Supplementary Information

Unraveling the original active sites of amorphous silica-alumina supported nickel catalyst for highly efficient ethylene oligomerization

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Supplementary Figures

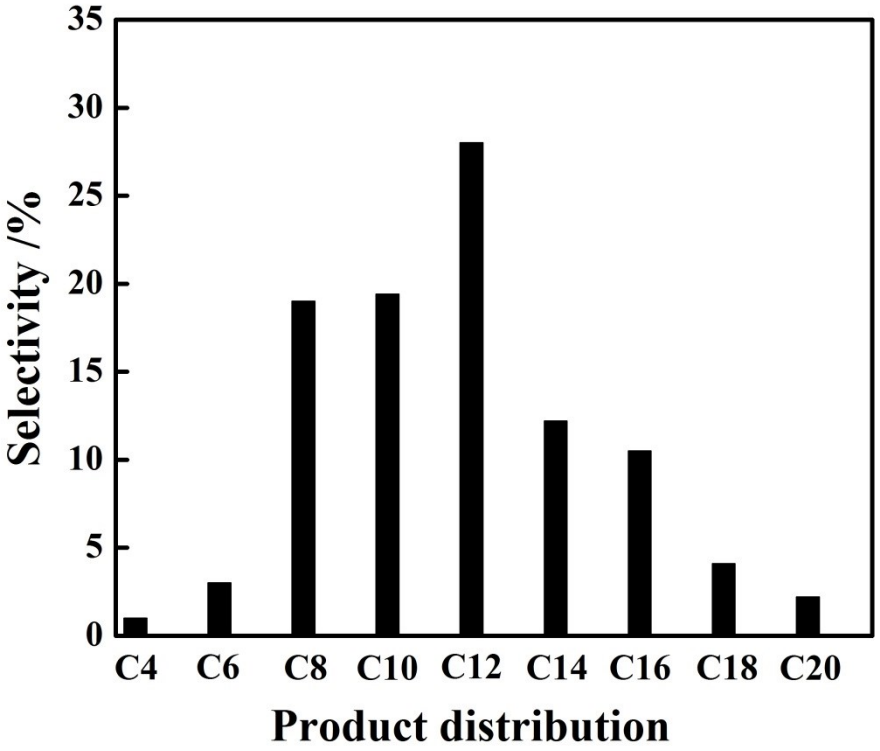

Fig. S1 The detailed product distribution of ethylene oligomerization on the N_2-Ni/ASA catalyst. Reaction conditions: 60 ^{o}C, 3.0 MPa, 0.5 g catalyst, 50% C_2H_4 - 50% N_2 with a flowrate of 15 mL min^{-1}.

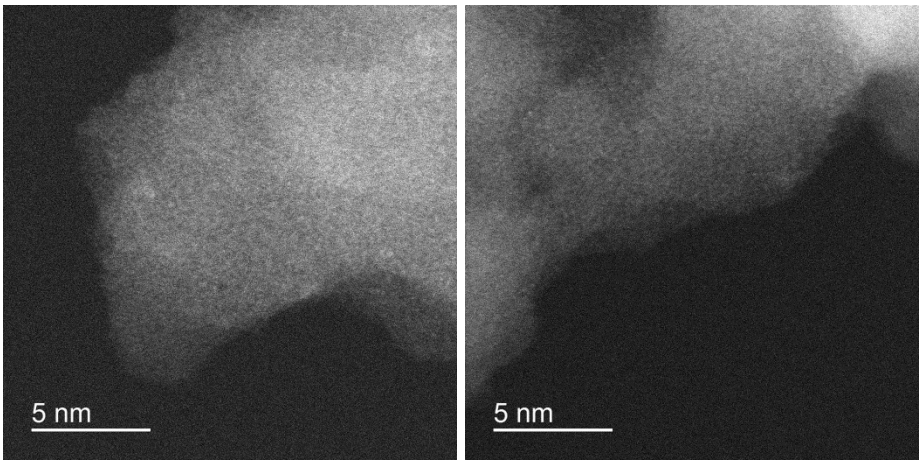

Fig. S2 HAADF-STEM images of the N_2-Ni-ASA sample.

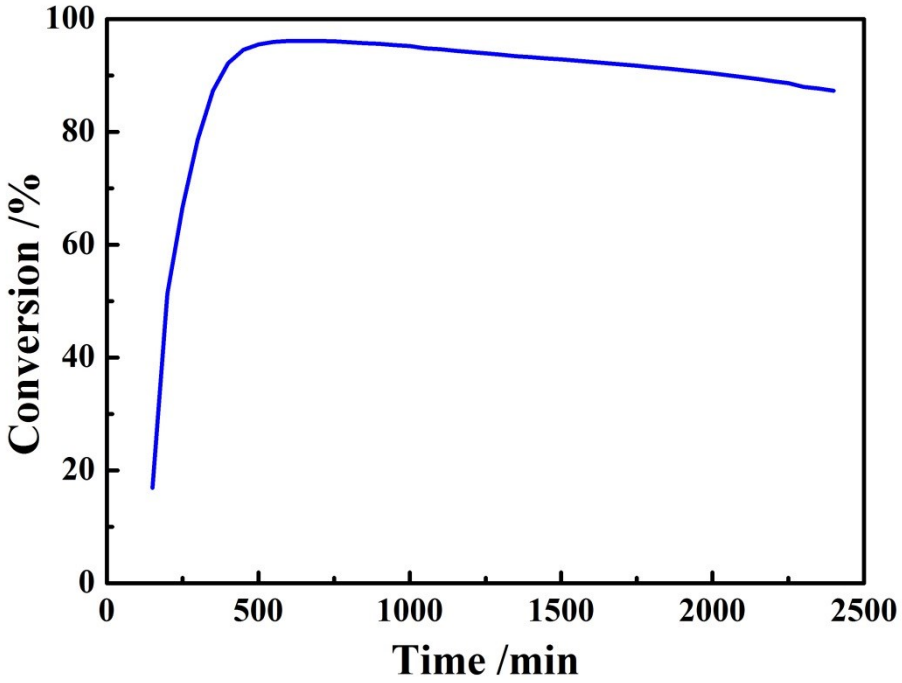

Fig. S3 The stability testing of the N_2-pretreated catalyst. Reaction condition: 0.5 g catalyst, reaction temperature is 60 ^oC, reaction pressure is 3 MPa, 50% C_2H_4 - 50% N_2 with a flowrate of 15 mL min^{-1}.

For the calculation of if the product follows a Schulz-Flory type distribution or not, the following equation of Schulz–Flory equation was used:

$\log(Wn/n) = n \log\alpha + \log((1-\alpha)2/\alpha)$

where, n is the number of monomer units in the oligomer, Wn is the mass fraction of the n^{th} oligomer, and α is the chain growth probability (growth factor).

We have further tested the ethylene oligomerization performance on the N_2-Ni/ASA catalyst at a high MHSV of 2.25 h^{-1}. Upon the product distribution (see Fig. S4), we plotted log(Wn/n) as a function of (n-1) by using the above equation, as shown in Fig S5. There is almost a linear relationship. Therefore, the product distribution at a high MHSV of 2.25 h^{-1} (by reducing the residence time) follows Schulz-Flory type distribution. A metallacycle mechanism for the oligomerization of ethylene over Ni^+ ions in such N_2-Ni/ASA catalyst can be proposed.

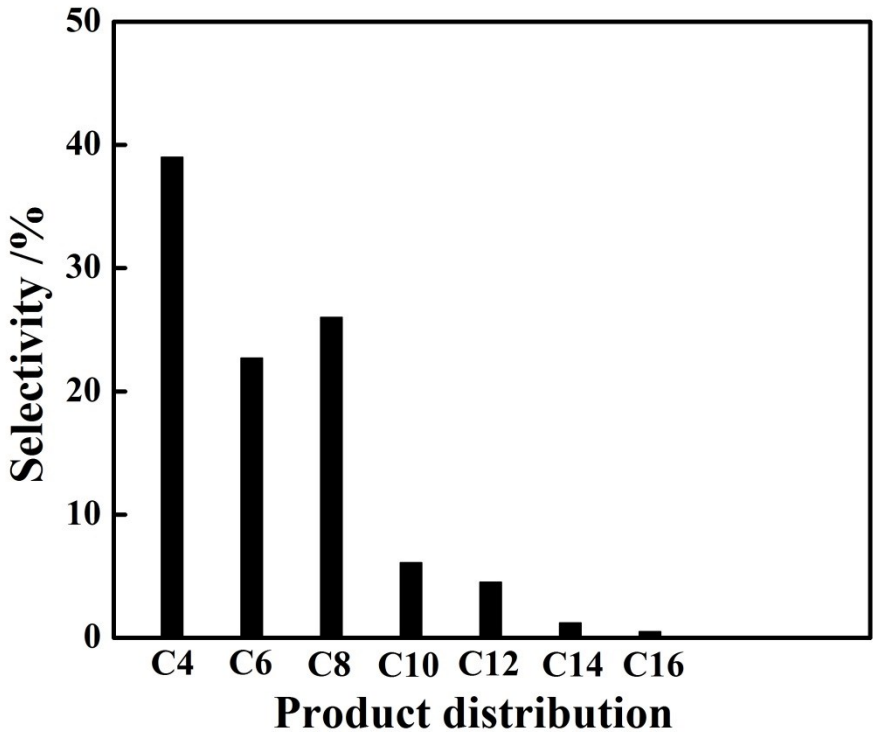

Fig. S4 The detailed product distribution of ethylene oligomerization on the N_2-Ni/ASA catalyst. Reaction conditions: 60 °C, 3.0 MPa, 0.5 g catalyst, 50% C_2H_4 - 50% N_2 with a flowrate of 15 mL min^{-1}, MSHV = 2.25 h^{-1}.

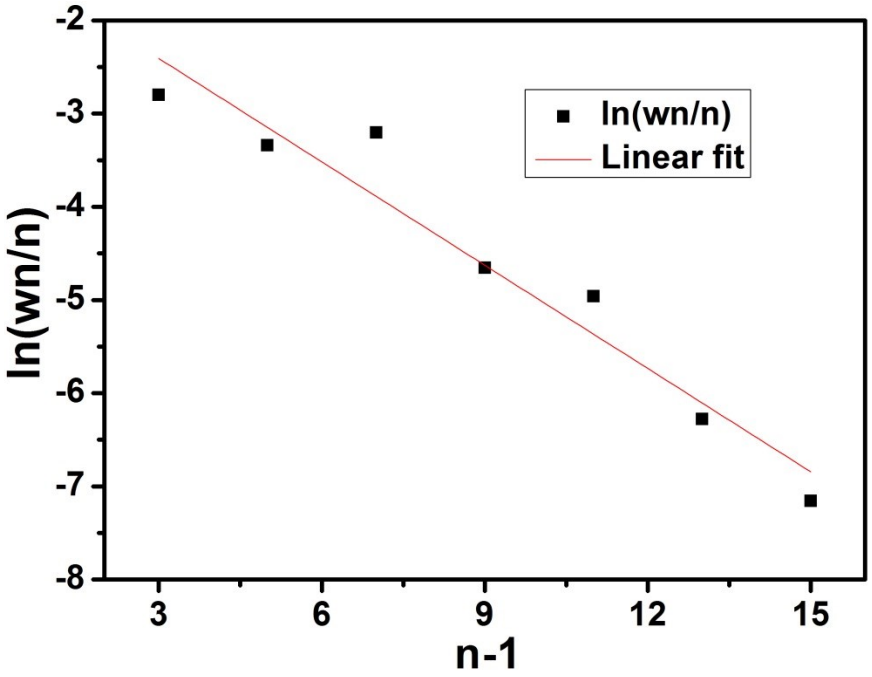

Fig. S5 The calculation of carbon chain growth probability. Reaction conditions: 60 ^{o}C, 3.0 MPa, 0.5 g catalyst, 50% C_2H_4 - 50% N_2 with a flowrate of 15 mL min^{-1}, MSHV = 2.25 h^{-1}.

Supplementary Tables

Table S1. Linear and branched C_4 - C_{12} products of the ethylene oligomerization reaction.

Sample	C_4 /%		C_6 /%		C_8 /%		C_{10} /%		C_{12} /%	
	LO	BO	LO	BO	LO	BO	LO	BO	LO	BO
N_2-pretreated	69.4	30.6	14.8	85.2	12.1	87.9	0.8	99.2	0.9	99.1

Note: LO means linear olefins; BO means branched olefins