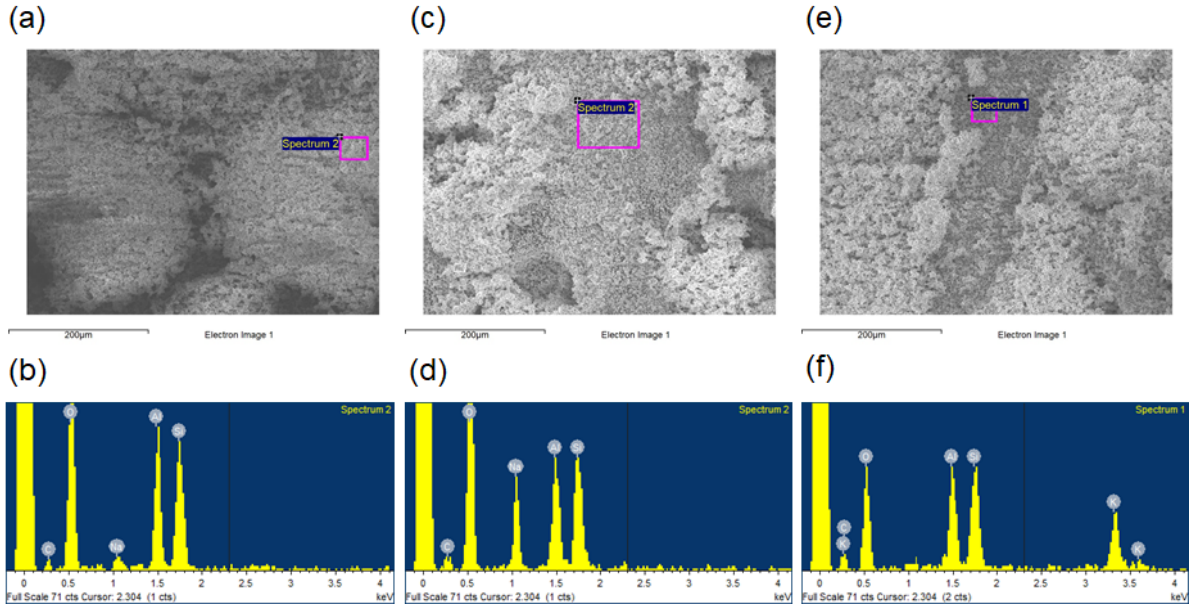


**Figure S2.** SEM images and EDX data of zeolite (a) and (b) XZ-Li, (c) and (d) XZ-Na, (e) and (f) XZ-K, respectively.

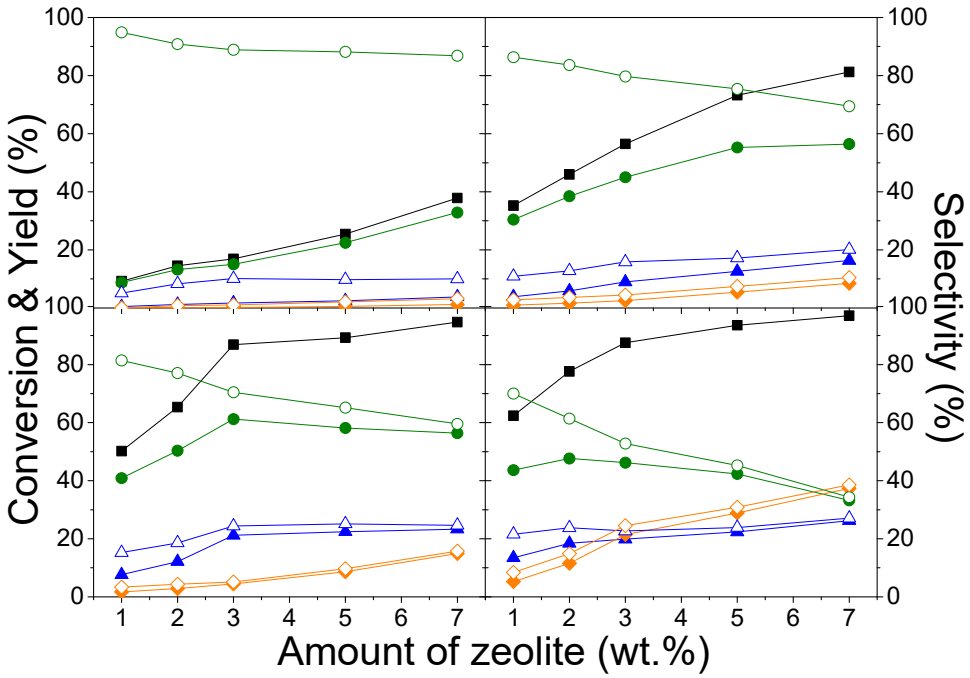


**Figure S3.** The influence of the amount of XZ-Li on the etherification reaction of glycerol at (a) 260 , (b) 270, (c) 280, and (d) 290 °C (-■-: Conversion of glycerol, -●-: Yield of DG, -▲-: Yield of TG, -◆-: Yield of others -○-: Selectivity of DG, -Δ-: Selectivity of TG, -◊-: Selectivity of others, reaction time: 2 h).

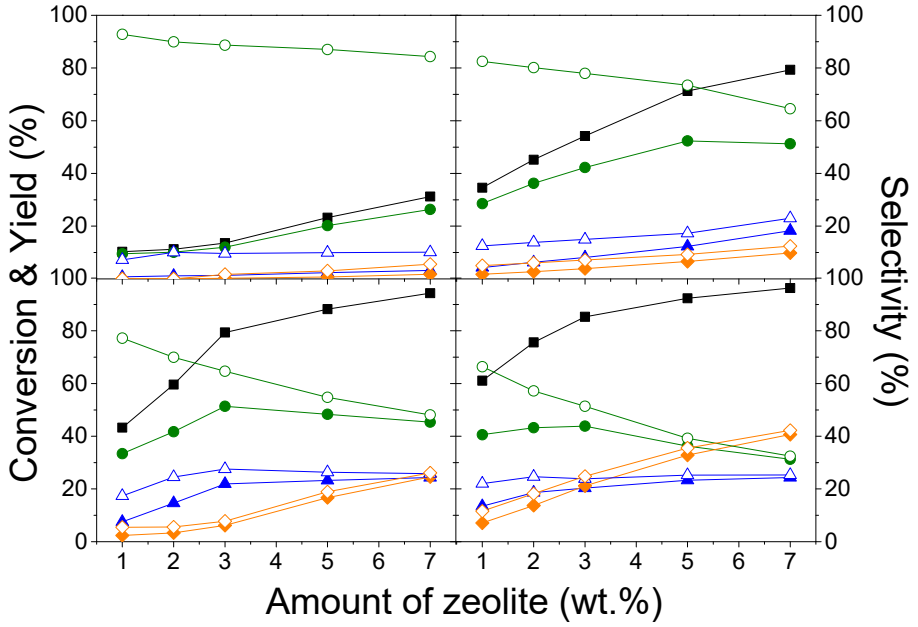


**Figure S4.** The influence of the amount of XZ-Na on the etherification reaction of glycerol at (a) 260, (b) 270, (c) 280, and (d) 290 °C (-■-: Conversion of glycerol, -●-: Yield of DG, -▲-: Yield of TG, -◆-: Yield of others -○-: Selectivity of DG, -Δ-: Selectivity of TG, -◊-: Selectivity of others, reaction time: 2 h).

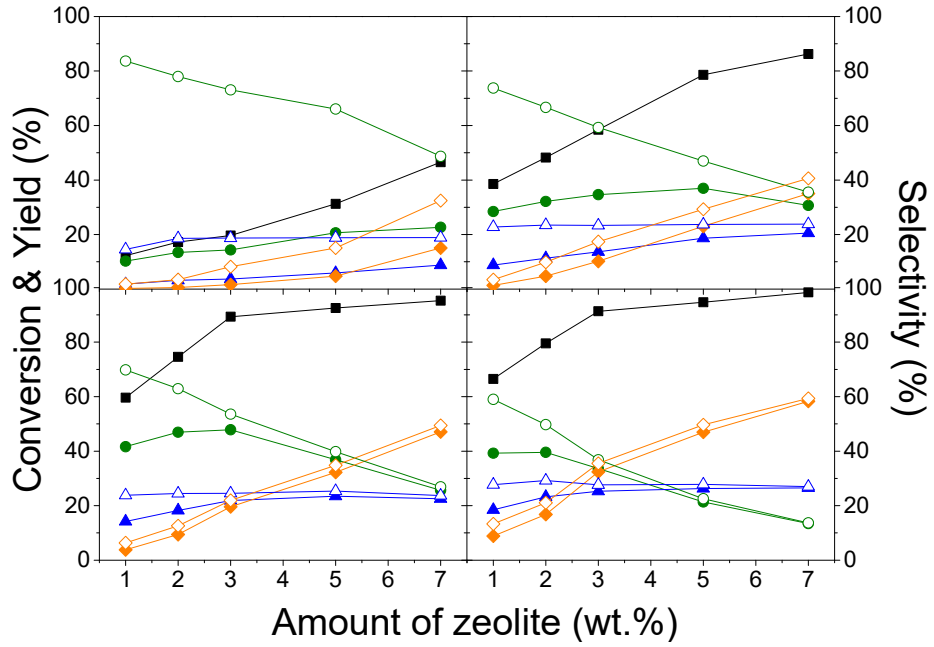


**Figure S5.** The influence of the amount of XZ-K on the etherification reaction of glycerol at (a) 260, (b) 270, (c) 280, and (d) 290 °C (-■-: Conversion of glycerol, -●-: Yield of DG, -▲-: Yield of TG, -◆-: Yield of others -○-: Selectivity of DG, -Δ-: Selectivity of TG, -◊-: Selectivity of others, reaction time: 2 h).

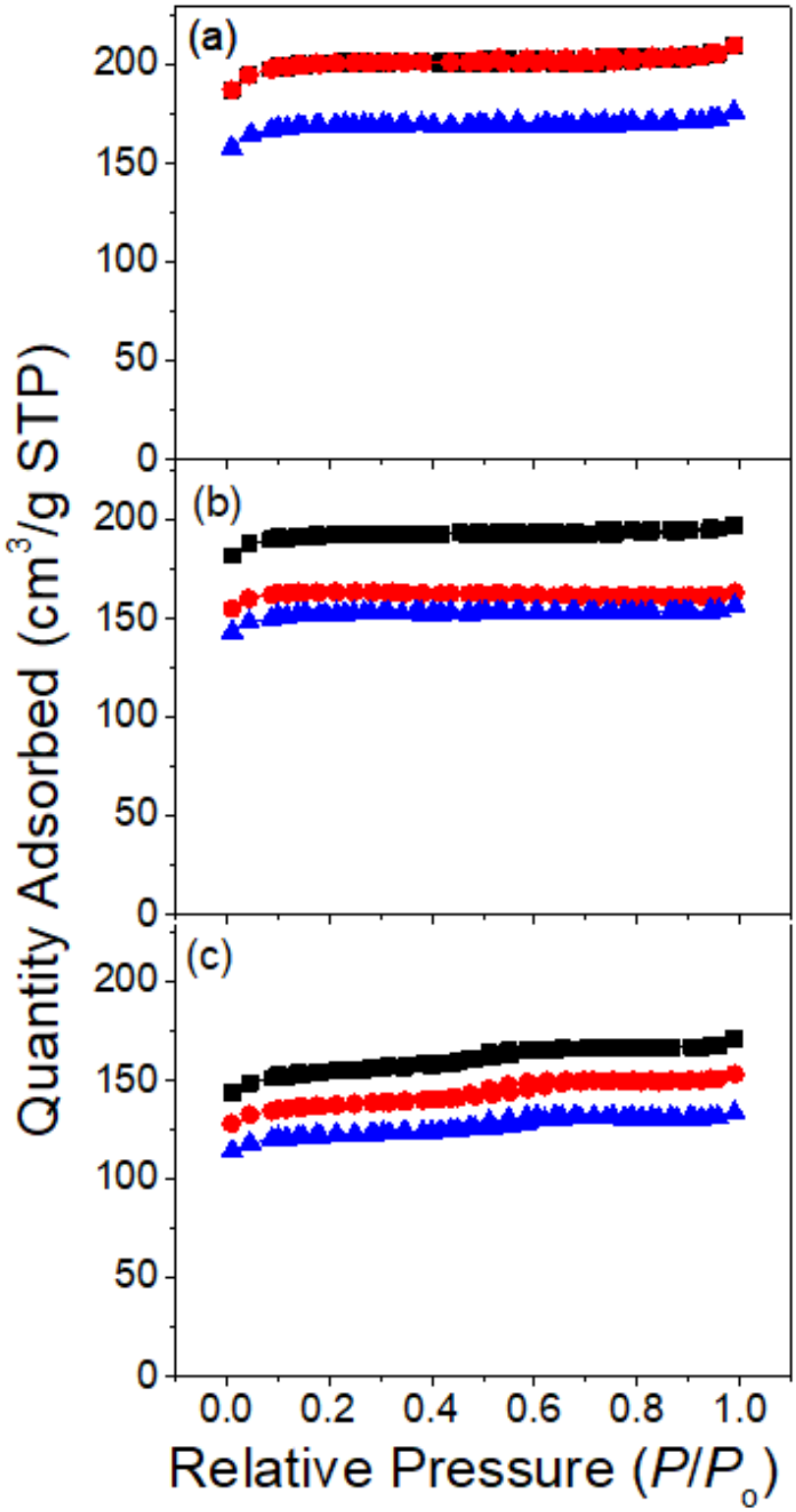


**Figure S6.** $N_2$ sorption isotherms of (a) XZ-Li, (b) XZ-Na, and (c) XZ-K (black: Pristine zeolite, red: After the first reaction, blue: After the fifth reaction).

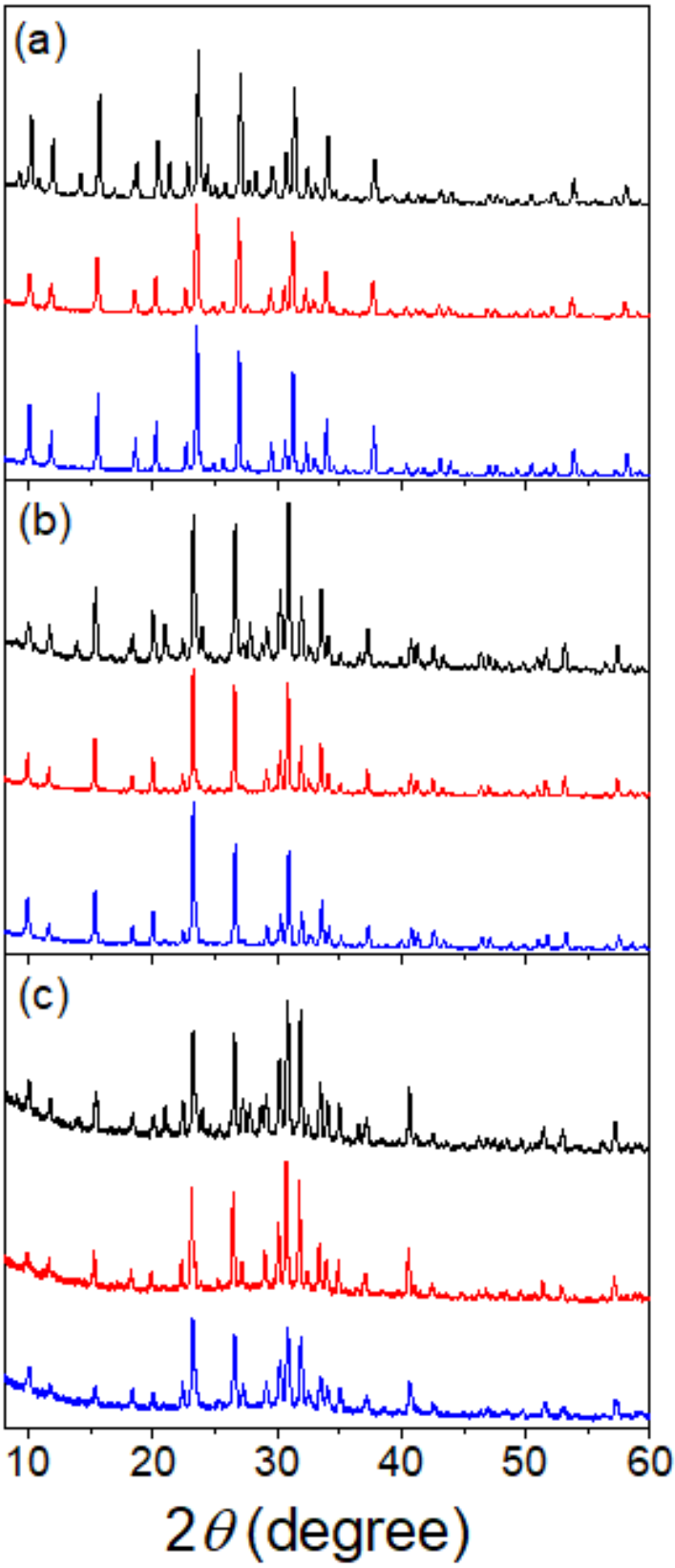


**Figure S7.** XRD patterns of (a) XZ-Li, (b) XZ-Na, and (c) XZ-K (black: Pristine zeolite, red: After the first reaction, blue: After the fifth reaction).

**Table S1.** Structural characterization of XZ-M.

| Catalyst | Atomic ratio (%) | | | | | Surface area ($m^2$ $g^{-1}$) | Pore volume ($cm^3$ $g^{-1}$) | Crystallinity (%) |
|---|---|---|---|---|---|---|---|---|
| | O | Na | Al | Si | K | | | |
| XZ-Li | 60.94 | 1.81 | 11.53 | 16.12 | - | 596 | 0.32 | 84.2 |
| XZ-Na | 64.65 | 10.26 | 10.47 | 14.62 | - | 541 | 0.27 | 87.7 |
| XZ-K | 61.11 | - | 11.56 | 16.23 | 11.10 | 465 | 0.26 | 78.9 |

**Table S2**. Recycling of XZ-M for the direct etherification of glycerol.

| | Cycle No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| XZ-Li | Conversion of glycerol | 86.9 | 58.8 | 87.2 | 83.1 | 81.2 |
| | Yield of DG | 61.2 | 60.1 | 61.0 | 58.2 | 56.8 |
| | Yield of TG | 21.2 | 20.6 | 20.9 | 19.9 | 19.5 |
| XZ-Na | Conversion of glycerol | 79.4 | 73.2 | 74.2 | 73.4 | 71.2 |
| | Yield of DG | 51.4 | 47.4 | 48.0 | 47.5 | 46.1 |
| | Yield of TG | 21.9 | 20.2 | 20.5 | 20.3 | 19.7 |
| XZ-K | Conversion of glycerol | 89.3 | 86.4 | 84.1 | 81.2 | 78.3 |
| | Yield of DG | 47.9 | 45.8 | 44.6 | 43.0 | 41.5 |
| | Yield of TG | 21.9 | 20.7 | 20.2 | 19.5 | 18.8 |