POLYOXOMETALATES

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HIGHLIGHT

Confined Anderson-type $PtMo_6O_{24}$ polyoxometalate clusters enable low-temperature, ultra-stable CO_2 hydrogenation to methanol

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ABSTRACT: Traditional heterogeneous catalysts for CO_2 hydrogenation to methanol typically require high temperatures (≥ 250 °C) and possess ill-defined active sites, which limit both energy efficiency and mechanistic understanding of the hydrogenation process. A recent study by Joseph T. Hupp, Zhihengyu Chen, Wentuan Bi, and Rachel B. Getman, published in *Nature Chemistry*, demonstrates that an atomically precise Anderson-type $PtMo_6O_{24}$ polyoxometalate cluster, when confined within the mesoporous channels of the zirconium-based metal–organic framework NU-1000, exhibits exceptional low-temperature catalytic activity (initiating at room temperature and operating stably at 100–200 °C) with no detectable deactivation over 3,600 h. We provide an in-depth analysis of how this study establishes a molecularly defined, MOF-confined cluster platform that decouples CO_2 activation and H_2 dissociation via a heterolytic mechanism, predominantly proceeding through a reverse water–gas shift pathway followed by CO* hydrogenation. This study highlights the unique advantages of well-defined cluster systems over conventional heterogeneous catalysts—namely, uniform active sites, precise structure–activity correlations, and ultrahigh stability (maintaining conversion, selectivity, and structural integrity)—and aims to inspire further exploration of multifunctional, confined cluster materials for low-temperature energy conversion and sustainable chemical synthesis.

KEYWORDS: polyoxometalate clusters, metal-organic frameworksm, pore confinement, CO_2 hydrogenation, methanol synthesis, low-temperature catalysis

The escalating atmospheric CO_2 concentration and the urgent need for carbon neutrality have spurred intense interest in converting CO_2 into value-added chemicals and fuels [1]. Among various transformation routes, the hydrogenation of CO_2 to methanol stands as a cornerstone reaction for establishing a closed-loop, sustainable carbon economy [2–5]. However, the high thermal demands of conventional catalysts—exemplified by industrial Cu-ZnO-Al_2O_3 operating above 250 °C—impose substantial energy penalties and thermodynamic constraints that limit single-pass yields [6, 7]. While the incorporation of H_2-activation components (e.g., Pd and Ni) into hydroxyl radical‑vacancy‑rich (Ni,Co)$(OH)_x$ nanoparticles or Npyridinic–carbon black can lower operating temperatures to 200–250 °C, such modifications often reduce methanol selectivity (defined as methanol relative to all carbon-containing products), favoring methane or CO instead via the reverse water–gas shift (RWGS) reaction [8, 9]. However, three fundamental scientific bottlenecks have long hindered low-temperature methanol synthesis. First, CO_2 activation at low temperature is thermodynamically and kinetically challenging. Second, kinetic mismatches between H_2 dissociation and CO_2 hydrogenation can divert the reaction toward RWGS or methanation, thereby lowering methanol selectivity. Third, ill-defined active sites in conventional catalysts obscure structure–activity correlations, impeding rational catalyst design. Addressing these bottlenecks requires catalytic systems that integrates efficient low-temperature CO_2 activation, precise control over reaction pathways, and a well-defined active-site architecture.

Offering a compelling departure from these challenges, a recent breakthrough by Joseph T. Hupp, Zhihengyu Chen, Wentuan Bi, and Rachel B. Getman—published in *Nature Chemistry*—demonstrates that an atomically precise Anderson-type polyoxometalate cluster, $PtMo_6O_{24}$, when confined within the mesoporous channels of zirconium-based metal–organic framework (MOF) NU-1000 (denoted NU1K), serves as an exceptionally stable and active catalyst for CO_2 hydrogenation to methanol at temperatures as low as 100 °C and even initiates the reaction at room temperature (Fig. 1(a)) [10]. The key design strategy lies in the integration of three elements: (i) The molecularly defined $PtMo_6O_{24}$ cluster provides a uniform, well-characterized active site; (ii) *c*-pores in MOF (8 Å × 10 Å) confine each cluster, preventing aggregation while maintaining accessible active interfaces; and (iii) a mild H_2 reduction step transforms the cluster into an active form ($PtMo_6O_{24}$–R) featuring a protruding, low-coordination Pt center and oxygen vacancies that are critical for CO_2 activation.

The performance metrics at 200 °C and 50 bar with an H_2/CO_2 ratio of 3:1 are striking. Specifically, $PtMo_6O_{24}$ confined in NU1K ($PtMo_6O_{24}$@NU1K) demonstrates methanol selectivity–dominated performance and achieves methanol yields two orders of magnitude

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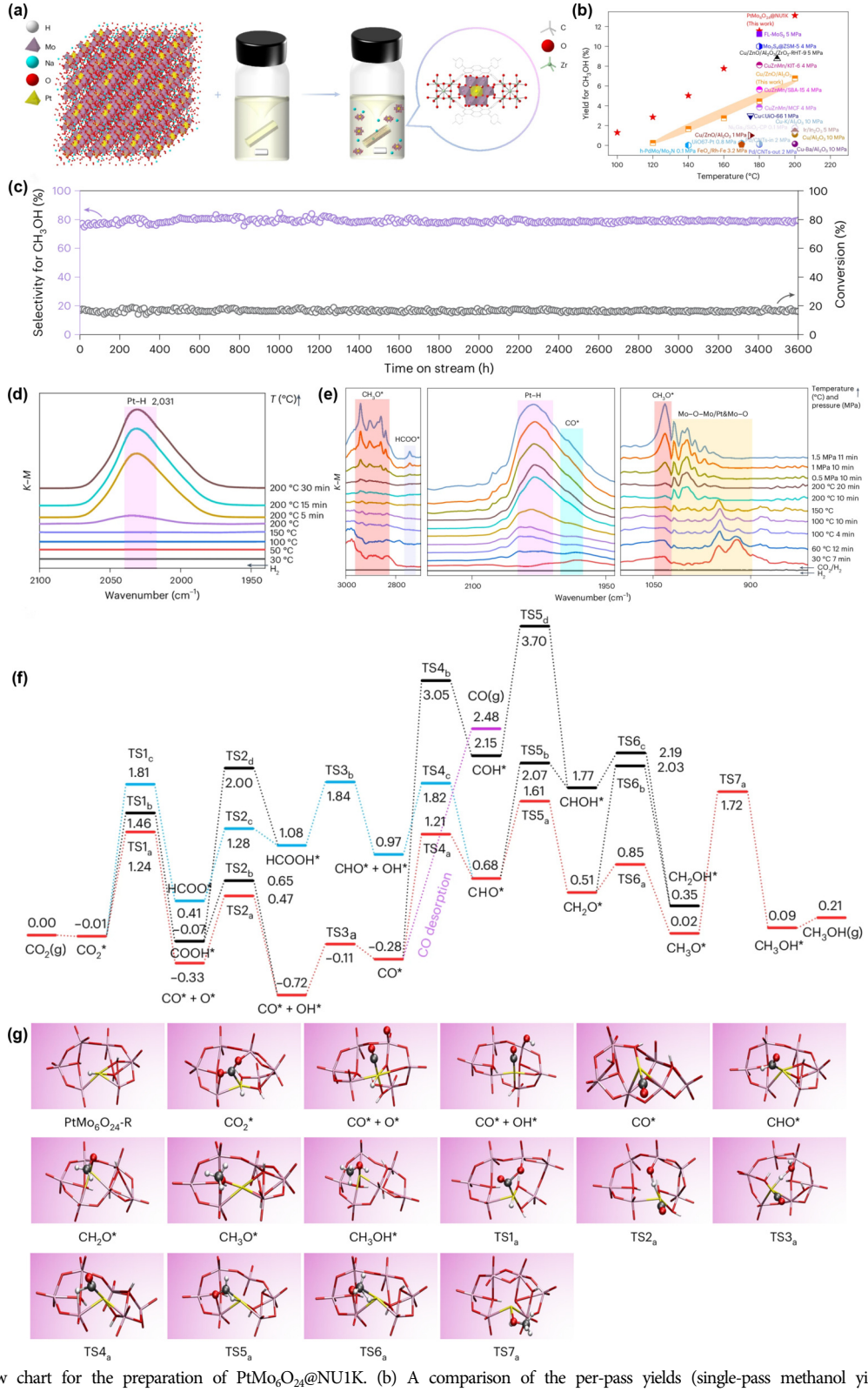


Figure 1 (a) A flow chart for the preparation of $PtMo_6O_{24}$@NU1K. (b) A comparison of the per-pass yields (single-pass methanol yield from CO_2) over $PtMo_6O_{24}$@NU1K and other state-of-the-art catalysts under 200 °C. (c) Stability testing of $PtMo_6O_{24}$@NU1K in CO_2 hydrogenation at 1,500 mL·$g_{cat.}^{-1}$·h^{-1}, with selectivity and conversion (consumed CO_2/total CO_2 ratio) monitored over 3600 h. The activity tests were conducted using a tubular fixed-bed reactor at 50 bar with an H_2/CO_2 ratio of 3:1. (d) *In situ* DRIFTS of H_2 activation on $PtMo_6O_{24}$@NU1K were recorded at different temperatures (*T*). (e) *In situ* DRIFTS of CO_2 hydrogenation over the $PtMo_6O_{24}$@NU1K catalyst under different reaction conditions. (f) Gibbs Free-energy diagram (ΔG_{vib}) of CO_2 hydrogenation to CH_3OH over the reduced $PtMo_6O_{24}$@NU1K catalyst. (g) Structural diagrams of the intermediates and transition states for each reaction step in the red line. Colour legend: Mo (purple), Pt (gold), O (red), C (grey) and H (white). Adapted from Ref. [10], © Liu, Q. et al., under exclusive licence to Springer Nature Limited 2026. Further details can be found in *Nature Chemistry* paper and its supplementary information [10].

higher than other polyoxometalate–MOF systems reported in the original study (e.g., PtV_3O_{28}@NU1K and PtW_6O_{24}@NU1K). Under identical conditions, the $PtMo_6O_{24}$@NU1K catalyst consistently delivers a higher net space–time yield of methanol than commercial $Cu/ZnO/Al_2O_3$ across the entire temperature range of 100–200 °C. At 180 °C, it achieves a CO_2 conversion of 15.7% with a methanol selectivity of ~ 79.0% (reaction conditions: 50 bar, 1,500 $mL{\cdot}g_{cat}^{-1}{\cdot}h^{-1}$, H_2/CO_2 = 3:1), corresponding to a per-pass yield of 13.1% at 200 °C—surpassing most state-of-the-art catalysts reported for operation below 200 °C (Fig. 1(b)). Even more remarkable is its durability: Over 3,600 h (150 days) of continuous operation at 180 °C, the catalyst shows no detectable decay in either activity (average conversion = 16.6%) or methanol selectivity (average ≈ 79.0%) (Fig. 1(c)). Control experiments underscore the indispensability of MOF confinement: Unsupported $PtMo_6O_{24}$ or the cluster supported on conventional ZrO_2 rapidly aggregates and loses activity, whereas Pt nanoparticles confined within NU1K (Pt@NU1K) are nearly inactive. Systematic variation of MOF topology (NU901 and NU1008) and node composition (Hf-NU1K) further confirms that the mesoporous *c*-pores (one-dimensional channels along the *c*-axis of NU-1K) of NU1K provides an optimal balance between mass transport and cluster stabilization, thereby enabling high catalytic activity, high methanol selectivity, and exceptional long-term durability in low- temperature CO_2 hydrogenation. Specifically, the *c*-pore dimensions and mesoporous environment of NU1K, comprising 8 Å × 10 Å *c*-pores together with 31 Å hexagonal mesopores and 12 Å triangular micropores, offers a uniquely balanced environment that simultaneously prevents cluster aggregation and facilitates efficient mass transport of reactants and products during CO_2 hydrogenation. This synergistic effect cannot be achieved by either the purely microporous NU901 or the highly spatially constrained NU1008.

Mechanistic investigations combining *in situ* X-ray total scattering (pair distribution function analysis and difference envelope density), X-ray absorption spectroscopy, electron paramagnetic resonance, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) provided a detailed picture of the catalytic cycle. Under H_2 activation, heterolytic dissociation of H_2 occurs at the isolated $Pt\delta^+$ site, generating a Pt-hydride species and a neighboring –OH group (Fig. 1(d)). Simultaneously, the Pt center dynamically evolves under reaction conditions, generating oxygen vacancies that participate in CO_2 activation rather than remaining in a static high-oxidation state. Isotopic labeling and in situ DRIFTS reveal that CO_2 hydrogenation proceeds predominantly via the RWGS pathway, followed by CO* hydrogenation (RWGS + CO-hydro), with formate (HCOO*) appearing only as a minor, high-temperature and high-pressure auxiliary route (Fig. 1(e)). Density functional theory calculations corroborate that CO_2 dissociation to CO* + O* is kinetically favored over alternative pathways (Fig. 1(f)–1(g)). Subsequent hydrogenation of CO* proceeds selectively through CH_3O* intermeditaes to methanol. The reconstructed atomic structure of the reduced cluster—a Pt center protruding from the Mo_6 framework with a two-coordinate PtO_2-like geometry—provides a clear, experimentally validated model for structure–activity correlations.

The significance of this work extends far beyond methanol synthesis. By demonstrating that a molecularly defined, MOF-confined polyoxometalate cluster can achieve low-temperature CO_2 hydrogenation with exceptional stability, the authors establish a generalizable platform for designing well-defined heterogeneous catalysts. The ability to isolate and stabilize discrete heteroatom-containing clusters within periodic frameworks opens new avenues for mechanistic studies that were previously inaccessible owing to catalyst heterogeneity. Moreover, the per-pass yield of $PtMo_6O_{24}$@NU1K (13.1% at 200 °C) under mild conditions rivals or exceeds that of many conventional systems, and the complete absence of deactivation over 3,600 h addresses one of the most persistent challenges in CO_2 hydrogenation—catalyst longevity. The $PtMo_6O_{24}$@NU1K system achieves a methanol selectivity of ~ 79.0% in the hydrogenation of CO_2 to methanol. Although this value is markedly higher than that of many existing systems, it remains suboptimal. Notably, the exceptional catalyst stability partially compensates for this moderate selectivity by reducing replacement downtime [3]; nevertheless, enhancing selectivity remains a key objective for future research. Beyond the above, several remaining issues warrant brief discussion. First, the catalyst relies on noble-metal Pt, raising concerns regarding cost and long-term sustainability. Second, the formate pathway was observed only under elevated temperature and pressure (> 1.5 MPa), leaving its relevance under milder conditions unclear. Third, the space–time yield of methanol under the reported conditions may still be insufficient for industrial requirements, despite the exceptional long-term stability. Inspired by the insights from this work, future efforts could be directed toward the following aspects: (1) modulating the electronic structure of the Pt center through heteroatom substitution or partially metal replacement; (2) engineering MOF pore environments to create a more favorable microenvironment for CO* hydrogenation; and (3) carefully regulating cluster aggregation within the pores while optimizing mass transport of CO_2 and CH_3OH through the pore network. These strategies hold promise for simultaneously enhancing methanol selectivity and maintaining the exceptional stability of the catalyst.

However, from a broader perspective, this study exemplifies how the integration of precise inorganic cluster chemistry and reticular chemistry can transform heterogeneous catalysis into a quasi-homogeneous, molecularly defined discipline. The $PtMo_6O_{24}$@NU1K system provides a high-performance catalyst for low-temperature CO_2 conversion and an ideal model system for elucidating reaction mechanisms at atomic resolution. As the demand for sustainable, energy-efficient chemical processes intensifies, such well-defined, ultra-stable catalyst architectures—where active site are uniform and structurally well controlled—will be instrumental in bridging the gap between fundamental understanding of structure–activity relationships and reaction mechanisms and industrial application of low- temperature CO_2 hydrogenation and related energy-efficient catalytic processes. The work by Joseph T. Hupp, Zhihengyu Chen, Wentuan Bi, and Rachel B. Getman thus charts a promising path toward the rational design of next-generation catalysts for CO_2 hydrogenation and beyond, including processes such as ammonia synthesis and selective oxidation (e.g., of alkanes or alkenes), where control over both the primary coordination sphere and the nanoconfined microenvironment is paramount.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors reports no conflict of interests in this work.

Author contribution statement

J. Y. Linghu: Writing – original draft. T. F.: Investigation, funding acquisition, writing – review & editing. X. Y.: Supervision, funding acquisition, project administration, writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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