Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Information

Boosting Acidity of SAPO-11 through Silicon Source Regulation: Towards High-Performance Ni-Based Catalysts for n-Dodecane Hydroisomerization

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1 Supplementary Synthesis Methods

In a typical synthesis of SAPO-11 (M. Y. Kim, K. Lee and M. Choi, Journal of Catalysis, 2014, 319, 232-238.), 36.7 g of aluminium iso-propoxate (AIP, 99%, Inno-Chem) was added to 77.8 g of deionized water and stirred at ambient temperature for 2 h. Then, 20.7 g of phosphoric acid (H_3PO_4, 85% aqueous solution, Hushi) was added dropwise, followed by continuous agitation for another 1 h. Subsequently, 10.9 g of di-n-propylamine (DPA, 99%, Hushi) was added as the structure-directing agent, followed by different amounts silicon sources (**TEOS, Silica sol and Fumed silica**). The precursor mixture was mechanically blended for 5 h to form a uniform synthesis gel. The as-prepared gel was heated and kept in a 90 °C water bath for 1 h to remove the isopropanol generated from the hydrolysis of AIP. The final molar composition of the precursor gel was fixed at 1.0 Al_2O_3 : 1.0 P_2O_5 : 1.2 DPA : 0.25 SiO_2 : 50 H_2O. After pre-treatment, the synthetic gel was transferred to a stainless-steel autoclave equipped with a tetrafluoro-polyethylene liner and subjected to rotary hydrothermal crystallization at 185 °C for 48 h under a rotating speed of 30 rpm. After crystallization, the solid product was filtered and repeatedly washed with deionized water, dried at 100 °C overnight, and calcined at 550 °C for 12 h to obtain white powdered SAPO-11 denoted as S11-TEOS、S11-Silica sol and S11- Fumed silica.

2 Existence forms of silicon atoms in SAPO-11 framework

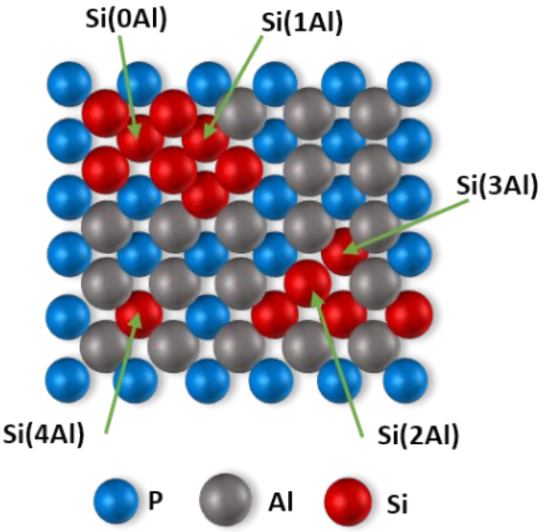

Figure S1 Schematic diagram of silicon species in the SAPO-11 molecular sieve framework.

3 Properties of SAPO-11 prepared from different silicon sources

The three samples displayed distinct characteristic diffraction peaks in their XRD patterns as displayed in Figure S2, all peaks were consistent with the typical peak profiles of different AEL framework structures. Furthermore, the XRD patterns corresponding to these two AEL-type structures have been documented in previous literature, confirming that all three groups of samples are indeed pure SAPO-11 molecular sieves.

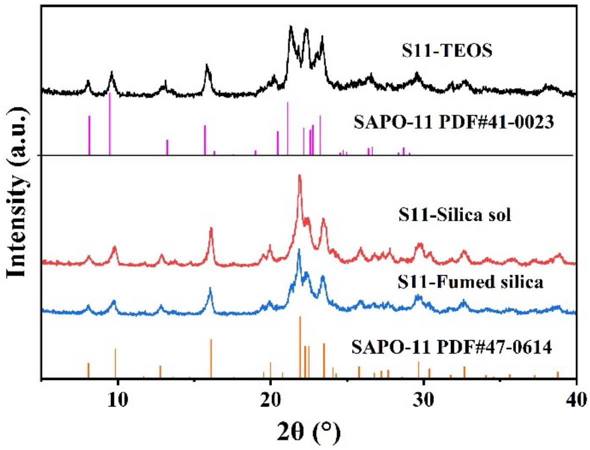

Figure S2 XRD pattern of SAPO-11 molecular sieves synthesized with different silicon sources.

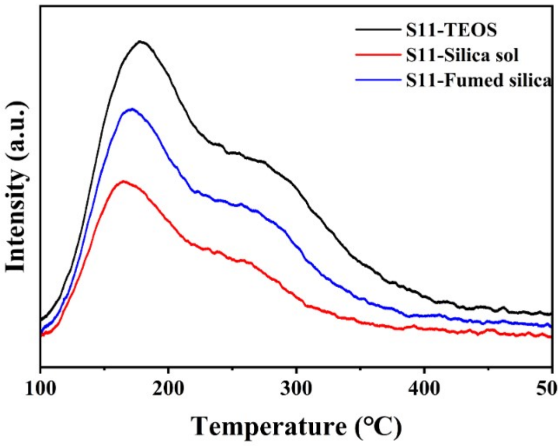

Figure S3 NH_3 adsorption and desorption curves of SAPO-11 molecular sieves synthesized from different silicon sources. The synthesis methods of SAPO-11 molecular sieves from different silicon sources are consistent with the synthesis methods in the main text, except that the silicon sources are changed to silica sol and fumed silica. The SiO_2/Al_2O_3 ratio of each group of samples was 0.25. The synthesized SAPO-11 was tested for NH_3-TPD using the same test method, and the results are shown in Figure S3. The sample with TEOS as the silicon source has the highest peak strength, indicating that TEOS is more suitable as the silicon source for synthesizing SAPO-11 molecular sieves to provide more acid sites.

4 The performance of Ni/S11-0.25 with different Ni loading content

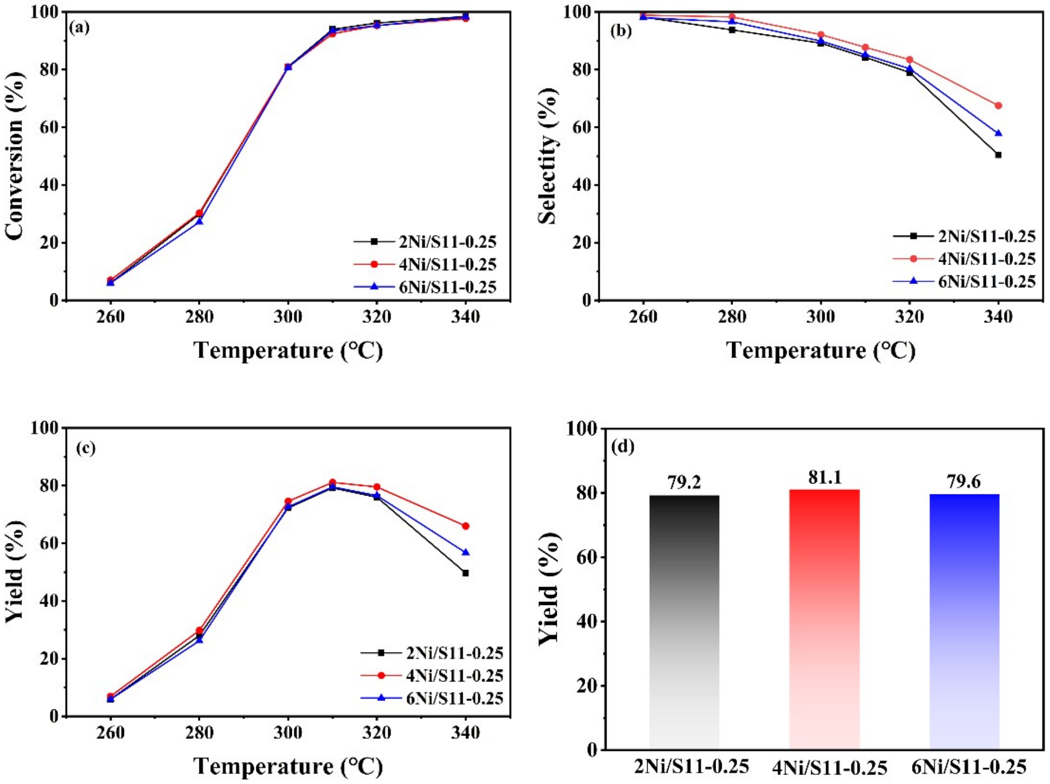

Figure S4 The n-dodecane hydroisomerization catalytic performance of *x*Ni/S11-0.25. (a) the conversion of n-dodecane, (b) the selectivity of iso-dodecane, (c) the yield of iso-dodecane, (d) the comparison diagram of the maximum isomer yield of xNi-S11-0.25. Reaction conditions: temperature 260-360 °C, pressure 2.0 MPa, H_2/n-dodecane = 1.5, WHSV = 1.5 h^{-1}. The results indicate that catalysts with different Ni loadings show similar trends in conversion and selectivity, with no significant performance differences among the three samples. Among them, 4Ni/S11-0.25 still exhibits the highest iso-dodecane yield at 310 °C. Therefore, we selected the catalyst with 4 wt% Ni loading for the performance studies presented in this work.

5 Ni dispersion determined by CO pulse chemisorption

The results reveal that Ni/S11-0.25Si presents the highest Ni dispersion (13.5%) with an active Ni particle size of 7.5 nm as shown in Table S1, which is in good agreement with the TEM results as shown in Figure S5. Although the three samples exhibit a trend of initial increase followed by decrease in Ni dispersion and particle size, these parameters vary within a relatively narrow range. Accordingly, such fluctuations are not considered as the decisive factor governing the final catalytic performance of the samples.

Table S1 Ni dispersion of Ni/S11-x by CO pulse chemisorption.

Sample	Dispersion / %	Diameter / nm
Ni/S11-0.10	11.7%	8.6
Ni/S11-0.25	13.5%	7.5
Ni/S11-0.40	12.4%	8.2

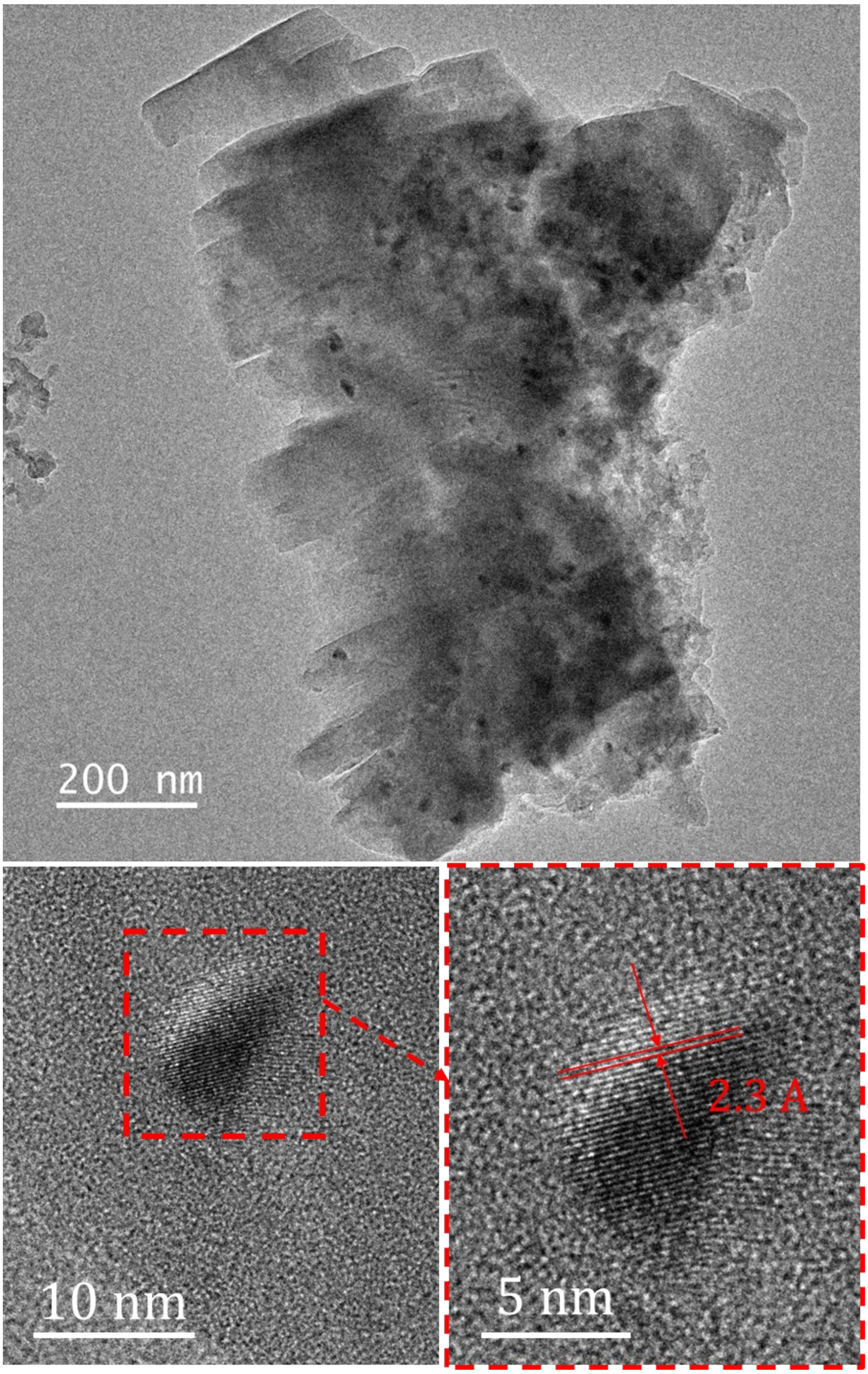

Figure S5 Transmission electron microscopy image of Ni/S11-0.25. The results indicate that the size of Ni particles is approximately 9 nm, and the measured interplanar spacing of the particles is 2.3 Å, which is consistent with the interplanar spacing of Ni reported in the literature. (*Applied Surface Science*, 2023, 636, 157736., *Journal of Materials Science & Technology*, 2021, 76, 86-94., *Journal of Nanoscience and Nanotechnology*, 2005, 5, 596-600.)

6 TOF of Ni/S11-x samples

For bifunctional catalytic, the overall reaction TOF is mainly governed by the rate of skeletal isomerization occurring on the acid sites, whereas the metal sites facilitate fast dehydrogenation of alkanes and subsequent hydrogenation of olefinic intermediates. S11-0.25Si exhibits the highest turnover frequency (TOF), indicating that the acid density of this catalyst maximizes the efficiency of the isomerization reaction while effectively suppressing cracking side reactions. This result demonstrates that the 0.25Si sample achieves the optimal acid–metal balance among the three catalysts.

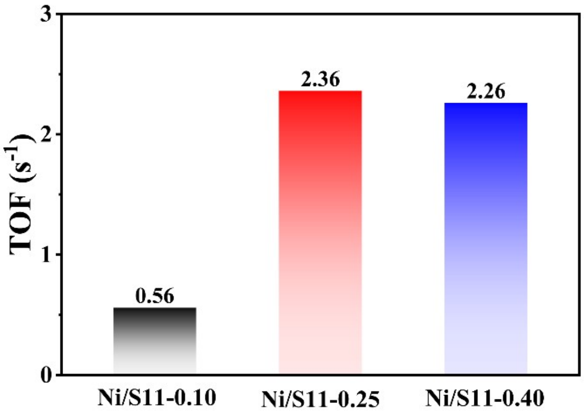

Figure S6 TOF (turnover frequency) of synthesized SAPO-11 in n-dodecane hydroisomerization. Reaction conditions: temperature 260 °C, pressure 2 MPa, H_2/n-dodecane = 1.5, WHSV = 1.5 h^{-1} to obtain an n-C_{12} conversion of 2%-7%.