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# Hydrogenation of $CO_2$ to LPG over CuZnZr/MeSAPO-34 Catalyst

Mingliang Tong[a+], Emmerson Hondo[a+], Linet Gapu Chizema[a], Ce Du[a,c], Qingxiang Ma[b], Shuting Mo[a], Chengxue Lu[a], Peng Lu[a,b]*, Noritatsu Tsubaki [d]*

*a Zhejiang Provincial Key Lab for Chem. & Bio. Processing Technology of Farm Product, School of Biological and Chemical Engineering, Zhejiang University of Science and Technology, Hangzhou, 310023, PR China*

*b State Key Laboratory Cultivation Base of Natural Gas Conversion, Ningxia University, Yinchuan 750021, PR China*

*c Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan*

[+]These authors have equal contribution

*Corresponding authors

Email: lvpeng0830@zust.edu.cn (Peng Lu)

Email: tsubaki@eng.u-toyama.ac.jp (Noritatsu Tsubaki)

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**Supporting information**

**Table S1.** $NH_3$-TPD results of *x*%ZrSAPO-34 catalysts

| Catalysts | Weak acid | | Strong acid | | Total amount (mmol·g$^{-1}$) |
|---|---|---|---|---|---|
| | Temperature (°C) | Acid amount (mmol·g$^{-1}$) | Temperature (°C) | Acid amount (mmol·g$^{-1}$) | |
| 1%ZrSAPO-34 | 175 | 0.44 | 392 | 0.31 | 0.75 |
| 3%ZrSAPO-34 | 188 | 0.34 | 362 | 0.24 | 0.58 |
| 5%ZrSAPO-34 | 176 | 0.36 | 368 | 0.18 | 0.54 |
| 7%ZrSAPO-34 | 172 | 0.33 | 360 | 0.11 | 0.44 |
| 10%ZrSAPO-34 | 172 | 0.25 | 359 | 0.09 | 0.34 |

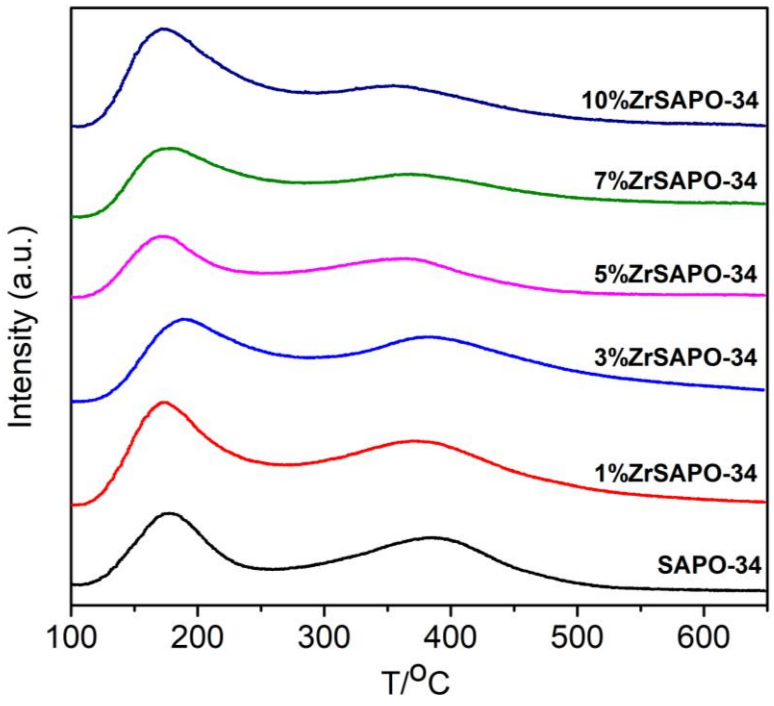


**Fig. S1.** $NH_3$-TPD profiles of *x*ZrSAPO-34 zeolite

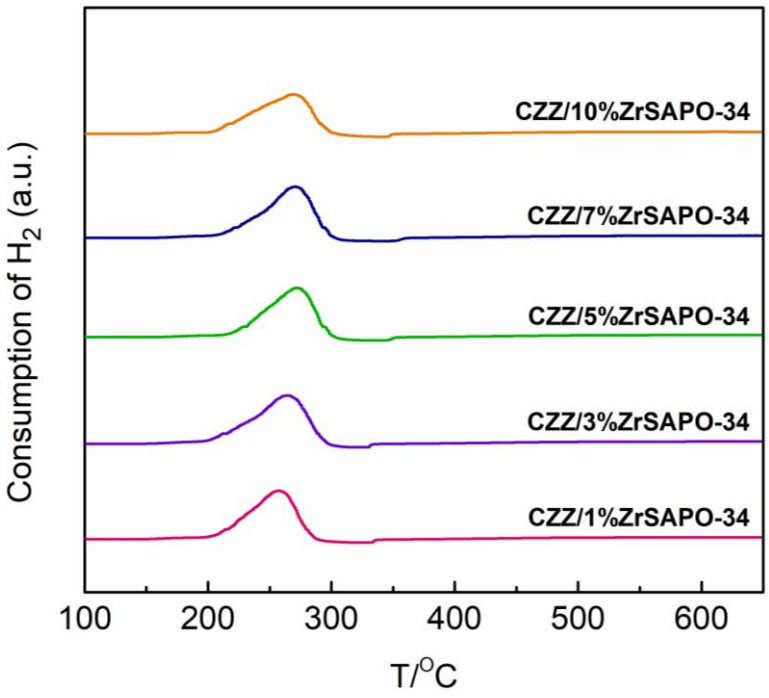


**Fig. S2.** $H_2$-TPR profiles of CZZ/*x*ZrSAPO-34 zeolite

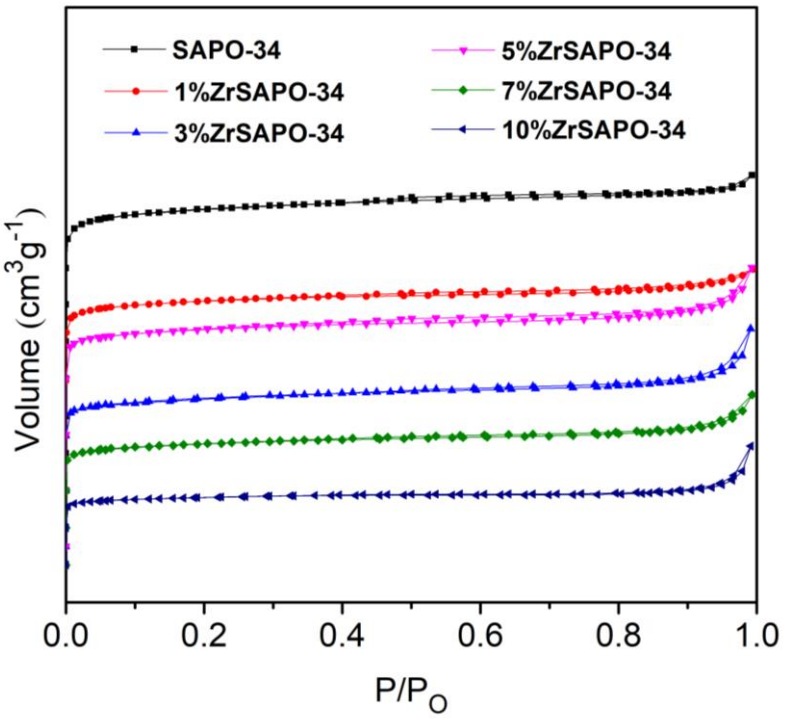


**Fig. S3.** $N_2$ adsorption-desorption isotherms of SAPO-34 and *x*ZrSAPO-34 zeolite catalysts

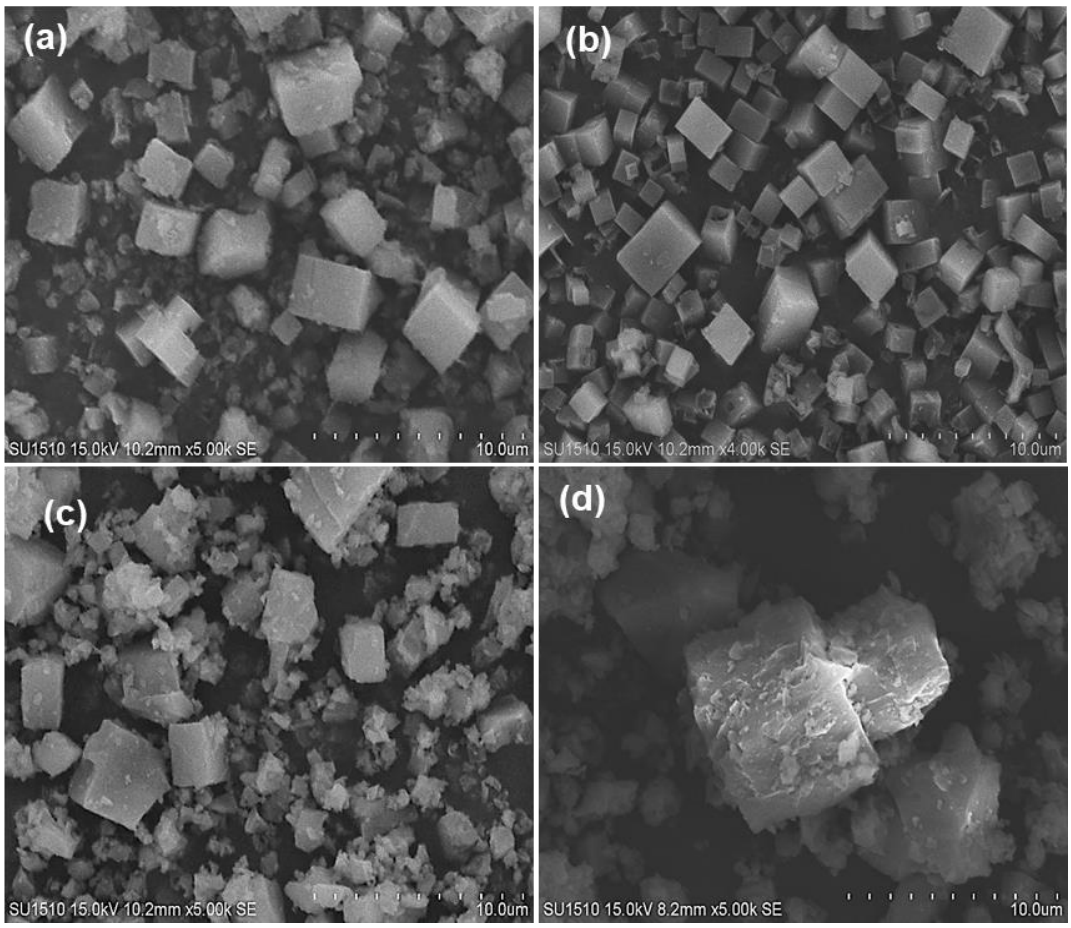


**Fig. S4.** SEM images of (a) 1%ZrSAPO-34; (b) 3%ZrSAPO-34; (c) 7%ZrSAPO-34; (d) 10%ZrSAPO-34

**Table S2.** Textural properties of the catalysts

| Catalysts | BET ($m^2g^{-1}$) | Total pore volume ($cm^{-3}g^{-1}$) |
|---|---|---|
| 1%ZrSAPO-34 | 305 | 0.195 |
| 3%ZrSAPO-34 | 263 | 0.165 |
| 7%ZrSAPO-34 | 190 | 0.109 |
| 10%ZrSAPO-34 | 136 | 0.072 |

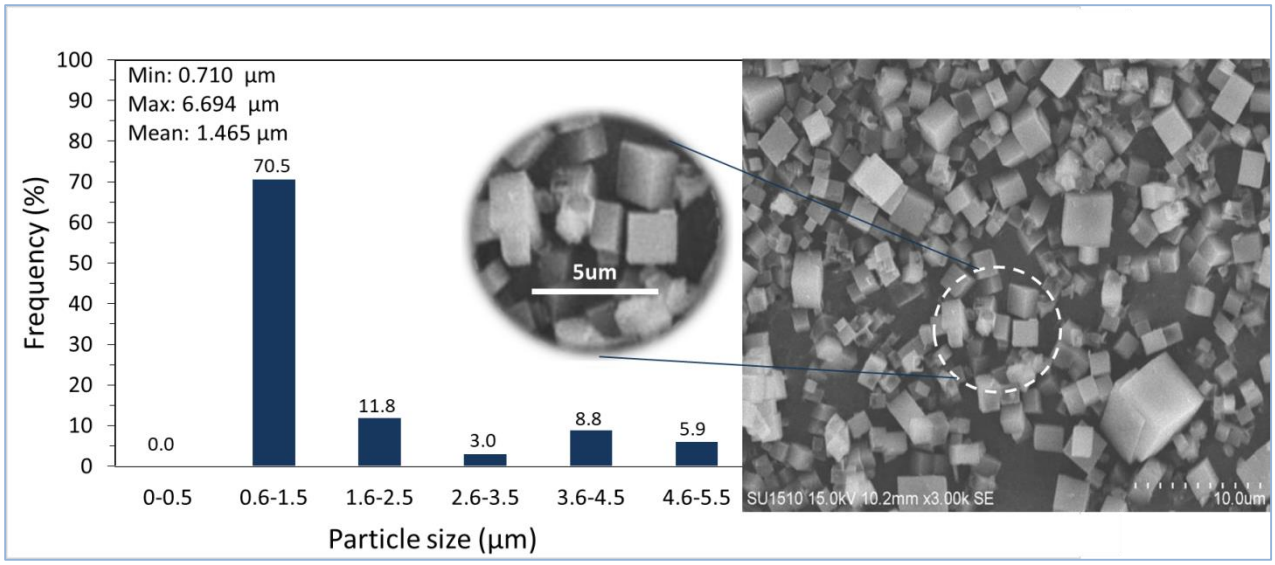


**Fig. S5.** Particle size distribution histogram of 5%ZrSAPO-34 catalyst

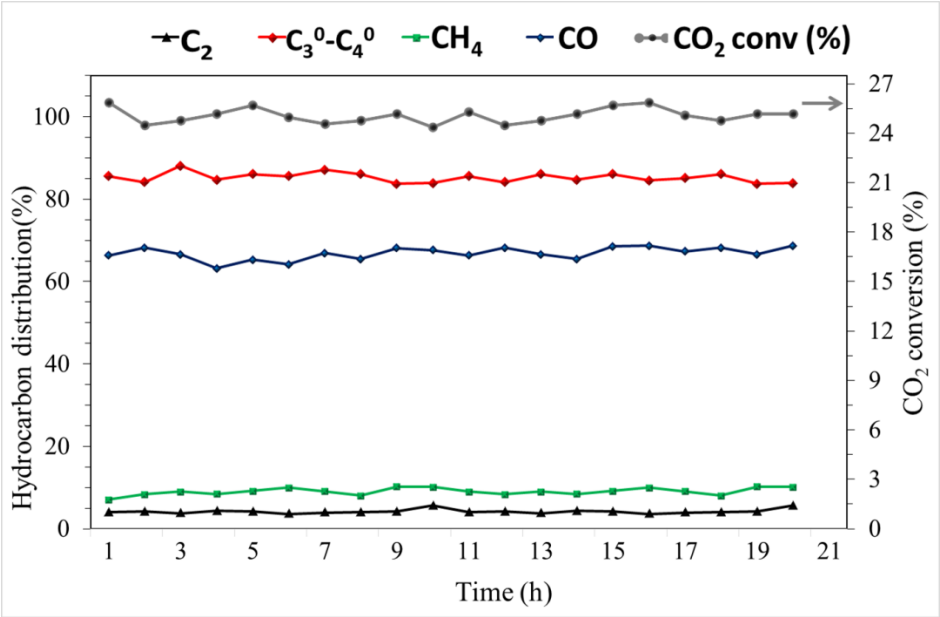


**Fig. S6**. Catalytic activity of CZZ/5%ZrSAPO-34 catalyst; Reaction conditions: pressure = 2.0 MPa, reaction temperature =350 ºC, GHSV=4200 $h^{-1}$, $C_3^0$-$C_4^0$ paraffins, ratio of CZZ to zeolite = 1, *all hydrocarbon selectivities were calculated CO free

**Table S3.** Effect of Zr concentration on catalytic performance

| Catalyst | $CO_2$ conversion (%) | Selectivity (%) | | Hydrocarbons distribution (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| Zr (wt%) | | CO | HC | $CH_4$ | DME/ ($CH_3OH$) | $C_2$ | $C_3$-$C_4$ | $C_{5+}$ |
| 0 | 24.0 | 58.6 | 41.4 | 22.8 | 1.5 | 0.6 | 75.1 | 0.6 |
| 1 | 23.9 | 68.2 | 41.4 | 18.8 | 0.0 | 0.9 | 78.7 | 0.3 |
| 3 | 24.2 | 71.4 | 28.6 | 18.1 | 0.0 | 0.0 | 80.9 | 0.0 |
| 5 | 25.7 | 68.4 | 31.6 | 9.7 | 0.0 | 4.2 | 86.1 | 0.0 |
| 7 | 24.4 | 73.5 | 26.5 | 21.5 | 0.0 | 3.3 | 75.2 | 0.0 |
| 10 | 24.2 | 76.3 | 23.7 | 23.3 | 0.0 | 5.1 | 71.6 | 0.0 |

Reaction conditions: Pressure = 2.0 MPa, reaction temperature = 350 ºC, GHSV=4200 $h^{-1}$, $C_2^0$-$C_4^0$ paraffins, TOS=360 mins, *all hydrocarbon selectivities were calculated CO free.

**Table S4.** Effect of metal oxide to zeolite ratio

| Catalyst | $CO_2$ conversion (%) | Selectivity (%) | | Hydrocarbons distribution (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | CO | HC | $CH_4$ | DME/ ($CH_3OH$) | $C_2$ | $C_3$-$C_4$ | $C_{5+}$ |
| CZZ/SAPO-34-0.5 | 24.8 | 61.1 | 38.9 | 26.2 | 3.7 | 1.1 | 68.2 | 0.8 |
| CZZ/SAPO-34-1 | 24.0 | 58.6 | 41.4 | 22.8 | 1.5 | 0.6 | 75.1 | 0.6 |
| CZZ/SAPO-34-2 | 24.4 | 73.1 | 26.9 | 30.5 | 2.5 | 1.2 | 65.1 | 0.7 |
| CZZ/5%ZnSAPO-34-0.5 | 24.6 | 64.4 | 35.6 | 13.8 | 2.2 | 0.0 | 84.0 | 0.0 |
| CZZ/5%ZrSAPO-34-1 | 25.7 | 68.4 | 31.6 | 9.7 | 0.0 | 4.2 | 86.1 | 0.0 |
| CZZ/5%ZrSAPO-34-2 | 24.1 | 75.5 | 24.5 | 12.0 | 3.3 | 0.0 | 83.5 | 1.2 |

Reaction conditions: Pressure = 2.0 MPa, reaction temperature = 350 ºC, GHSV=4200 $h^{-1}$, $C_2^0$-$C_4^0$ paraffins, TOS=360 mins, *all hydrocarbon selectivities were calculated CO free.