Entrapped Single Tungstate Site in Zeolite for Cooperative Catalysis of Olefin Metathesis with Brønsted Acid Site

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Supporting Information

ABSTRACT: Industrial olefin metathesis catalysts generally suffer from low reaction rates and require harsh reaction conditions for moderate activities. This is due to their inability to prevent metathesis active sites (MASs) from aggregation and their intrinsic poor adsorption and activation of olefin molecules. Here, isolated tungstate species as single molecular MASs are immobilized inside zeolite pores by Brønsted acid sites (BASs) on the inner surface. It is demonstrated that unoccupied BASs in atomic proximity to MASs enhance olefin adsorption and facilitate the formation of metallocycle intermediates in a stereospecific manner. Thus, effective cooperative catalysis takes place over the BAS−MAS pair inside the zeolite cavity. In consequence, for the cross-metathesis of ethene and trans-2-butene to propene, under mild reaction conditions, the propene production rate over WOx/USY is ca. 7300 times that over the industrial WO3/SiO2-based catalyst. A propene yield up to 79% (80% selectivity) without observable deactivation was obtained over WOx/USY for a wide range of reaction conditions.

1. INTRODUCTION

Olefins are essential feedstocks for the production of many petrochemicals, oleochemicals, polymers, and specialty chemicals. Catalytic olefin metathesis is an important reaction in the chemical industry. For example, the cross-metathesis of ethene and 2-butene to propene and the reverse reaction play a significant role in buffering the global supply of ethene and propene. Over the past 50 years, a number of metal oxides including Re2O7, MoO3, and WO3 supported on SiO2 and/or Al2O3 have been found to be effective as olefin metathesis catalysts under continuous flow conditions. For various reasons, an inexpensive and robust WO3/SiO2-based material is the only widely employed catalyst in the industry for the cross-metathesis of ethene and 2-butene to propene and the reverse reaction. High temperature (300−550 °C) and high pressure (>20 bar) are required for moderate activities to meet the industrial requirement. Active site isolation shifting from WO3 nanocrystals to surface polymeric WOx and ultimately to isolated WOx has been found to be effective as olefin metathesis catalysts under continuous flow conditions. Considerable efforts have been made on immobilizing isolated organometallic complexes on SiO2 and/or Al2O3 for high activities despite the fact that they tend to aggregate on open surfaces. The industrial application of these catalysts requires further development. Another way to improve the activity of the industrial WO3/SiO2-based catalyst becomes clear when one studies the fundamental olefin metathesis reaction mechanism. It is generally accepted that olefin metathesis proceeds via metallocycle intermediates in the rate-determining steps (Scheme 1). The efficient formation

Scheme 1. Reaction Mechanism of the Cross-Metathesis of Ethene and trans-2-Butene to Propene over Isolated WOx MASs

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of metallocycle intermediates requires fast adsorption of olefin molecules and appropriate alignment between the C=C bond of adsorbed olefin molecules and the W=O/W≡C bond of metathesis active sites (MASs) for [2 + 2] cycloaddition. This may be difficult to achieve with a catalyst that contains only isolated MASs. There is an indication from previous studies that the introduction of acidic sites to olefin metathesis catalysts can increase the rate of olefin metathesis reactions. Thus, enhanced activity is obtained when supported WO3 or MoO3 is blended with zeolites. However, the ill-defined interface between bulk acidic zeolite and MASs does not lead to significant rate enhancement, indicating the cooperative catalysis is not yet optimized.

Thus, we designed a new type of bifunctional olefin metathesis catalyst by placing an isolated tungstoxide as a WO3 MAS in a zeolite cavity where unoccupied Bronsted acid sites (BASs) are in atomic proximity for efficient cooperative catalysis. As a result, we show for the first time that, at 200 °C and 1 bar, the propene production rate over WO3-USY is ca. 7300 times that over the industrial WO3/SiO2-based catalyst. A propene yield up to 79% with 80% selectivity without observable deactivation can be achieved over WO3/USY for a wide range of reaction conditions. The structure of the WO3/USY catalyst was elucidated by synchrotron X-ray powder diffraction (SRXD) and Rietveld refinement, supported by aberration-corrected scanning transmission electron microscopy (STEM), extended X-ray absorption fine structure (EXAFS) spectroscopy, and so on. These characterization results and density functional theory (DFT) calculation suggest that olefin adsorption can be enhanced by unoccupied BASs, and the formation of metallocycle intermediates over the isolated WO3 MAS can be greatly facilitated by the nearby unoccupied BAS through the appropriate alignment between the C=C bond of adsorbed olefin molecules and the W≡O/W≡C bond of WO3 MAS for [2 + 2] cycloaddition. This accounts for the exceptional olefin metathesis rate observed.

2. EXPERIMENTAL SECTION

Catalyst Preparation. WO3/SiO2 was commercially available. WO3/zeolite catalysts (WO3/USY, WO3/ZSM-5, WO3/SAPO-11, WO3/SAPO-34, and WO3/β) were prepared by wet impregnation. WO3/USY was obtained from Tosoh. ZSM-5 and β were provided by Sinopec. SAPO-11 and SAPO-34 were purchased from ACS Material. The chemical composition of zeolite supports was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the chemical composition of (NH4)6H2W12O40·2(H2O) was determined using an element analyzer equipped with an SGE BP-1 column (100% dimethylpolysiloxane, 30 m length, 0.53 mm inner diameter, 50 μm film thickness) and a flame ionization detector. The trans-2-C2= conversion, propene (C3H6) selectivity, and carbon balance were calculated as follows:

\[
\text{conversion (trans-2-C2=)} = \frac{n(\text{trans-2-C2= in feed}) - n(\text{trans-2-C2= remaining})}{n(\text{trans-2-C2= in feed})}
\]

\[
\text{selectivity (C3H6)} = \frac{n(\text{C3H6})}{n(\text{all products})}
\]

\[
\text{carbon balance} = \frac{n(\text{C}) \text{ in products}}{n(\text{C}) \text{ in feed}}
\]

\[
\text{yield (C3H6)} = \text{conversion (trans-2-C2=)} \times \text{selectivity (C3H6)} \times \text{carbon balance}
\]

High-Resolution STEM. High-resolution electron microscopy was carried out using an aberration-corrected JEOL ARM200F. The microscope was operated at 200 kV in high-angle annular dark-field (HAADF)-STEM mode with HAADF detector collection semiangles from 73 to 236 mrad. The convergence semiangle was 31.48 mrad with probe array sizes of 1024×1024 and a dwell time of 0.8 μs per pixel. The probe current was 11 pA.

EXAFS and XANES. The local environment of W atoms in WO3/USY and WO3/ZSM-5 was probed by analyzing their k3-weighted W 1s-edge EXAFS spectra collected at beamline B18, Diamond Light Source, UK. The energy resolution (ΔE/E) was 2×10−4. Fluorescence mode was used. To ascertain data reproducibility, at least two data sets were collected for each sample. W metal was used as a reference to avoid energy shift of the measured EXAFS spectra. Data analysis was performed using IFEFFIT 1 with Horae packages 2 (Athena and Artemis). The amplitude parameter was set as a fixed input parameter to allow the refinement of the coordination number of W. This parameter was obtained from the analysis of the EXAFS spectrum of W metal. First-shell data analysis was performed under the assumption of single scattering with the errors estimated by an R-factor. The oxidation states of W in WO3/USY samples were evaluated by analyzing their k3-weighted W L2,3-edge X-ray absorption near-edge structure (XANES) spectra. These XANES spectra were compared with that of (NH4)6H2W12O40·2(H2O) in which the oxidation state of W is +6.

SXRD. High-resolution SXRD data were collected at beamline I11, Diamond Light Source, UK. The energy of the incident X-ray was 15 keV. The wavelength and the 2θ zero point were determined by fitting the diffraction data of high-quality silicon powder (SRM640c). SXRD data were collected for a WO3/USY sample, a WO3/ZSM-5 sample, a WO3/Na-USY sample, and a trans-2-butene-adsorbed WO3/USY (t2b-WO3/USY) sample. Before data collection, WO3/USY and WO3/ZSM-5 were treated under vacuum at 300 °C for 2 h. Adsorbed water should have been removed completely. The adsorption of trans-2-butene (2% in N2) on WO3/USY was performed at room temperature using a Schlenk line. The sample was treated under vacuum at 300 °C for 2 h beforehand. Adsorbed water should have been removed completely. Liquid N2 was used to quench the adsorption of trans-2-butene.

All samples were loaded into borosilicate glass capillaries (0.7 mm inner diameter) in a glovebox. Glass wool was packed on top of the sample. SXRD data were collected in a Debye–Scherrer geometry using multianalyzer crystal (MAC) detectors in the 2θ range of 0–150° with 0.001° data binning. Each data set was collected for 1 h for good statistics.

DFT Calculation. All periodic calculations were performed using spin-polarized DFT within the generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package J. Am. Chem. Soc. XXX, XXX, XXX–XXX

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Figure 1. Catalytic activities of WOx/zeolite catalysts. (A) Trans-2-butene conversion, propene selectivity, propene yield, and carbon balance over WOx/zeolite catalysts compared to those over WO3/SiO2 at T = 400 °C and p = 1 and (B) 20 bar. Time on steam (TOS) = 1 h. (C) Propene yield over WO3/SiO2, WO3/USY, and WO3/Na-USY at T = 100–550 °C, p = 1 bar, and (D) at T = 400 °C, p = 1, and 20 bar. TOS = 0.25 h. Carbon balance is above 95% in all experiments. (E) Propene yield over WO3/SiO2 [WOx/SiO2] + USY, WO3/(SiO2 + USY), and WO3/USY at T = 400 °C and p = 1 bar. SiO2 to USY mass ratio = 19/1. TOS = 1 h. Carbon balance is above 95% in all experiments. (F) Arrhenius plots for WO3/SiO2 and WO3/USY at T = 100–500 °C and p = 1 bar. (G) Dependencies of propene production rate on the partial pressure of trans-2-butene over WO3/SiO2 and WO3/USY at T = 450 °C and p = 1 bar. α: order of reaction.

3. RESULTS AND DISCUSSION
Catalytic Activities. Laboratory characterization results indicate that WOx MASs are well dispersed over all WOx/zeolite catalysts except for WOx/SAPO-34 (Figures S1–S4, Table S3). Figure 1A shows that the catalytic activities of all WOx/zeolite catalysts are superior to that of WO3/SiO2 at 1 bar, which can be indicative of a synergy between WOx MASs and the acidic sites in zeolites. Figure 1B shows that the catalytic activity of WO3/SiO2 can be significantly improved at 20 bar. This can be due to the increased rate of olefin adsorption over WOx MASs under higher applied pressure. It is interesting that the catalytic properties of all WOx/zeolite catalysts remain similar at the two different applied pressures, indicating that olefin adsorption could have readily taken place at a lower pressure in the presence of acidic sites. The difference in the catalyst acidity and zeolite structure can be seen as the primary cause of the variation in the catalytic activities of WOx/zeolite catalysts. WOx/ZSM-5, WOx/SAPO-11, and WOx/β with high acidic strength and/or large acid quantity (Figure S5) can give high trans-2-butene conversions but low propene selectivities and poor carbon balances. These materials favor the formation of heavy hydrocarbons and carbonaceous deposition due to their strong acidity and characteristic porous structures (Figures S6–S9). Less effective WOx dispersion is found in WO3/SAPO-34, as the smaller SAPO-34 pores inhibit the immigration of WOx during
Among all the catalysts studied, \( \text{WO}_x/\text{USY} \) exhibits the highest catalytic activity. As shown in Figures 1C and 1D, with \( \text{WO}_x/\text{SiO}_2 \) as a reference, \( \text{WO}_x/\text{USY} \) achieves significantly and consistently higher trans-2-butenes conversions (85–92%), propene selectivities (78–88%), and propene yields (70–79%) over a wide range of reaction conditions (\( T = 200–400 ^\circ \text{C}, p = 1–20 \text{ bar} \)). \( \text{WO}_x/\text{USY} \) also shows good stability for at least 20 h in our academic laboratory (Figure S10). Under mild conditions (\( T = 200 ^\circ \text{C}, p = 1 \text{ bar} \)), the propene production rate over \( \text{WO}_x/\text{USY} \) (3.5 mmol·g\(^{-1} \text{cat} \)·h\(^{-1} \)) is ca. 7300 times that over the industrial \( \text{WO}_x/\text{SiO}_2 \)-based catalyst (4.8 × 10\(^{-4} \) mmol·g\(^{-1} \text{cat} \)·h\(^{-1} \)) (see SI for rate calculation and number of active sites). We attribute this unprecedented high reaction rate to an essential cooperative catalysis of olefin metathesis.

Isolated \( \text{WO}_x \text{ MAS} \). The isolation of \( \text{WO}_x \text{ MAS} \) in USY pores was confirmed by high-resolution STEM. Isolated W-containing species can be clearly identified in the HAADF-STEM image of \( \text{WO}_x/\text{USY} \) (Figures 2A, 2B, and S11). They appear to locate inside USY pores. The USY framework underwent significant radiation damage during the image acquisition process due to the well-known electron beam sensitivity of zeolites.\(^{3,32} \) Thus, it is acceptable that part of the W-containing species aggregated and formed small clusters on the particle surface with increased electron beam exposure and consequent damage. Isolated \( \text{WO}_x \text{ MAS} \) was subsequently revealed to be a discrete molecular dioxo tungstate (\( \text{O} \equiv \text{W} \equiv \text{O} \)) of \( \text{WO}_4 \text{ MAS} \) by the best fitting of the \( k^2 \)-weighted W L\(_3\)-edge EXAFS spectra of \( \text{WO}_x/\text{USY} \) (Figures 2C, S12, and S13, Tables 1 and S4).

It is anticipated that \( \text{WO}_x \text{ MAS} \) inside USY pores may interact with BASs nearby. This is illustrated by comparing the catalytic activities of \( \text{WO}_x/\text{USY} \) and \( \text{WO}_x/\text{Na-USY} \) (Figures 1C and 1D). In the absence of BASs (\( \text{H}^+ \) replaced by \( \text{Na}^+ \)), \( \text{WO}_x/\text{Na-USY} \) clearly delivers inferior catalytic activity to \( \text{WO}_x/\text{USY} \) despite that its catalytic activity is still superior to that of \( \text{WO}_x/\text{SiO}_2 \). This supports our hypothesis that BASs in zeolite work in synergy with \( \text{WO}_x \text{ MAS} \) to enhance the overall catalytic activity. As shown in Figure 1E, the catalytic activity of our bifunctional catalyst is critically dependent on the interface between \( \text{WO}_x \text{ MAS} \) and BASs. The physical mixture of \( \text{WO}_x/\text{SiO}_2 \) and USY (\( \text{WO}_x/\text{SiO}_2 + \text{USY} \)) and the \( \text{WO}_x \)-deposited mixture of \( \text{SiO}_2 \) and USY (\( \text{WO}_x/\text{SiO}_2 + \text{USY} \)) have an ill-defined interface between \( \text{WO}_x \text{ MAS} \) and BASs. Thus, they are far less active than \( \text{WO}_x/\text{USY} \) in the cross-metathesis of ethene and trans-2-butene to propene. The high catalytic activity of \( \text{WO}_x/\text{USY} \) appears to be due to the effective interaction(s) between \( \text{WO}_x \text{ MAS} \) and BASs inside zeolite.

### Table 1. Structural Data for \( \text{WO}_x \text{ MAS} \) in \( \text{WO}_x/\text{USY} \) from Its Best Fitted \( k^2 \)-Weighted W L\(_3\)-Edge EXAFS Spectra

<table>
<thead>
<tr>
<th>scattering path</th>
<th>bond length (Å)</th>
<th>coordination number</th>
<th>Debye–Waller factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W-O_1 )</td>
<td>1.75(1)</td>
<td>2.2(1)</td>
<td>0.003(1)</td>
</tr>
<tr>
<td>( W-O_2 )</td>
<td>1.90(2)</td>
<td>0.8(1)</td>
<td>0.002(2)</td>
</tr>
<tr>
<td>( W-O_3 )</td>
<td>2.12(1)</td>
<td>1.1(2)</td>
<td>0.006(2)</td>
</tr>
</tbody>
</table>

(\( R = 0.33, \) \( E_{\text{calc}} = 4.1 \))

The structural details of unmodified USY along with the strength, quantity, and location of BASs have been reported in our previous work.\(^{38} \) BASs (\( \text{H}^+ \)) locate on \( \text{O}_4 \) of the USY framework with various strengths. We determined the location of \( \text{WO}_x \text{ MAS} \) in USY by refining the crystal structure of \( \text{WO}_x/\text{USY} \) using the Rietveld method in TOPAS-Academic.\(^5,39 \) Based on its high-resolution SXRD data (see SI for the general Rietveld refinement procedure). The rigid bodies describing \( \text{WO}_x \text{ MAS} \) were built based on EXAFS results and were added into the USY framework one by one, following the indication from a difference Fourier map. Weighted-profile R-factor (\( R_{wp} \)) and goodness-of-fit (GOF) were used to gauge the quality of Rietveld refinement. After the first \( \text{WO}_4 \) rigid body was added, \( R_{wp} \) and GOF were found to decrease, indicating the addition of the \( \text{WO}_4 \) rigid body was appropriate. The site occupancy of the second \( \text{WO}_4 \) rigid body added turned to be almost zero. Thus, the existence of the second \( \text{WO}_4 \) rigid body was not considered. As a result, one \( \text{WO}_4 \) rigid body was used to fit the SXRD data (Figures 3A and S14). The resulting crystallographic model of...
It is shown that the isolated WO₄ MAS is trapped in the USY cavity by W-O···(H)O₄ hydrogen bonding (O_WO₄···O₄ = 2.73(1) Å) on the inner surface (Figures 3C and 3D). The DFT calculation indicates the interaction energy between WO₄ MAS and (H)O₄ (BAS) is -141 kJ·mol⁻¹ (see the DFT calculation section and SI for details). The BAS directly bound to the WO₄ MAS has been demonstrated to be reinforced by the extra-framework Al³⁺ (EFAI) in the sodalite cage due to the polarization effect of EFAI on O₆. These strong BASs (sBASs) are fully taken up by WO₄ MASs for immobilization according to their resolved site occupancies (sBASs: 2.1 per unit cell (u.c.), WO₄ MAS: 2.8 per u.c.). There are remaining weak BASs (wBASs: 5.1 per u.c.) in close proximity to the immobilized WO₄ MAS in the USY cavity. The unoccupied wBASs in WO₄/USY can be selectively replaced by Na⁺. This is confirmed by the crystallographic position and resolved site occupancy (5.0 per u.c.) of Na⁺ in WO₄/Na-USY (Figure 3E, see SI for the detailed Rietveld refinement procedure and Figure S15 for data fitting). As described previously, the inhibition of wBASs results in a dramatic decrease in catalytic activity. This reflects the important role of unoccupied BASs in atomic proximity to WO₄ MASs for enhanced reaction rates.

We also found a similar entrapment and site isolation of WO₄ MASs in W_O₆/USY (400 °C and 1 bar). This reactivity loss of WO₄ in USY framework T sites were replaced by Al³⁺, leading to poor propene selectivity and rapid catalyst deactivation, as in the case of WO₄/USY. The weak unoccupied BASs in WO₄/USY guarantee high olefin metathesis catalytic activity and stability of the catalyst without significant side products and extensive carbon formation. In addition, the weak unoccupied BASs in WO₄/USY appear to be capable of catalyzing 1-butene (present in industrial reformat gases) to form 2-butene which participates in the cross-metathesis reaction with ethene to form propene. As a result, ca. 55% propene yield with ca. 95% 1-butene conversion can be achieved over WO₄/USY at 400 °C and 1 bar. This reflects the highly cooperative adsorption–metathesis mechanism in this well-designed catalyst.

Cooperative Catalysis over the BAS–MAS Pair.

Effective cooperative catalysis over the BAS–MAS pair is envisaged to be due to the appropriate alignment between the C=C bond of olefin molecules adsorbed over the BAS and the W=O bond of the WO₄ MAS. To confirm this hypothesis, trans-2-butene was loaded in WO₄/USY for the study of its adsorption geometry by SXRD and Rietveld refinement (Figure 3B, see SI for detailed Rietveld refinement procedure and Figure S19 for data fitting). The trans-2-butene molecule was found to be adsorbed over the unoccupied BAS with an O₄(H)···C₄t2be distance of 4.14(2) Å (t2be: trans-2-butene) (Figure 3F). This distance is expected for a significant interaction between the electron-rich C=C bond of trans-2-butene and the unoccupied BAS (H⁺). This could easily lead to the protonation of trans-2-butene at elevated temperature.

Perhaps the most intriguing observation is that the C=C bond of trans-2-butene appears to have aligned with the W=O bond of nearby WO₄ MAS at room temperature with a noticeable interaction (W_WO₄···C₄t2be = 2.86(1) Å). The C=C bond of trans-2-butene and the W=O bond of WO₄ MAS show a distorted square arrangement, which resembles the anticipated oxametallocycle intermediate formed in the initiation step (pseudo-Wittig initiation mechanism, Scheme 1). The oxametallocycle intermediate will lead to the formation of a reactive W carbene (W=CHCH₃) to start the metallacyclobutane catalytic cycle for catalytic olefin metathesis (Chauvin reaction mechanism, Scheme 1). In the metallacyclobutane catalytic cycle, it is envisaged that the BAS facilitates the adsorption and alignment of ethene to the nearby W carbene with stereospecificity in a similar manner to form a metallacyclobutane intermediate before propene is produced.

DFT Calculation. DFT calculation was carried out to study the metallacyclobutane catalytic cycle. The USY model (T₈⁺O₁₈⁶⁺ T = Si or Al) was built based on our previous work. It has a lattice parameter of 24.2680 Å and 7 BASs. Nine Si⁺⁺ at specific framework T sites were replaced by Al³⁺, and 2 extra-framework Al³⁺ were added in the sodalite cage. The resulting negatively charged USY framework was
compensated by adding 7 H⁺ at the O²⁻ directly connected to Al³⁺ (framework) and adding 2[(O==)₆W(−O)]²⁻ (WO₄ MAS) at random positions. These added H⁺ are active BASs of USY. Structure optimization shows that WO₄ MASs inside USY are most likely bound to H−O⁻ of the framework (Figure S20). This is in line with the results from Rietveld refinement.

We first calculated the adsorption and conversion of ethene and trans-2-butene over WO₄ MASs, in order to determine which of the two, W═CH₂ or W═CH₂CH₃, is the intermediate to initiate the metallacyclobutane catalytic cycle. As shown in Figure S21, the formation of W═CH₂CH₃ from trans-2-butene is thermodynamically more favored due to its lower Gibbs reaction energies. In particular, the formation of W═CH₂CH₃ in the presence of an unoccupied neighboring BAS is kinetically feasible. Therefore, a W═CH₂CH₃ with an unoccupied BAS nearby was used as the intermediate to initiate the metallacyclobutane catalytic cycle.

Figure 4 shows the energy diagram of the metallacyclobutane catalytic cycle over a W═CH₂CH₃ in the presence/absence of an unoccupied BAS nearby. The metallacyclobutane catalytic cycle is initialized by ethene being adsorbed at the W═CH₂CH₃ to form a W cyclobutane intermediate. This is followed by the concerted C−C and W−C bond scissions leading to the formation of the first propene. This step is exothermic with a reaction energy (ΔG) of −21 kJ·mol⁻¹ in the absence of BAS. The calculated Gibbs energy of activation (ΔG‡) is 94 kJ·mol⁻¹. This is comparable to the experimental apparent activation energy (E_a) obtained for WO₄/SiO₂ which does not have a BAS close to its MAS (108.6 kJ·mol⁻¹, Figure 1F). This kinetically relevant step in the first half of the metallacyclobutane catalytic cycle is significantly promoted when an unoccupied neighboring BAS is present. A dramatically low ΔG‡ (62 kJ·mol⁻¹) was obtained, and the concerted C−C and W−C bond scissions are more exothermic (ΔG = −103 kJ·mol⁻¹). The cooperation between the active W═CH₂CH₃ and the unoccupied neighboring BAS is shown to play a key role in increasing olefin metathesis reaction rate, despite that the experimental E_a for WO₄/USY (29.9 kJ·mol⁻¹, Figure 1F) cannot allow a direct comparison with the activation barrier obtained from DFT calculation. The value of experimental E_a is indicative of diffusion limitation which leads to a complex rate−temperature relationship. Upon releasing the first propene, a reactive W═CH₃ is formed and is ready for the adsorption of trans-2-butene to form a W cyclobutane intermediate subsequently. It is found that the adsorption of trans-2-butene and the formation of the W cyclobutane intermediate are affected by the presence of the unoccupied neighboring BAS. More importantly, the calculated ΔG‡ of the second concerted C−C and W−C bond scissions in the presence of the unoccupied neighboring BAS (53 kJ·mol⁻¹) is much lower than that without the BAS present (86 kJ·mol⁻¹).

The order of reaction with respect to trans-2-butene in excessive ethene was evaluated for WO₄/SiO₂ (1.8 ± 0.1) and WO₄/USY (1.3 ± 0.1), respectively (Figure 1G). The apparent higher order of reaction with respect to trans-2-butene in the case of WO₄/SiO₂ again suggests WO₄/SiO₂ has a stronger dependence on the availability of adsorbed olefin. This reflects that the higher activation energy process of surface trans-2-butene adsorption is rather difficult to proceed in WO₄/SiO₂. In contrast, as demonstrated, the presence of unoccupied BASs in USY makes a significant contribution to increasing the availability of trans-2-butene (with a lower E_a and a lower order of reaction, Figure 1F and Figure 1G) and ethene to WO₄ MASs in the atomic vicinity. Thus, both experimental and theoretical evaluations suggest that the cooperative catalysis between BASs and MASs leads to an overall enhanced catalytic activity.

4. CONCLUSIONS

We have designed a new type of bifunctional olefin metathesis catalyst by immobilizing isolated single WO₄ MASs in a zeolite cavity where unoccupied BASs are in atomic proximity. Within the confined zeolite cavity, we demonstrate that BASs facilitate the adsorption and activation of olefin molecules for the metathesis reaction over WO₄ MASs. This leads to a dramatically enhanced olefin metathesis reaction rate. We report an exceptional propene production rate and thermal stability of WO₄/USY under industrially applicable conditions.

In general, the concept of cooperative catalysis presented here, using two active sites of different functionalities within atomic proximity in a molecular cavity, can provide new opportunities for designing synergistically adsorptive and catalytic materials.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03012.

Methods and additional results of catalyst testing, structure refinement, physical characterization, and suggested future work (PDF)

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