Supporting Information

Facile Preparation of Ni-imidazole Compound with High Activity for Ethylene Dimerization

Zhaohui Liu,[1] Guanxing Li,[2] Mohammed R. Alalouni,[3] Ziyin Chen,[4] Xinglong Dong,[5,*] Jianjian Wang,[1] Cailing Chen[2,*]

[1] School of Chemistry and Chemical Engineering & Institute of Advanced Interdisciplinary Studies, Multi-scale Porous Materials Center, Chongqing University, Chongqing, 401331, China.

[2] Advanced Membranes and Porous Materials (AMPM) Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

[3] Catalyst Center of Excellence (CCoE), Research and Development Center, Saudi Aramco, Dhahran 31311, Saudi Arabia

[4] Gas and Particulate Metrology Group, National Physical Laboratory, Teddington, London TW11 0LW, UK

[5] School of Chemistry, University of Lincoln, Brayford Pool, Lincoln, LN6 7TS, UK

*Corresponding authors: cailing.chen@kaust.edu.sa (Dr. C. Chen); xinglong.dong.uk@gmail.com (Dr. X. Dong)

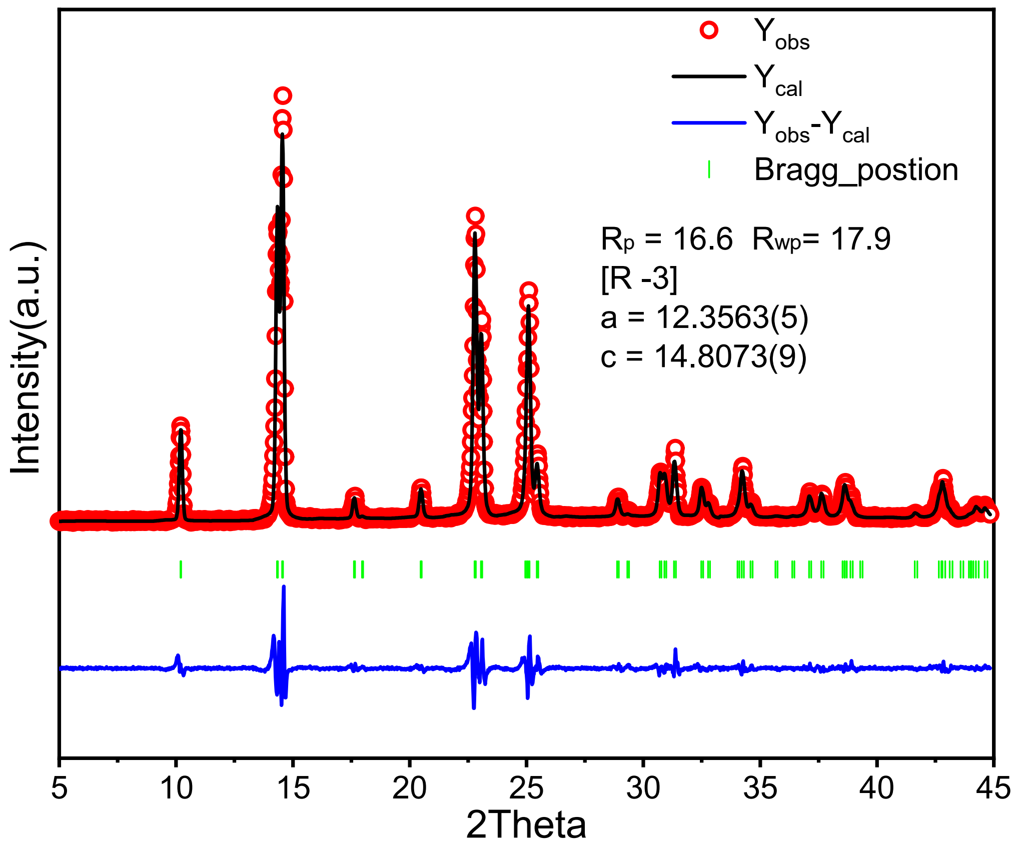

Fig. S1 XRD patterns of Ni-imidazole with the experimental profiles (dot line, red), Pawley refined profiles (solid black line), Bragg positions (green), and differences between experimental and refined PXRD patterns (blue).

Note: we performed an XRD Rietveld refinement for this sample and the fitting results was indexed to a trigonal R-3 space group with a unit cell of a=12.36 Å, c = 14.81 Å (R_P=5.76% and R_{WP}=7.95%), which perfectly matches the previously reported structure.

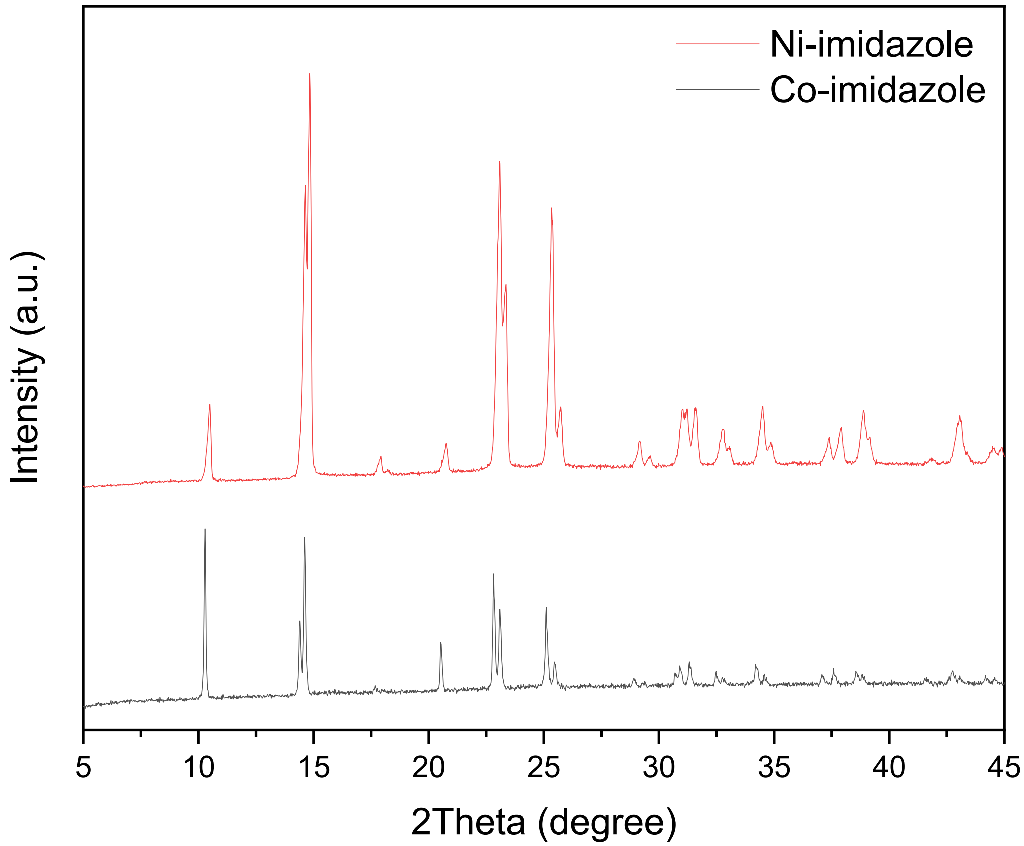

Fig. S2 XRD patterns of Ni-imidazole and Co-imidazole.

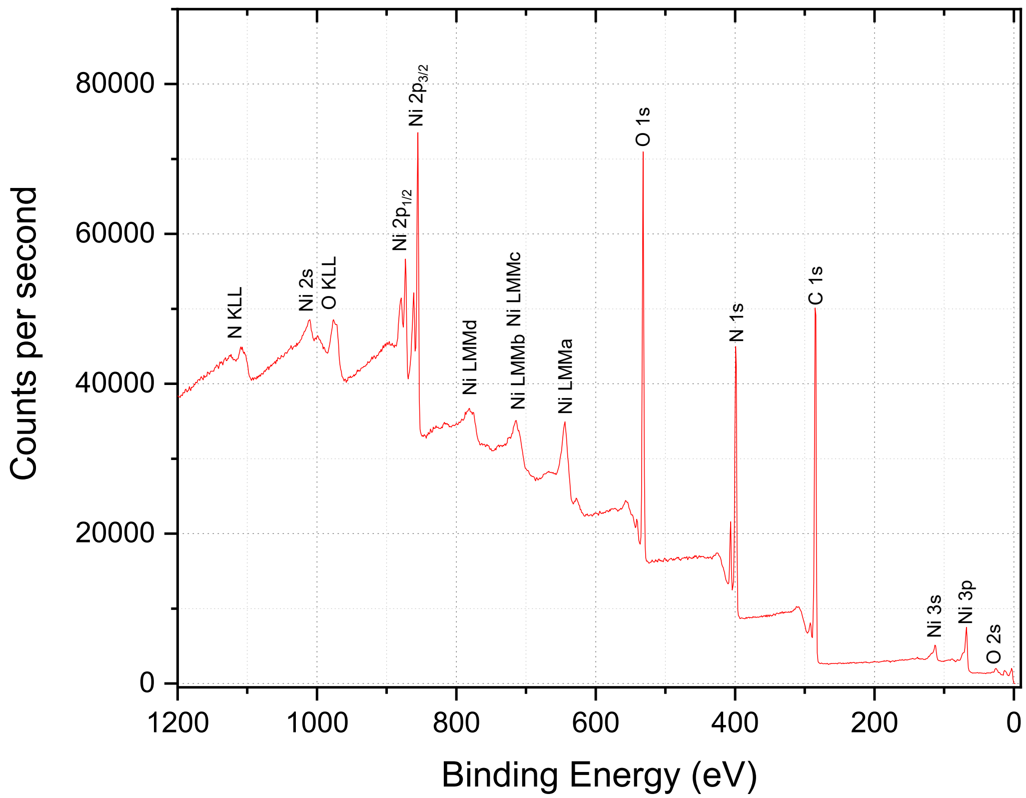

Fig. S3 XPS survey scan of Ni-imidazole.

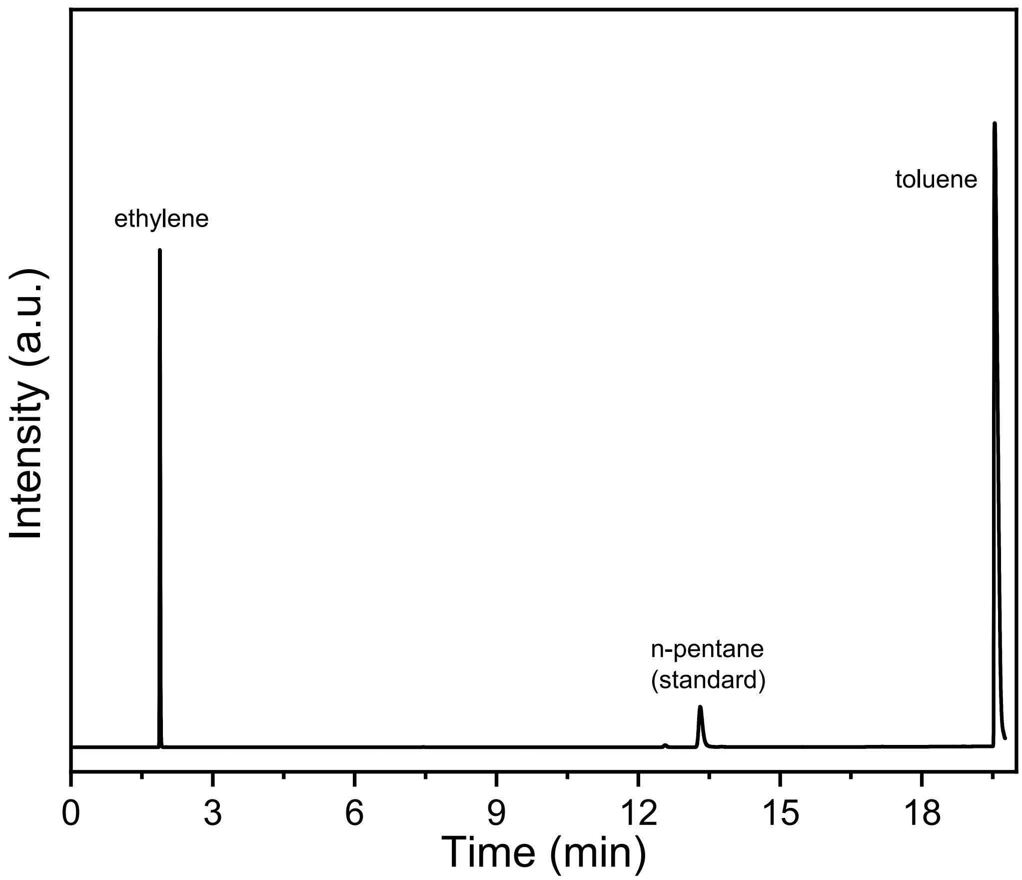

Fig. S4 Gas Chromatography record of blank test. Ethylene dimerization as feed gas, toluene as solvent, MAO as co-catalyst under 35 °C and 30 bar of ethylene. No butenes or hexenes were detected, suggesting that no catalytic performance without catalysts.

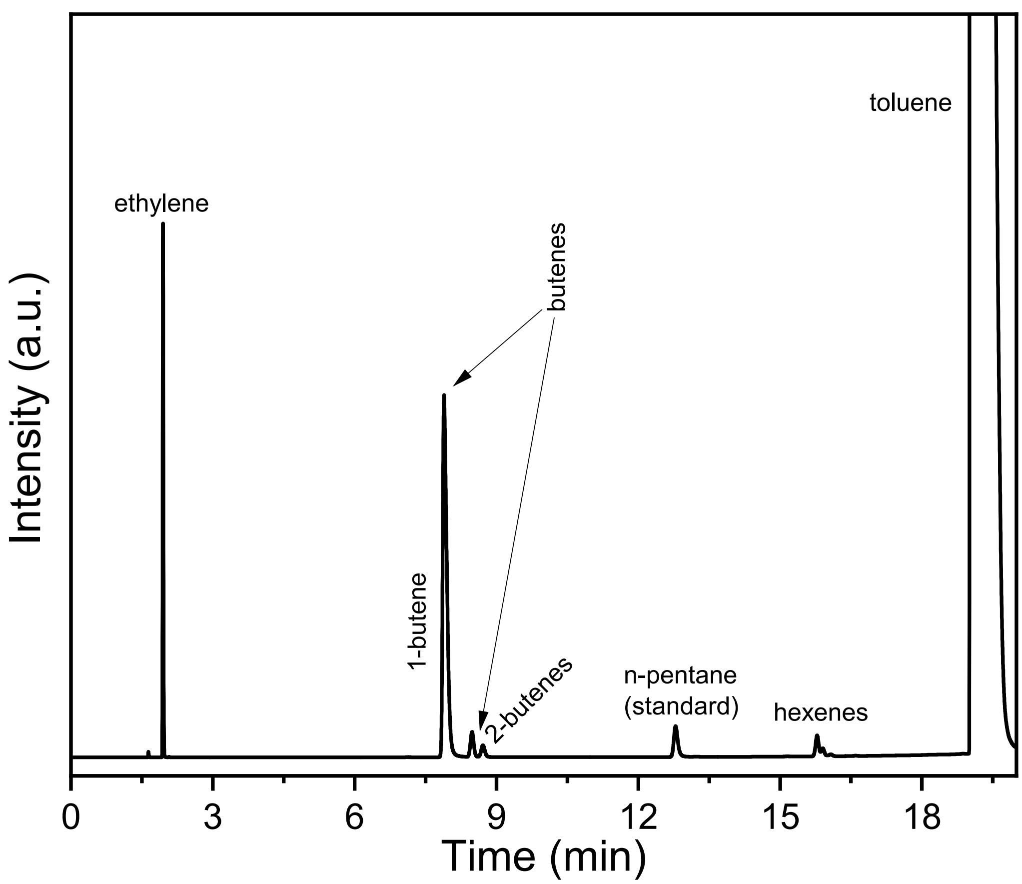

Fig. S5 Gas Chromatography record of ethylene dimerization over Ni-complex.

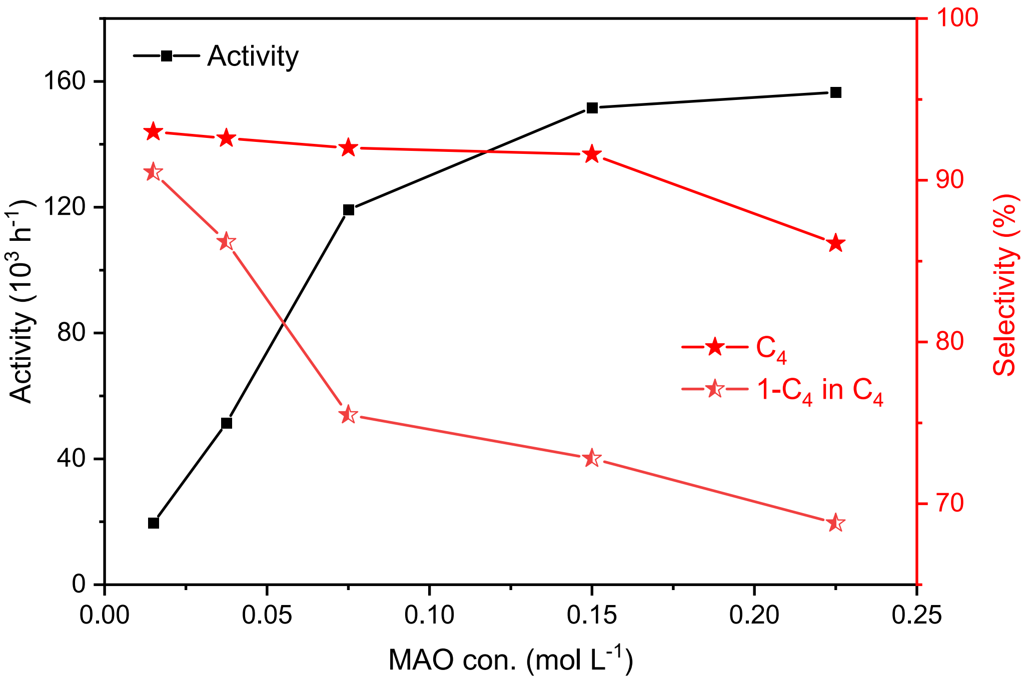

Fig. S6 MAO concerntration dependent activity and selectivity of ethylene dimerization catalyzing by Ni-imidazole in the liquid phase

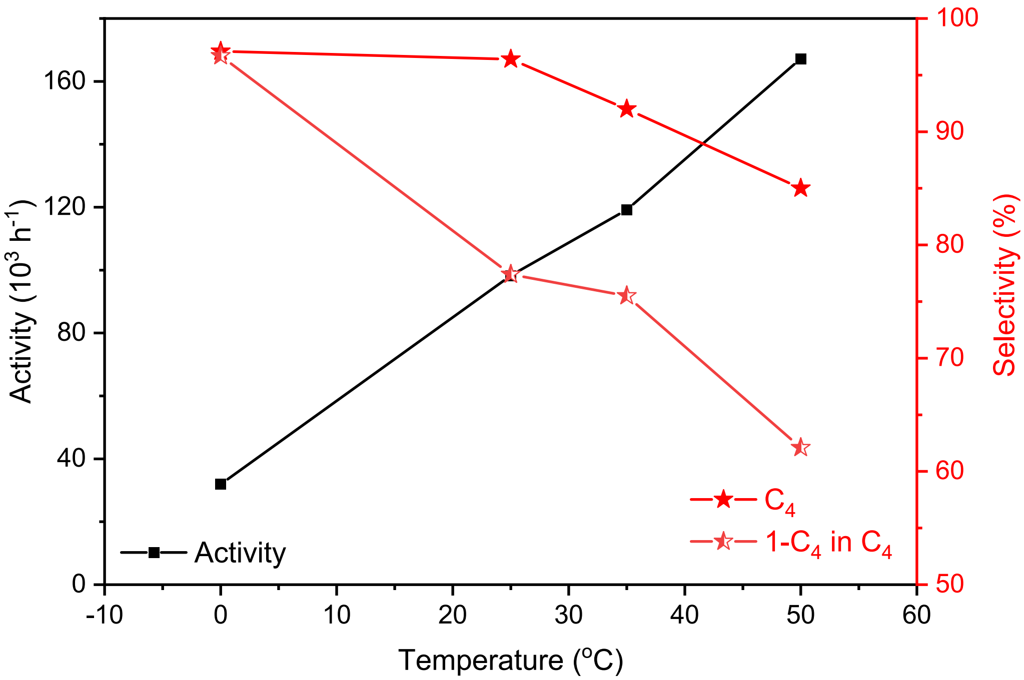

Fig. S7 Temperature dependent activity and selectivity of ethylene dimerization catalyzing by Ni-imidazole in the liquid phase

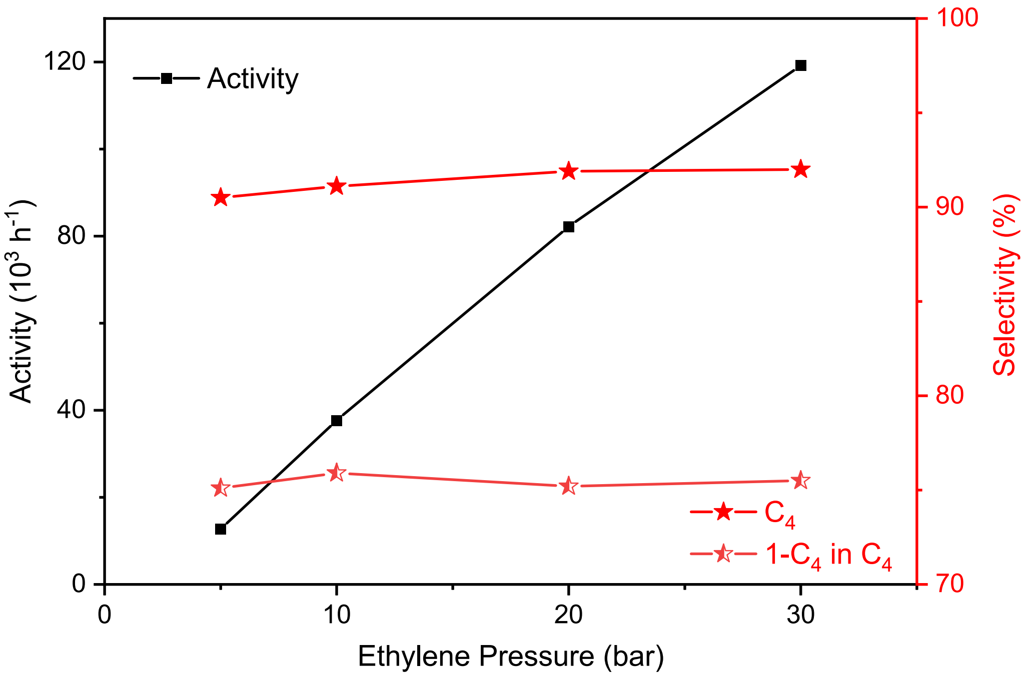

Fig. S8 Ethylene pressure dependent activity and selectivity of ethylene dimerization catalyzing by Ni-imidazole in the liquid phase

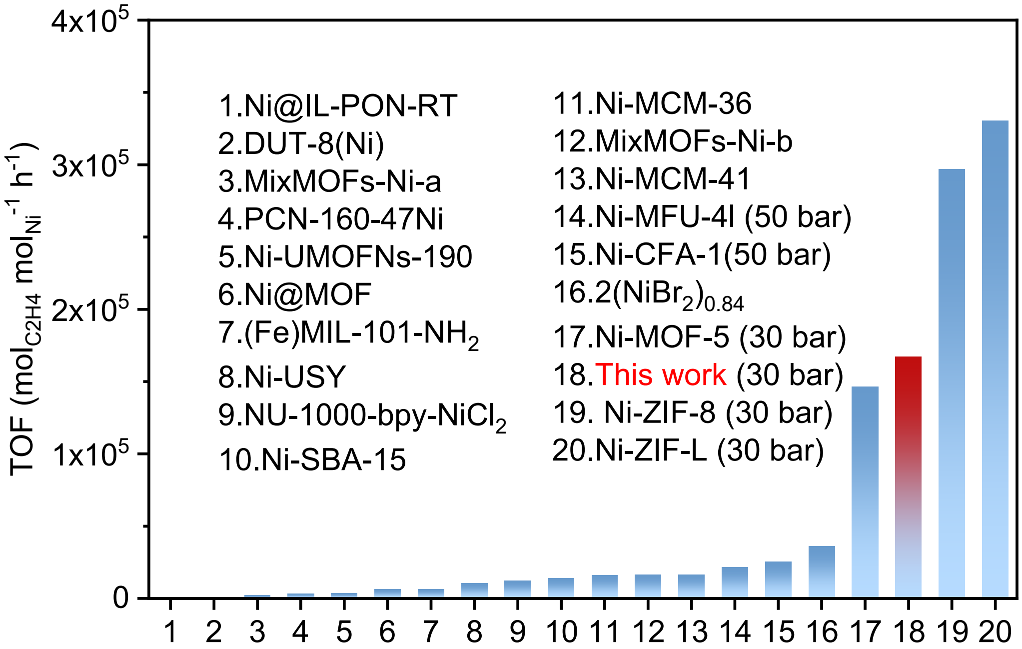

Fig. S9 Comparison of turnover frequency of various high-performance heterogeneous catalysts for ethylene dimerization.

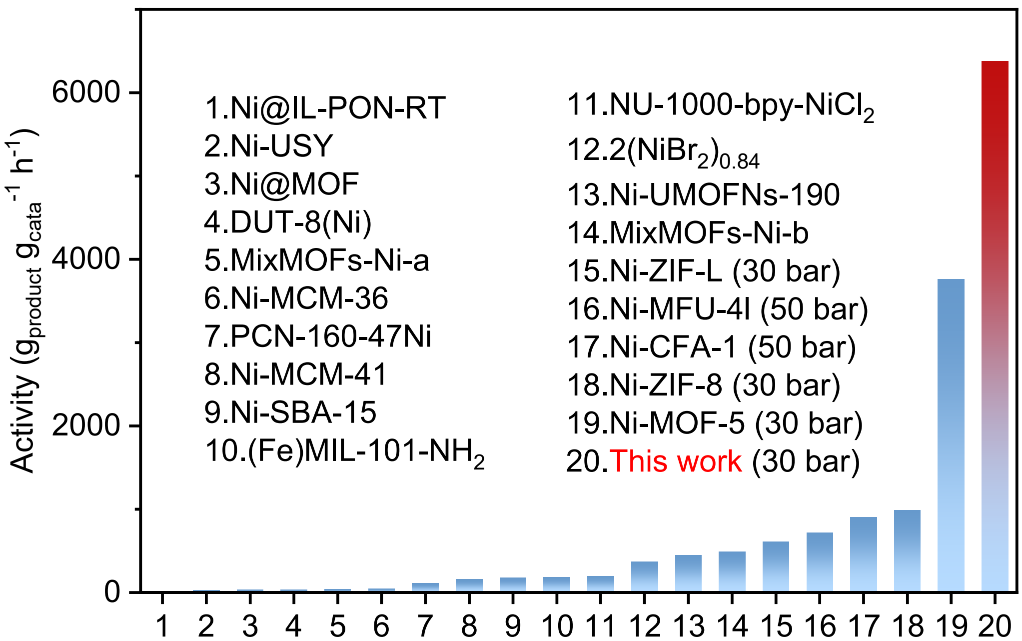

Fig. S10 Comparison of mass activity of various high-performance heterogeneous catalysts for ethylene dimerization.

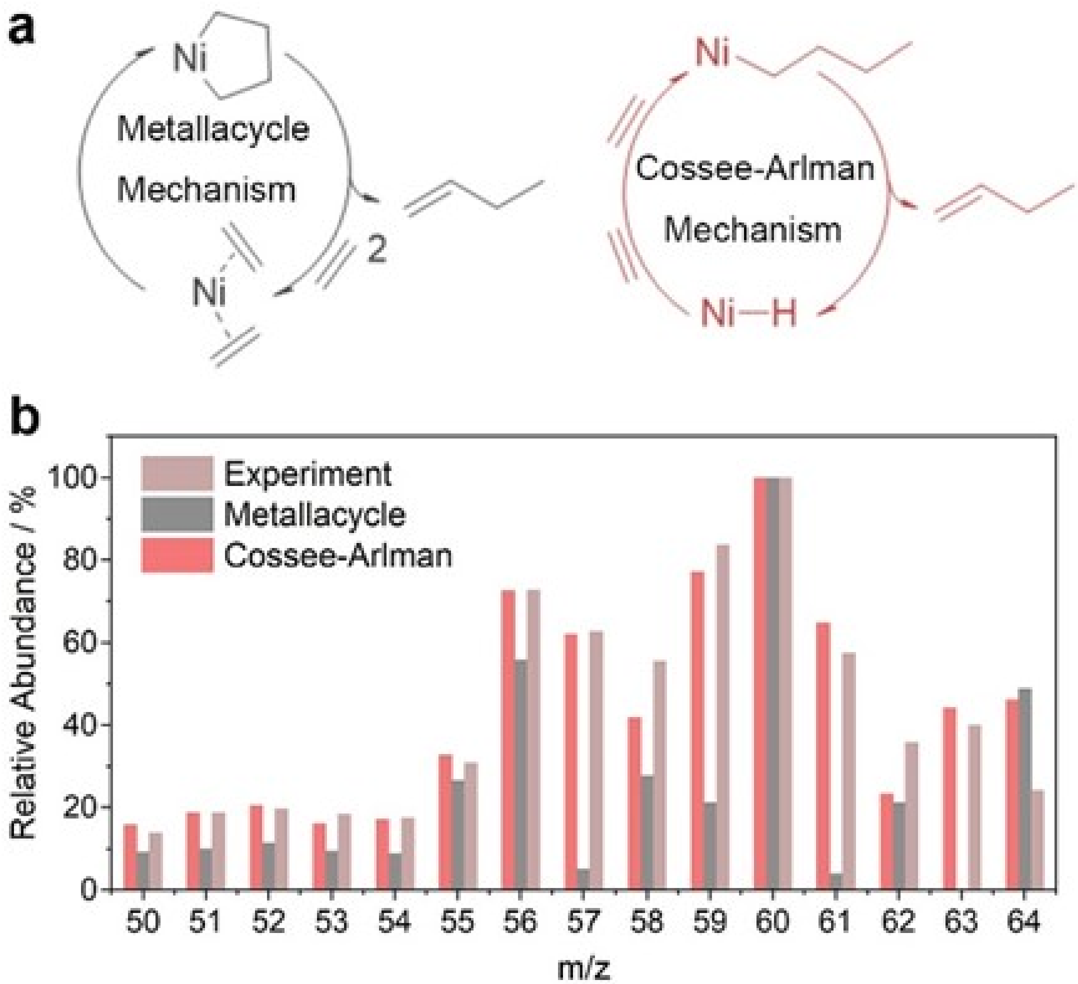

Fig. S11 (a) Two proposed catalytic ethylene dimerization mechanism. (b) The fragmentation patterns of 1-butene from a mixed 1:1 C2H4/C2D4 gas, based on experimental results and predictions from the proposed mechanisms.

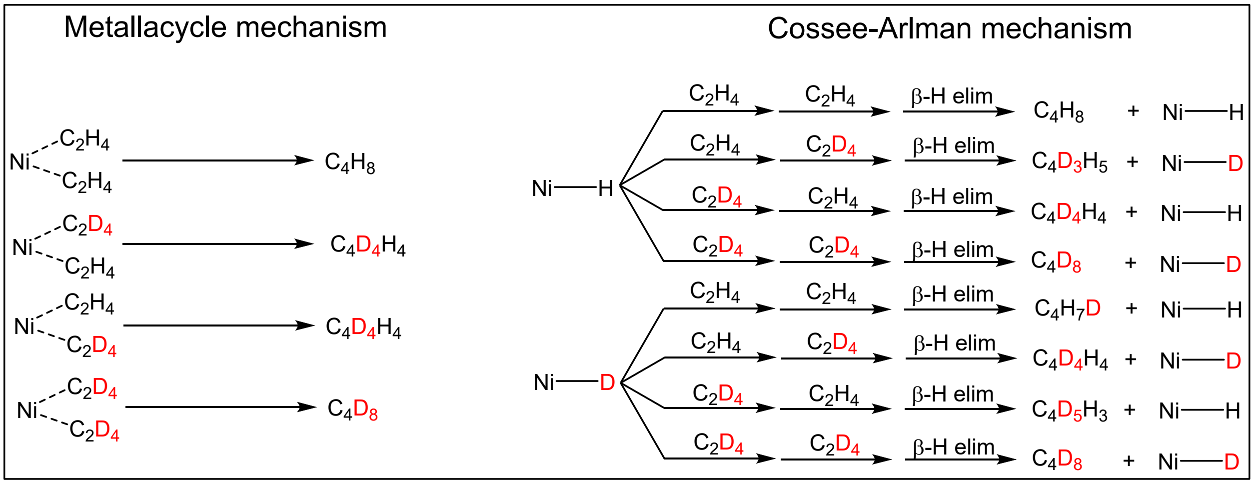

Fig. S12 Ethylene dimerization to butene isotopomers via the Metallacycle and Cossee-Arlman mechanisms.

Note: The metallacycle mechanism and Cossee–Arlman mechanism can be distinguished by designing an isotope labeling experiment, that is, ethylene dimerization experiments using a 1:1 mixture of ethylene (C_2H_4) and perdeutero ethylene (C_2D_4) as the feed gas. Theoretically, isotope labeling experiment results should be in a 1:2:1 ratio of C_4H_8, $C_4H_4D_4$ and C_4D_8 if the reaction proceeds according to the metallacycle mechanism, whereas the result should be in a 1:1:1:2:1:1:1 ratio of C_4H_8, C_4H_7D, $C_4H_5D_3$, $C_4H_4D_4$, $C_4H_3D_5$, C_4HD_7, and C_4D_8 if the reaction proceeds according to the Cossee–Arlman mechanism. Isotope products can be distinguished by analyzing their fragmentation peaks using mass spectrometry (Fig. S11).