

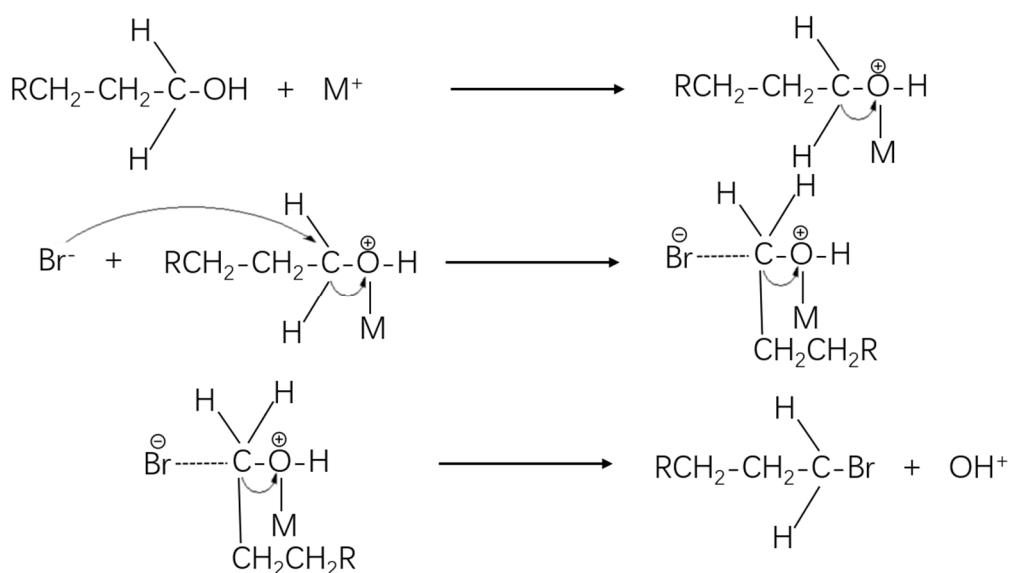
Supporting Information

# Synthesis of Brominated Alkanes via Heterogeneous Catalytic Distillation over $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}/\text{ZrO}_2$

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**Figure S1.**  $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$  catalytic reaction mechanism

**Table S1.** TOF of the  $\text{Al}_2\text{O}_3/\text{SO}_4^{2-}/\text{ZrO}_2$  catalyst and comparison with other catalysts.

Catalyst	T/°C	TOF/h <sup>-1</sup>	Yield/%	Ref.
$\text{H}_3\text{PW}_{12}\text{O}_{40}-$ [bmim][FeCl <sub>4</sub> ]	135	12.5	83	[1]
$\text{SO}_4^{2-}/\text{ZrO}_2-\text{ZnO}$	130	1.79	70.22	[2]
methyl trioctyl ammonium chloride	110	0.83	72.8	[3]
$\text{H}_2\text{SO}_4$	70-130	4.17	93.2	[4]
$\text{Al}_2\text{O}_3/\text{SO}_4^{2-}/\text{ZrO}_2$	110	13.33	96.1	This work

**Table S2.** Conversion substrate application of the Al<sub>2</sub>O<sub>3</sub>/SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst

Substrate	T/°C	Time/h	Yield/%
Ethanol	90	3	93.72
N-propanol	110	3	96.18
Isopropanol	110	3	95.55
N-butanol	120	4	92.26

**References:**

1. Iraj, M. B.; Majid, M.; Shahram, T. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-[bmim][FeCl<sub>4</sub>]: A novel and green catalyst-medium system for microwave-promoted selective interconversion of alkoxyethyl ethers into their corresponding nitriles, bromides and iodides. *C. R. Chim.* **2010**, *13*, 1468-1473.
2. Hu, G. Q.; Tan, L. Y.; Cui, L. M. Synthesis of 1-Bromoocetane Catalyzed by Solid Super Acids SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-ZnO. *Asian. J. Chem.* **2014**, *26*, 1212-1214.
3. Loupy, A.; Pardo, C. A Convenient and Efficient Method for the Conversion of Alkyl Chlorides to the Corresponding Bromides. *Synth. Commun.* **1988**, *18*, 1275-1281.
4. Kamm, O.; Marvel, C. S. Preparation of Alkyl and Alkylene bromides. *J Am Chem Soc.* **1920**, *42*, 299-309.