Accelerated discovery of stable, extra-large-pore nano zeolites with micro-electron diffraction

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Abstract: Stable zeolites with extra-large pores and nano dimensions, capable of processing large molecules, are in high demand but have been difficult to discover. Their complex structures and nanoscale crystal sizes present challenges for analysis using conventional X-ray diffraction techniques, leading to inefficiencies in material development. We report NJU120-1 and NJU120-2, two robust and fully connected aluminosilicate nano zeolites featuring interconnected channel systems with extra-large pores of 22-ring. NJU120-1 is a nanosheet with only ~8 nm thickness, corresponding to 1.5 unit cells, and NJU120-2 is a nanorod with 50 nm by 250 nm dimensions. Their synthesis optimization was greatly accelerated through rapid structure determination with MicroED, revealing their multidimensional pore structures. Their very large largest-free-sphere diameters of approximately 1.2 nm coupled with nano morphologies enabled catalytic cracking of large molecules.

Main Text: Zeolites are crystalline microporous materials that are decorated with controllable acid centers for size- and shape-selective catalysis (*1, 2*). Access of molecules through diffusion into and out of their inner confined space−where adsorption and reactions occur−are crucial to their functionalities and is determined by their pore apertures and lengths for mass transfer. However, current industrial zeolites are commonly larger crystal bulk and have micropores with aperture diameters < 1 nm (*3*). These properties hinder the molecular diffusion of reactants and products and often lead to rapid coking and unwanted side reactions.

To overcome these challenges, the synthesis of nanosized or extra-large-pore (ELP) zeolites provides promising approaches (*4, 5*). Nano zeolites, especially nanosheet ones, have much shorter diffusion pathways and an increased fraction of accessible external surface with exposed active sites compared to bulk counterparts, which enhances mass transfer (*6, 7*). They are commonly realized by strategies such as exfoliating layered zeolites, templated crystallization, introducing mesopores, and employing additive-assisted synthesis. Unfortunately, these methods necessitate expensive surfactants, specially designed organic structure-directing agents (OSDAs) with long chain alkyl groups, as well as intricate processes like swelling, pillaring, and delamination, which make them uneconomical for industrial use. Moreover, they are typically applicable only to a limited range of zeolites, including **MFI** (*6*), **FAU** (*8*), **MOR** (*9*), **MWW** (*10, 11*), and **FER** (*12*) types, none of which qualify as ELP zeolites that can process molecules larger than those currently manageable.

ELP zeolites, characterized by larger pore apertures delimited by rings encircled with over twelve TO_4 tetrahedra (where T represents framework atoms coordinating with O, like Si and Al) and larger largest free sphere (LFS) that can pass through the framework by at least one lattice translation, provide another effective strategy to overcome the mass transfer limitations through broadened diffusion pathways (*13, 14*). Specifically, molecules are blocked if their sizes surpass the pore aperture or LFS diameter of a given zeolite. For example, the LFS diameter of industrial ultrastable Y (USY) zeolite (**FAU** topology) with a 12-membered ring (12MR) channel system is only 0.74 nm, which seriously restricts its catalytic application in processing heavier hydrocarbons (*15*). This limitation has spurred demands for ELP zeolites with pore apertures exceeding 12MR and LFS diameters >1 nm.

During the past 30 years, 40 ELP zeolites have been identified (table S1); however, 30 of them have interrupted frameworks with terminal −OH groups or contain elements such as Ge, Ga, P, and Be (*16*). These features diminish their thermal and hydrothermal stability and limit practical applications. However, the few stable pure silicate or borosilicate ELP zeolites have failed to fully meet catalytic requirements because of the challenges in incorporating sufficient active aluminum into their frameworks. High-silicon ELP zeolites with stable catalytic sites remain exceedingly rare. Notable exceptions include ZEO-1 (*17*), and ZMQ-1 (*18*), which is characterized by large crystal dimensions.

The combination of nano dimensions with extra-large pores, or nano ELP zeolites, could have both shortened and broadened diffusion pathways, which would greatly boost mass transfer and enable higher catalytic performance compared to conventional zeolites. Despite their great potential, such nano ELP zeolites remain underexplored, and their development has many challenges. Specifically, during synthesis, various factors, including reagents (especially OSDAs) and their ratios, as well as synthetic temperature and duration, require careful selection and optimization (*19*). High-throughput can screen many variables in a timely manner but requires equally effective phase identification and structure determination. For nano ELP zeolites, this requirement poses difficulties because such zeolites often have rather complex framework structures and crystallize as nanocrystal powders mixed with other phases, which complicates their analysis by routine techniques like X-ray diffraction (XRD).

We present a strategy to accelerate nano ELP zeolite development by combining state-of-the-art MicroED (microcrystal electron diffraction) with combinatorial chemistry. First, a wide range of compositions are tested and the resulting compounds are characterized in parallel with a combinatorial approach. Subsequently, their phase elucidation and structure determination are rapidly completed within multiphase polycrystalline samples by high-throughput MicroED, which can isolate crystallites with different phases and compositions. Based on these findings, synthetic conditions are then pertinently optimized and pure products are finally obtained.

With this strategy, two stable and fully connected nano ELP aluminosilicate zeolites, NJU120-1 and NJU120-2 (Nanjing University zeolites 1 and 2 discovered on the occasion of the 120th anniversary of Nanjing University) with high Si/Al ratios, were developed within similar systems. Notably, NJU120-1 has an impressive nanosheet morphology characterized by multilamellar stacks with only 1.5 unit-cell thickness, whereas NJU120-2 exhibits a nanorod morphology with dimensions of 50 nm by 250 nm. These zeolites feature in their structures multidimensional and interconnected channels with 22 × 10 × 10 MR and 22 × 12 × 10 MR pores, respectively. Moreover, their 22MR pore apertures surpass all of our previously reported stable ELP zeolites, including ZEO-1 (aluminosilicate with 16MR pores, **JZO** topology) (*17*), ZEO-3 (pure silicate with 16MR pores, **JZT** topology) (*20*), and ZEO-5 (pure silicate with 20MR pores, **HZF** topology) (*21*).

Both NJU120-1 and NJU120-2 demonstrate impressive LFS diameters of approximately 1.2 nm, exceeding most known zeolites and only slightly smaller than ZMQ-1. Coupled with intrinsic aluminum catalytic active centers embedded in their ELP structures and nano morphologies, NJU120-1 and NJU120-2 enabled efficient heavy-oil conversion and selectivity to fuels during fluid catalytic cracking (FCC) process, and outperformed ZEO-1 and the highly optimized USY zeolite. This work not only showcases the effectiveness of our powerful strategy by applying MicroED to accelerate the discovery of new nano ELP zeolites like NJU120-1 and NJU120-2 but also paves the way for future innovations in zeolite synthesis and characterizations.

Preparation and structure determination of NJU120-1 and NJU120-2

Di(1-adamantyl)-*n*-butyl-methylphosphonium was utilized as the OSDA (fig. S1) for synthesizing NJU120-1 and NJU120-2 in the absence of HF. In the initial synthesis batch for the combinatorial approach, 16 gel compositions (table S2) were prepared and subjected to crystallization under two hydrothermal conditions: 463 K for 24 days and 448 K for 42 days. Powder XRD (PXRD) analysis revealed that 12 of them crystallized into products with unknown phases under the first condition, whereas 8 yielded distinct crystalline products under the second (figs. S2 and S3).

Because of the PXRD complexity of the obtained mixtures, high-throughput MicroED was used for rapid phase identification and structure analysis. Prior to this, these products were calcined at 873 K for 6 hours to recognize those potentially containing new stable zeolites, and entries E01a and E11b were selected for further analysis because of the persistence of their PXRD peaks after calcination (fig. S3). Remarkably, within just two MicroED sessions (~8 hours), two new nano ELP zeolites, NJU120-1 and NJU120-2, were identified with 10 and 3 datasets, respectively (Fig. 1, A and C; tables S3 and S4). After the initial synthesis of impure NJU120-1 and NJU120-

2, gel compositions and synthetic conditions were accordingly optimized, and pure products were quickly obtained just in the second synthesis, as confirmed by the synchrotron PXRD (SPXRD) measurements (Fig. 1, B and D).

NJU120-1 and NJU120-2 are both nanocrystals, with the former possessing a nanosheet morphology of ~8 nm in thickness and the latter exhibiting a nanorod morphology with dimensions of ~50 nm by 250 nm (figs. S4 and S5). Such small sizes made it rather challenging to achieve their accurate structures, especially with routine XRD methods. We thus used the advanced continuous rotation electron diffraction (cRED) technique to implement MicroED, which effectively overcame the difficulties associated with nanocrystals and electron-beam damage during structure determination (*22-27*). Typical reconstructed reciprocal lattices from the cRED datasets are shown in Fig. 1, A and C, and figs. S6 and S7. The complex structures of NJU120-1 and NJU120-2 were then determined with exceptional details using high-quality MicroED data, achieving 82.7% and 94.2% completeness and 0.8 and 1.0 Å resolution after merging 10 and 3 datasets, respectively.

NJU120-1 crystallized in an orthorhombic unit cell, with the systematic extinctions indicative of the *Imma* space group and dimensions of a = 19.040(4) Å, b = 20.560(4) Å, c = 40.910(8) Å, whereas NJU120-2 crystallized in a monoclinic unit cell with the space group $P2_1/n$ and dimensions of a = 12.860(3) Å, b = 26.457(5) Å, c = 28.927(6) Å, and β = 98.28(3)° (table S5). All of their T and O atoms were located directly ab initio with *SHELXLT* (*28*), and the resulting framework structures were refined using *SHELXL*, yielding an unweighted residual factor (*R1*) of 0.1622 for NJU120-1 and 0.1433 for NJU120-2. These structures further underwent Rietveld refinement against synchrotron PXRD (SPXRD) for both as-made and calcined NJU120-1 and NJU120-2, achieving more accurate structures with chemically reasonable bond lengths and angles while also confirming sample purity (Fig. 1, B and D, and figs. S8 and S9; tables S6 to S17).

OSDAs within NJU120-1 and NJU120-2 frameworks were determined through a combined MicroED and SPXRD refinement on as-made samples. Specifically, difference electronic potential density maps revealed two crystallographically independent OSDA molecules occupying 22MR pores for both zeolites (figs. S10 and S11). Their number from Rietveld refinement was 14.51 and 8.0 per unit cell for NJU120-1 and NJU120-2, respectively, consistent with the compositions from various chemical analyses: $|C_{25}H_{42}P|_{14.13}\cdot[Si_{179.04}Al_{12.96}O_{384}]$ for NJU120-1 and $|C_{25}H_{42}P|_{8.12}\cdot[Si_{102.23}Al_{9.77}O_{224}]$ for NJU120-2 (fig. S12 and table S18). In NJU120-1, OSDAs extended their long butyl chains into the 10MR pores, whereas in NJU120-2, one crystallographically distinct OSDA stretched an adamantyl group and the butyl chain into the supercage via 12MR pore aperture, along with the latter oriented towards 10MR aperture. These findings suggest that the large adamantyl head and long butyl tail of the OSDA are crucial in directing 22MR, 12MR, and 10MR pores in NJU120-1 and NJU120-2.

Structures of NJU120-1 and NJU120-2

NJU120-1 contained 14 T and 31 O atoms in its crystallographic asymmetry unit (tables S7, S10, and S19), whereas NJU120-2 featured 28 T and 56 O atoms (tables S13, S16, and S20), indicating their complex structures. The large number of unique atoms in NJU120-2 makes it one of the most intricate fully connected zeolites resolved to date, even surpassing the recently reported ZMQ-1 with 18 T and 40 O atoms, despite having larger pores. Only zeolites PST-20 (no assigned code so far) and the disordered SSZ-57 (***SFV** topology), with respective 29 and 99 T atoms, are more complex (*29, 30*).

NJU120-1 can be formally viewed as a layer-pillared framework structure and featured a multidimensional 22 × 10 × 10 MR channel system (Fig. 1, E to G, and figs. S13 and S14; table S21). The straight elliptical extra-large 22MR pore runs along the [010] direction (Fig. 1E), whereas the straight 10MR pore in the pore wall and the sinusoidal 10MR pore in the porous layer both extend along the [100] direction (Fig. 1F), all of which are interconnected (Fig. 2G and fig. S15). Further topological analysis of the layer-pillared structure, combined with nanosheet morphology and preferred orientation of NJU120-1 (see below) and informed by the principles of reticular chemistry in porous materials (*29*, *31*), enabled us to propose a new and fully connected ELP zeolite family named NJU120-1-G*n* (*n*th generation of NJU120-1). This family uses the porous layer and pore pillar as its structural elements and can be systematically tailored by modulating the layer gliding and the number of interlayer pillars (fig. S16). NJU120-1 represents the 3rd generation, while interestingly, the recent ZMQ-1 also belongs to this family as the 4th generation (*18*). Their successful synthesis strongly demonstrates the feasibility of this predicted ELP zeolite family.

The most distinctive structural feature of NJU120-2 is the presence of a large supercage, whose cavity dimension approaches 2 nm (Fig. 2H) and surpasses that of the cage in USY zeolite (1.12 nm). It opens through two 12MR and two 10MR pore apertures that are connected through the inner cavity (fig. S17). These supercages are stacked on top of each other along the [100] direction to form two columns, as colored by gold and orange in Fig. 1I and fig. S18, which are related by the operation (-*x*+1/2, *y*+1/2, -*z*+1/2) and connected by additional T pairs. With this configuration, the NJU120-2 framework structure was achieved, characterized by a multidimensional interconnected 22 × 12 × 10 MR channel system (Fig. 1J, and figs. S19 and S20; table S22). The straight extra-large 22MR pore extends along the [100] direction, while the sinusoidal 12MR and 10MR pores run along the [010] and [001] direction, respectively. These pores were all mutually connected through the supercage cavity and 22MR pores, providing a confined yet extended space to facilitate guest diffusion.

The pores in NJU120-1 and NJU120-2 interconnect through 22MR apertures as well as other 10MR or 12MR apertures, forming multidimensional channel systems (Fig. 2, A to H, and figs. S15 and S20). The crystallographic dimension of the 22MR pore aperture in NJU120-1 measured approximately 15.49 × 12.34 Å (Fig. 2B; table S23), accommodating an LFS with the diameter of 12.05 Å. This LFS surpasses in sizes those found in other stable and fully connected zeolites, including USY (7.29 Å) and our previously reported ZEO-1 (9.45 Å), ZEO-3 (8.44 Å), and ZEO-5 (11.07 Å) (Fig. 2I and fig. S21). It is also near the LFS of ZMQ-1 (12.15 Å) with larger 28MR pores, which can be attributed to the nearly fixed spacing between adjacent pore walls in the NJU120-1-G*n* family (fig. S16).

These findings indicated that, besides the number of pore membered rings, LFS diameter may be crucial for evaluating zeolite pore dimensions, as the former cannot guarantee a pore shape adequate for applicable diffusion. In addition, the two 10MR pores in NJU120-1 are also larger than those in industrial ZSM-5 and TS-1 zeolites (both **MFI** topology) (Fig. 2, C and D). While for NJU120-2, its 22MR pore is also impressive, with a larger crystallographic aperture of approximately 16.64 × 11.43 Å (Fig. 2F) and an LFS of diameter of 12.01 Å. Besides, the 12MR and 10MR pore apertures in NJU120-2 were comparable to those in industrial USY and **MFI** zeolites, respectively. Such exceptional pore characteristics endowed NJU120-1 and NJU120-2 with a low calculated density of 1.296 and 1.272 g/cm^3 (in SiO_2 form) and a low framework density (FD) of 12.99 and 12.75 T/1000 Å^3, respectively. Although the FD of NJU120-1 and NJU120-2 is higher than that of ITQ-70 (10 T/1000 Å^3), a recent pure silica zeolite with smaller 18MR pores and highly concentrated ordered defects (*32*), only ZMQ-1 and ZEO-5 have lower FD than them among fully connected zeolites (table S23). These remarkable pore properties place NJU120-1 and NJU120-2 among the few zeolites with the largest pores and most open framework structures.

Physicochemical properties and catalysis

The structures of NJU120-1 and NJU120-2 were further validated by spherical aberration (Cs)-corrected scanning transmission electron microscopy (STEM). Examination of the cross-section of NJU120-1 revealed that the overall thickness of the multilamellar stacked nanosheets was approximately 8 nm, which corresponded to the *c*-axis dimension of just 1.5 unit cells (Fig. 3, A to D and figs. S22, A and B, and S23). The nanosheets were so thin that they were even flexible. Remarkably, these ultrathin NJU120-1 nanosheets were directly synthesized without precursor exfoliation or the use of expensive surfactants with associated treatments. Such a low thickness is also exceptionally rare among all known zeolites, and, to our knowledge, NJU120-1 is the first reported ELP zeolite with an ultrathin nanosheet morphology of unit-cell thickness.

The NJU120-1 nanosheets extend in the *ab* plane, with the 22MR and 10MR pores aligned parallel to the nanosheet plane (fig. S22, C and D). This preferential growth might result from the inherent layer-pillared structure of NJU120-1, likely driven by the higher crystallization energy along the *c*-axis (perpendicular to the porous layers). In terms of NJU120-2, which features a nanorod morphology with an average diameter of ~50 nm and a length of ~250 nm, STEM investigation on its cross-section uncovered that its 22MR pores run along the long axis of the nanorod, indicating its preferential crystallization along the [100] direction (Fig. 3, E to G, and fig. S22, E to H). These findings supported the NJU120-1 and NJU120-2 structures obtained from MicroED.

During synthesis, the OSDA remained intact within the NJU120-1 and NJU120-2 pores, as confirmed by the ^{31}P and ^{13}C nuclear magnetic resonance (NMR) measurements (figs. S24 and S25). Upon calcination at 873K in air, these OSDA molecules decomposed, leaving behind phosphate-like species, while the framework structures were well preserved, as seen from the ^{29}Si and ^{27}Al NMR spectra, despite that some Al species became six-coordinated and slightly pentacoordinated during this process (figs. S26 and S27). After treatment with an NH_4Cl solution, the phosphate-like species was removed and the six-coordinated and minor pentacoordinated Al atoms disappeared by both removal and reversion to tetrahedral sites (figs. S24 and S27), resulting in phosphorus-free (P-free) zeolites with clean and accessible pores and increased Si/Al ratio (table S18).

Both NJU120-1 and NJU120-2 exhibited Ia-type N_2 adsorption behavior (figs. S28 and S29), and their specific surface areas and micropore volumes were calculated to be as high as 957 and 1007 m^2/g and 0.32 and 0.35 cm^3/g, respectively. In addition, the pore size distributions, determined from the Ar adsorption measurements using nonlocal density functional theory (NLDFT) methods, peaked at approximately 10.16 and 16.86 Å for NJU120-1 and 10.9 and 16.88 Å for NJU120-2, which matched the 22MR pore apertures and aligned well with their crystallographic values (figs. S30 and S31). Furthermore, NJU120-1 and NJU120-2 both displayed an H4 hysteresis loop in their adsorption/desorption profiles, indicative of the presence of an amount of mesopores corresponding to the accumulated voids formed between nanocrystals. Notably, the

P-free NJU120-1 and NJU120-2 frameworks demonstrate high thermal stability at temperatures up to 1273 K and relatively high hydrothermal stability upon steaming at 1073 K under 50% relative humidity (figs. S32 and S33).

The aluminum species within the NJU120-1 and NJU120-2 frameworks can serve as the solid-state acid centers for catalysis, which largely remain preserved after steam treatment, as shown by NH_3 temperature programmed desorption (NH_3-TPD; figs. S37 and S39; table S25). To assess their intrinsic catalytic capabilities without the influence of occluded phosphorus, we conducted benchmark FCC tests using commercial vacuum gas oil (VGO; table S26) on P-free NJU120-1 and NJU120-2, with P-free ZEO-1 and commercial zeolites USY and Beta as the controls. Remarkably, NJU120-1 exhibited superior cracking efficiency for VGO, with less coke formation coke and higher conversion of heavy oil (Fig. 4; table S27). Besides, it favored a larger fraction of high-value fuels, particularly gasoline and diesel, which together accounted for nearly 60% of the total products.

In contrast, although NJU120-2 initially exhibits lower heavy oil conversion with higher coke formation, its FCC performance notably improves after regeneration: the fraction of high-value fuels approaches 51% in the 5th run, alongside reduced coke formation and enhanced heavy oil conversion (fig. S40; table S28). In addition, among the liquefied petroleum gas (LPG) products, both NJU120-1 and NJU120-2 demonstrated a higher selectivity for propylene, an essential petrochemical feedstock, over propane, a performance not observed with any of the control catalysts. Importantly, even after consecutive catalytic runs, the product distribution of NJU120-1 remains nearly unchanged, while it becomes favorable for NJU120-2, indicating activity retention and catalytic activation, respectively (fig. S40; table S28). This was further corroborated by their retained framework structures after FCC cycles, despite a slight decrease in specific surface area and micropore volume (figs. S32 to S35; table S24). These preliminary catalytic tests underscore the potential of NJU120-1 and NJU120-2 as efficient acid-based heterogeneous catalysts. Their exceptional performance can be attributed to the larger 22MR pores and nano morphologies for facilitated mass transfer, highlighting the importance of developing nano ELP zeolites with enhanced catalytic activity.

Outlook

Stable and fully connected zeolites with extra-large pores and nano dimensions are highly sought after for their ability in boosting diffusion pathways for enhanced applications, well exemplified by NJU120-1 and NJU120-2 reported herein. Although the designed synthesis of such nano ELP zeolites faces considerable challenges, our study offers a compelling example for the future development of this field. A key factor in achieving these targeted structure features and properties lies in the OSDAs applied. The MicroED technique for the rapid polycrystalline multiphase structure analysis combined with combinatorial chemistry synthesis could help develop new nano ELP zeolites, including the missing members of the NJU120-1-G*n* family, but also our understanding of the relationships among synthetic conditions, OSDAs, and resulting zeolite structures.

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Author contributions: J.L. conceived the project and supervised the study. C.M. and M.D.Z. performed the synthesis. Z.H.Z. conducted structure analysis and the (S)TEM characterizations. C.L., G.C.L., T.W.B. L., and K.F.Y. performed the structure and topology analysis, SPXRD, and NMR measurements. L.H., H.T.S., and W. L. worked on the catalytic tests. X.D.T. and L. X. carried out the NH_3-TPD experiments. J.L., C.L., and M.A.C. prepared the initial draft of the manuscript. All authors discussed the results and contributed to revising the final manuscript.

Competing interests: J. L. and C. M. have filed a patent on NJU120-1 and NJU120-2 (Chinese patent application no. 202410861721.5). Nanjing University holds the rights on that patent.

Data and materials availability: All datasets generated and/or analyzed in the present study are available in the main text or the supplementary materials. The adsorption Information Files (AIFs) for NJU120-1 and NJU120-2 used in adsorption studies have been deposited at Zenodo (*34*). The crystallographic information files (CIFs) for the structures of NJU120-1 and NJU120-2, refined using cRED data and Rietveld refinement against SPXRD data, have been deposited at the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/) under the reference numbers of 2427489 (NJU120-1_as-made_cRED), 2427488 (NJU120-2_as-made_cRED), 2427920 (NJU120-1_as-made_SPXRD), 2427486 (NJU120-2_as-made_SPXRD), 2427485 (NJU120-1_cal_SPXRD), and 2427487 (NJU120-2_cal_SPXRD).

Supplementary Materials

Materials and Methods

Physicochemical Characterizations

Structure Determination and Characterizations

Catalytic Tests

Supplementary Texts

Figs. S1 to S40

Tables S1 to S28

References (*35*-*85*)

Fig. 1. Identification and structures of NJU120-1 and NJU120-2. (**A** to **D**) Typical reciprocal lattices reconstructed from MicroED and Rietveld refinement plots of SPXRD for as-made NJU120-1 (A and B) and NJU120-2 (C and D). (**E** and **F**) Framework structure of NJU120-1 viewed along [010] (E) and [100] (F) directions, highlighting the 10MR in the pore wall (light jade), 10MR in the porous layer (light sky blue), and the pillar (or pore wall, orchid). (**G**) 3D channel system of NJU120-1 with the structure superimposed. (**H** and **I**) NJU120-2 supercage (H) and framework structure formed by two supercage columns (gold and orange) with additional T pairs (translucent green) and viewed along [100] direction (I), highlighting the 12MR and 10MR pores and apertures (light jade and light sky blue, respectively), supercage cavity (light gold), 22MR pores (light red), and connection among supercages and additional T pairs (translucent green). (**J**) 3D channel system of NJU120-2 with the structure superimposed.

Fig. 2. Pores of NJU120-1 and NJU120-2. (**A**) 3D interconnected channel system of NJU120-1. (**B** to **D**) Crystallographic pore apertures of NJU120-1. (**E**) 3D interconnected channel system of NJU120-2. (**F** to **H**) Crystallographic pore apertures of NJU120-2. (**I**) Comparison of the LFS diameters of zeolites USY, ZEO-3, ZEO-1, ZEO-5, ZMQ-1, and present NJU120-1 and NJU120-2.

Fig. 3. Electron microscopy structures of NJU120-1 and NJU120-2. (**A**) SEM image of NJU120-1 nanosheets. (**B**) Unit-cell-thick NJU120-1 nanosheets with clear extra-large 22 MR pores, treated by Wiener filter to reduce low-frequency signals for enhanced contrast (*33*). (**C** and **D**) Images of integrated differential phase contrast (iDPC)-STEM (C) and annular bright-field (ABF)-STEM (D) of a single NJU120-1 nanosheet with straight and elliptical 22MR pores viewed along the [010] zone axis. (**E** to **G**) iDPC-STEM (E and F) and high-angle annular dark-field (HAADF)-STEM (G) images of NJU120-2, with the straight and rhombic extra-large 22MR pores viewed along the [100] zone axis (E), sinusoidal 10MR pores viewed along the [001] zone axis (F), and overlapped sinusoidal 12MR and 10MR pores viewed along the [011] zone axis (G). Superimposed insets highlighted by white dotted boxes in (C to G): corresponding framework structures (left) and simulated STEM images (right); scale bars, 200 nm for (A), 10 nm for (B), and 5 nm for (C to G).

Fig. 4. FCC performance of VGO over zeolite catalysts. Note that the performance of NJU120-2 shown is from the 5th run. Reaction conditions: 0.18-0.45 mm fraction, catalyst/oil of 1, 1 atm, 773 K, and weight hourly space velocity (WHSV) of 51.4 h^{-1}.