



Enhanced Olefin Metathesis Performance of Tungsten and Niobium Incorporated Bimetallic Silicates: Evidence of Synergistic Effects

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Abstract: Tungsten and niobium incorporated KIT-6 (WNb-KIT-6) materials were synthesized by a one-pot sol-gel method. During 2-butene + ethylene metathesis with these materials at 450°C, the propene yield is maximized (~70%) at a certain metal composition (~20 wt% W and ~1 wt% Nb), significantly surpassing those reported with an industrial WO₃/SiO₂ catalyst. The enhanced propene yield is attributed to better dispersion of W species on the catalyst surface and the formation of new active site precursors (O=)₂W(O-Si)(O-Nb), as confirmed by XRD, TEM, H₂-TPR, XPS, EXAFS, and ToF-SIMS techniques. Complementary DFT calculations reveal a positive correlation between the O=W=O bond angle and the propene yield. We therefore speculate that the -O-Nb moiety tunes the electronic environment around the W atom and increases the propene yield.

Introduction

Metathesis involving light alkenes is gaining importance as an atom economical route to augment the supply of certain olefinic feedstocks based on demand.^[1] Catalysts investigated widely for olefin metathesis include WO₃, MoO₃, and Re₂O₇ supported on either SiO₂ or Al₂O₃.^[2-24] Because of its robustness towards poisons and relatively low cost, the WO₃/SiO₂ catalyst has been

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widely used in industry to produce propene from ethylene and butenes. Recently, several groups (Wachs^[8,25], Stair^[11], Bell^[12], Subramaniam^[26]) have reported on the structure-activity relationship of supported W catalysts. These studies suggest that W-O-Si type species are the active site precursors for metathesis and that maximizing such species via catalyst synthesis techniques is a key to increasing propene yield.

A recent patent^[27] reported that the addition of 0.01-10 wt% of niobium or its oxide into the WO₃/SiO₂ catalyst (0.1-20 wt% W loading) promotes the disproportionation of butene to produce propene. Verpoort et al.[28] reported that anchoring aryloxy tungsten complexes on NbOx/SiO2 yields higher 2-pentene metathesis activity than catalysts without NbOx. However, a detailed understanding of the active sites in these supported multi-metallic oxides is still lacking. In organometallic chemistry, ligands are used to tune the electronic and/or steric influence on metal centers to enhance the yield towards targeted products.[29-^{31]} A similar analogy may be invoked to explain the functioning of a WO₃/SiO₂ catalyst in which the active site precursor $(O=)_2W(O-)_2^{[8,12]}$ is grafted on the SiO₂ framework (Scheme 1a). In such a scenario, the SiO₂ framework alters the electronic nature of the W center to render it active for metathesis. The active site precursor (O=)₂W(O-)₂ possesses two (O-) moieties that provide the possibility for tuning the electronic nature of the W center by replacing one Si atom with another element (such as Nb, Scheme 1b). The sol-gel method^[7,15,32,33] allows the synthesis of such types of structures wherein the Si and Nb sources are first hydrolyzed to form the framework, following which the W species are grafted onto the Nb₂O₅-SiO₂ framework.

Motivated by this hypothesis, we synthesized a series of WNb-KIT-6 mesoporous catalysts with different W and Nb loadings by sol-gel method. We find that the catalyst performance is indeed enhanced at certain bimetal loadings, with the W₁₀Nb₁-KIT-6 catalyst (~20 wt% W loading and ~1 wt% Nb loading) yielding up to ~70% propene yield at steady state. This substantially exceeds the performances of W-KIT-6^[15] and W-EISA^[17] catalysts (~60% propene yield) at identical reaction conditions. The enhanced performance is attributed to the traditional W dioxo species and the formation of new active site precursors (O=)₂W(O-Si)(O-Nb), which were confirmed by H₂-TPR, XPS, EXAFS and ToF-SIMS techniques. Our results suggest that such synergy imparted by the second metal can be systematically exploited in heterogeneous catalysis.

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Scheme 1. (a) 2-Butene and ethylene react on WO₃/SiO₂ catalysts (W-KIT-6 and W-EISA) to generate propene. The W surface active precursor is bonded to the SiO₂ framework. (b) 2-Butene and ethylene react on WNb-KIT-6 catalyst to form propene. The W surface active precursor is bonded to Si and Nb atoms. The framework structures (-O-Si and -O-Nb) influence the chemical environment around the W center.



Results

Synthesis and Characterization of the WNb-KIT-6, Nb-KIT-6, and W-KIT-6 catalysts. Figure 1 shows the wide-angle XRD patterns of WNb-KIT-6, Nb-KIT-6, and W-KIT-6 catalysts. The W10-KIT-6 (Na) catalyst (synthesized from Na2WO4, labeled with "Na" in the parentheses) displays a strong signal corresponding to crystalline WO₃ species, while the W₁₀-KIT-6 catalyst (synthesized from ammonium metatungstate, represented without any label) shows a weak signal of crystalline WO₃ species, indicating better W dispersion on the surface. This may be due to the Na₂WO₄ reagent possessing a higher hydrolysis rate than ammonium metatungstate in the presence of HCI. The Nb1-KIT-6 exhibits only a broad band of amorphous SiO₂ between 15° and 30°, indicating the Nb species are well dispersed in the framework, which is also confirmed by TEM mapping results (Figure S6). The incorporation of Nb in W10Nbx-KIT-6 yields a new peak at approximately 22.8° which gradually increases between 1 - 10 Nb/Si mol% but not seen at 0.25 and 0.5 Nb/Si mol% (Figure 1). This new peak is attributed to Nb_xW_yO_z species (Figure S1). Interestingly, no crystalline WO₃ reflections were observed when Nb was incorporated into the SiO₂ framework of KIT-6 during the synthesis, indicating that Nb increases the dispersion of surface WO_x species. Small angle XRD results (Figure S2) show a peak centered around $0.89\text{-}0.91^\circ$ for $W_{10}Nb_{0.25\text{-}2.5}\text{-}KIT\text{-}6$ catalysts, indicating these WNb-KIT-6 catalysts have ordered structure. However, the W10Nb10-KIT-6 and W10Nb5-KIT-6 catalysts show either poorly resolved or no peak below 1°, indicating that these two catalysts have low ordering in their structures. This conclusion is also confirmed by TEM images (Figures S4a, S4b).



Figure 1. Wide angle XRD patterns of W₁₀-KIT-6 (Na), W₁₀-KIT-6, Nb₁-KIT-6, and W₁₀Nb_x-KIT-6 catalysts (x = 0.25 - 10). The broad band between 15° and 30° is due to amorphous SiO₂.

 N_2 sorption isotherms and the corresponding pore size distributions of WNb-KIT-6, W_{10} -KIT-6, and Nb₁-KIT-6 catalysts reveal that these catalysts exhibit type IV isotherm and H1 hysteresis loop (Figure S3 and Table S1). The BET surface area, pore volume, and average pore size of the WNb-KIT-6 catalysts are in the range of 545–448 m²/g, 0.59–0.53 cm³/g, and ~9.6 nm, respectively (see Table S1). When the Nb element was incorporated into the framework of W_{10} -KIT-6 catalyst (S_{BET} = 450 m²/g), the BET surface area increased gradually reaching 545 m²/g in $W_{10}Nb_{10}$ -KIT-6 catalyst. The values of the (Si/W) and (Si/Nb) ratios in the synthesis gel are close to those measured by ICP-OES, indicating that the W and Nb species were fully incorporated into the catalyst (Table S1).

Representative transmission electron microscopy (TEM) image, scanning transmission electron microscopy-high angle annular dark-field (STEM-HAADF) image and energy dispersive X-ray spectroscopy (EDX) mapping of W₁₀Nb₁-KIT-6 catalyst are shown in Figure 2. The TEM images of all WNb-KIT-6 catalysts are shown in Figure S4. Highly ordered pores and channels are clearly visible in the TEM image (Figure 2a) and STEM-HAADF image (Figure 2c), which are consistent with the results from N₂ physisorption study (Figure S3). The presence of less resolved diffraction spots (Figure 2a insert) indicates that the W10Nb1-KIT-6 catalyst may contain nanocrystals (nano-WO₃, as also confirmed by UV/Vis experiment, vide infra). The nanocrystals (~1 nm) are more clearly seen in the high-resolution STEM-HAADF image (Figure 2b). The EDX mapping results (Figure 2d) show a uniform distribution of W, Nb, Si, and O species throughout the W10Nb1-KIT-6 catalyst. Comparative TEM results of W10-KIT-6 and Nb₁-KIT-6 catalysts (Figures S5 and S6) show that the size of nano-WO₃ on W₁₀-KIT-6 is slightly larger (1-2.5 nm, as inferred from Figure S5b) lending further credence to the hypothesis that Nb incorporation enhances the dispersion of W species.

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Figure 2. TEM images of the W₁₀Nb₁-KIT-6 catalyst. TEM image (a) and STEM-HAADF image (c) show the highly ordered pores and channels of the W₁₀Nb₁-KIT-6 catalyst. The insert in the TEM image (a) shows the less resolved diffraction spots, indicating the W₁₀Nb₁-KIT-6 catalyst contains some nanocrystals. The high-resolution STEM-HAADF image (b) shows the presence of nanocrystals. The orange box in Figure 2c is chosen for EDX mapping. W, Nb, Si, and O distributions (d-g) are shown in green, cyan, yellow, and orange, respectively.

The nature and the coordination of W species in the W-KIT-6 and WNb-KIT-6 catalysts were studied by DR UV/Vis spectroscopy in the range of 190-800 nm under ambient conditions (Figure 3). The absorption band at 233 nm is due to the hydrated isolated tetrahedral [WO₄]²⁻ species.^[32,34,35] The band around 270 nm is attributed to hydrated octahedral polytungstate species.^[32,34,35] A well-resolved band around 400 nm is observed on W10-KIT-6 catalyst, which is due to the crystalline WO3 species.^[32,34,35] However, the WO₃ species (400 nm) disappeared in the case of W10Nb2.5-10-KIT-6 materials. At lower Nb loadings, broad and less-resolved bands around 400 nm were observed in W10Nb0.25-1-KIT-6 catalysts similar to the W10-KIT-6 catalyst. These results further strengthen the explanation that Nb incorporation into the catalyst improves the dispersion of W species on the catalyst surface, which is in agreement with wideangle XRD (Figure 1) and TEM (Figures 2 and S5) results. A weakly resolved band around 190 nm, in the background of hydrated isolated tetrahedral $[WO_4]^{2-}$ species, is attributed to the hydrated tetrahedral NbO₄ units,^[36-38] This band (~190 nm) is more clearly observed in the Nb1-KIT-6 catalyst sample (Figure S7).



Figure 3. DR UV/Vis spectra of fresh W_{10} -KIT-6 and W_{10} Nb_x-KIT-6 catalysts (x = 0.25 - 10). The UV/Vis measurements were performed at ambient conditions.

Metathesis of Ethylene and 2-Butene to Make Propene. The metathesis activity of Nb₁-KIT-6, W₁₀-KIT-6 (Na), W₁₀-KIT-6, and W₁₀Nb_x-KIT-6 catalysts (x = 0.25 - 10) were compared at the following conditions: $T = 450^{\circ}$ C, P = 1 atm, WHSV (ethylene and 2-butene) = 2.0 h⁻¹, n(ethylene)/n(2-butene) = 3/1 (Figures 4, S8 and S9). Compared with the W₁₀-KIT-6 (Na) catalyst,^[15] the W₁₀-KIT-6 catalyst (prepared with ammonium metatungstate as source) showed a remarkable increase in 2-butene conversion from 46.6 ± 0.7% to 71.7 ± 0.6% and propene yield from 36.6 ± 0.5% to 60.7 ± 0.7%. This enhancement is consistent with better W dispersion based on wide-angle XRD results (Figure 1).

To further understand the influence of Nb incorporation on the W-KIT-6 catalysts, the metathesis activities of the W10Nbx-KIT-6 catalysts listed in Figure 3 were measured in continuous runs. Figure S9 provides the temporal profiles for 2-butene conversion, propene selectivity and propene yield for the various catalysts. The equilibrium propene yield at T = 450 °C, P = 1 atm, n(ethylene)/n(2-butene) = 3/1 is ~83 %, which was estimated with Aspen Plus[®] 8.6 software (Figure S10). As shown in Figure 4, the W10Nb1-KIT-6 catalyst provides the maximum values of 2-butene conversion (79.1 \pm 0.6%), propene selectivity (87.9 \pm 0.2%), and propene yield (69.6 ± 0.6%). Temporal 2-butene conversion as well as propene, 1-butene, and pentenes selectivity profiles for W₁₀Nb₁-KIT-6 are shown in Figure S11. At higher Nb loadings, these values decrease and are either similar to or less than those observed with the W10-KIT-6 catalyst. For example, the performance of W10Nb10-KIT-6 was significantly worse when compared to the W10-KIT-6 catalyst, which is attributed to the formation of inactive NbxWyOz species (Figure S1). In contrast, the performances of W10Nb0.25-KIT-6 and W10-KIT-6 are similar. This suggests that W and Nb exhibit synergy only at certain relative loadings.

We hypothesise that the bimetallic silicate possesses a combination of the two types of sites shown in Scheme 1b. The enhanced metathesis activity results from both the conventional W dioxo species anchored to only Si (Scheme 1a) and the more active W sites anchored to adjacent Si and Nb (Scheme 1b, M = Nb). For a given W loading, there exists an optimum Nb loading that maximizes the number of adjacent Nb and Si sites. Higher Nb loading results in a progressively increasing population of Nb_xW_yO_z, isolated Nb, and polymeric Nb species that are less active than either of the two active species shown in Scheme 1. Consequently, the optimum Nb loading that maximizes the population of the active sites (and the propene yield) is relatively low compared to the W loading. The propene yield of $69.6 \pm 0.6\%$, observed with W10Nb1-KIT-6, exceeds those reported with other W-incorporated mesoporous silicates [59.2 ± 0.5% for W-KIT-6 (Na)^[15] and 60.1 ± 1.4% for W-EISA^[17]] at the same reaction conditions. The apparent activities of various catalysts from our work and those reported by others are compared in Table 1. Clearly, the W₁₀Nb₁-KIT-6 catalyst shows the best apparent activity value of 9.92 mmol g⁻¹h⁻¹. Interestingly, as seen from Figure 4, the propene yield and the total acidity follow an identical trend, as also reported in previous studies. [15,17,39]

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Figure 4. 2-Butene conversion, propene selectivity, propene yield and total acidity of Nb₁-KIT-6, W₁₀-KIT-6 (Na), W₁₀-KIT-6, and W₁₀Nb_x-KIT-6 catalysts (x = 0.25 - 10) at $T = 450^{\circ}$ C, P = 1 atm, WHSV (ethylene and 2-butene) = 2.0 h⁻¹, n(ethylene)/n(2-butene) = 3/1. The propene yields represent the mean of the steady state values between 5-7 h. The "KIT-6" are omitted in the caption for brevity.

 Table 1. The compared apparent activity for some W-based catalysts.

Catalyst	W loading (wt%)	Propen e yield (%)	Apparent activity (mmol g ⁻¹ h ⁻¹)
W ₁₀ -KIT-6 ^a	19.2	60.7	8.66
W ₁₀ Nb ₁₀ -KIT-6 ^a	16.9	31.6	4.50
W ₁₀ Nb ₅ -KIT-6 ^a	19.1	45.6	6.50
W ₁₀ Nb _{2.5} -KIT-6 ^a	20.0	62.6	8.93
W ₁₀ Nb ₁ -KIT-6 ^a	20.9	69.6	9.92
$W_{10}Nb_{0.5}$ -KIT-6 ^a	20.0	61.7	8.79
$W_{10}Nb_{0.25}\text{-}KIT\text{-}6^a$	19.2	59.6	8.50
W-KIT-6 (2 h, 9.2) ^{[15],a}	9.2	59.2	8.44
W-EISA (22.2) ^{[17],a}	22.2	60.1	8.57
WO ₃ /SiO ₂ ^{[34],b}	24.0	79.7	3.03
WO _x -imp-Si ^{[40],c}	9.8	N.A.	~2

^a 1 g of catalyst, $T = 450^{\circ}$ C, P = 1 atm, WHSV (ethylene and 2butene) = 2.0 h⁻¹, n(ethylene)/n(2-butene) in feed = 3/1; ^b 3 g of catalyst, $T = 200^{\circ}$ C, P = 3 atm, WHSV (ethylene and 2butene) = 1.6 h⁻¹, n(ethylene)/n(2-butene) in feed = 3/1; ^c 0.1 g of catalyst, $T = 250^{\circ}$ C, 8 mL/min reaction feed consisting of ethylene and trans-2-butene (1:1 molar ratio) together with 10 vol.%N₂.

Relationship between Metathesis Activity and the Structure of the Active Sites. To elucidate the nature of the active sites, the H₂-TPR experiments were performed on Nb₁-KIT-6, W₁₀-KIT-6, W₁₀Nb_x-KIT-6, and WO₃/Nb₂O₅ samples (x = 0.25 – 10, Figure 5). The Nb₁-KIT-6 catalyst showed a silent signal from 100 to 1050°C, indicating strong interaction of the Nb species with the framework. In contrast, the W₁₀-KIT-6 catalyst exhibited three reduction peaks at 800, 868, and 928°C, which may be attributed to the stepwise reduction from WO₃ to W(0) [WO₃(VI) \rightarrow W₂₀O₅₈ (V, VI) \rightarrow WO₂(IV) \rightarrow W(0)]^[41]. Upon the incorporation of Nb element into the W₁₀-KIT-6 catalyst, a new reduction peak at

800°C was observed on W₁₀Nb₁₀-KIT-6 catalyst and this peak shifted to lower temperatures (700-718°C) with decreasing Nb/Si mol%, indicating the existence of W-Nb interaction. The reduction peak at 718°C observed with the W₁₀Nb₁-KIT-6 catalyst was assigned to the W-O-Nb structure based on the observation of a reduction peak with a WO₃/Nb₂O₅ model catalyst at 714°C. The peak around 818°C on WO₃/Nb₂O₅ catalyst is attributed to the reduction of Nb₂O₅ interacted with W species, based on the reduction peak of Nb₂O₅ at 860°C (Figure S14).



Figure 5. H₂-TPR profiles of (a) Nb₁-KIT-6, (b) W_{10} -KIT-6, (c) W_{10} Nb₁₀-KIT-6, (d) W_{10} Nb₅-KIT-6, (e) W_{10} Nb₂-KIT-6, (f) W_{10} Nb₁-KIT-6, (g) W_{10} Nb_{0.5}-KIT-6, (h) W_{10} Nb_{0.25}-KIT-6, and (i) WO_3 /Nb₂O₅ catalysts.

To further understand the enhanced metathesis activity on the $W_{10}Nb_1$ -KIT-6 catalyst, W 4f XPS studies were performed on $W_{10}Nb_1$ -KIT-6 and W_{10} -KIT-6 catalysts (Figure 6). Compared to W_{10} -KIT-6, the $W_{10}Nb_1$ -KIT-6 catalyst exhibited a higher peak intensity at approximately 33.9 eV. This result suggests that Nb incorporation into W_{10} -KIT-6 catalyst increases the population of the active site precursors. Quantitative estimates of surface enrichment by W species from XPS data are shown in Table S2.



Figure 6. Photoemission W 4f feature of $W_{10}Nb_1$ -KIT-6 and W_{10} -KIT-6 catalysts.

The XAFS technique is a powerful tool that can provide information on the local symmetry, coordination and oxidation state of an atom of interest in the catalyst.[42] The Nb L3-edge XANES spectra for Nb₂O₅, W₁₀Nb₁-KIT-6 and Nb₁-KIT-6 samples under total electron yield (TEY) and fluorescence yield (FY) modes are shown in Figure 7. Double-featured peaks (2372.95 eV at peak A and 2375.80 eV at peak B) are dominant in Figure 7, accompanied by a weak signal at approximately 2387.05 eV (peak C). The peaks at A and B are due to the $2p_{3/2} \rightarrow 4d_{5/2}$ transition, while the weak signal at C is attributed to the $2p_{3/2} \rightarrow 5s$ transition.^[42-44] The observed double-featured peaks at A and B originate from the ligand field splitting of d-orbitals of Nb atom.^[44,45] For the $W_{10}Nb_1$ -KIT-6 and Nb_1 -KIT-6 samples, the intensity of peak A is greater than peak B, which indicates that the Nb atom is in octahedral coordination.^[42, 45] At the same time, the W10Nb1-KIT-6 and Nb1-KIT-6 samples show the same absorptionedge as Nb₂O₅ (+5) reference, which demonstrates that the oxidation state of the Nb in W10Nb1-KIT-6 and Nb1-KIT-6 samples is +5.[42] Besides, we noticed that the total peak area (A and B) of W₁₀Nb₁-KIT-6 catalyst is higher than that of Nb₁-KIT-6 when the W and Nb elements co-exist in the KIT-6 matrix, implying the depletion of Nb 4d electron density in the W10Nb1-KIT-6 sample.^[42] This points to an interaction between W and Nb elements.



Figure 7. Nb L₃-edge XANES spectra for Nb₂O₅, W₁₀Nb₁-KIT-6 and Nb₁-KIT-6 samples at ambient condition. The Nb₂O₅ sample was measured with total electron yield (TEY) mode, while the W₁₀Nb₁-KIT-6 and Nb₁-KIT-6 samples were measured with fluorescence yield (FY) mode.

The normalized tungsten L₃-edge XANES spectra for W₁₀-KIT-6, W₁₀Nb₁-KIT-6 catalysts, and the reference WO₃ at ambient condition are shown in Figure 8. The W₁₀-KIT-6 and W₁₀Nb₁-KIT-6 catalysts show the same absorption edge as the reference sample WO₃, indicating that the W element in calcined W₁₀-KIT-6 and W₁₀Nb₁-KIT-6 catalysts are in the oxidation state of +6.^[46] Besides, the W₁₀Nb₁-KIT-6 catalyst has greater peak intensity than W₁₀-KIT-6 catalyst, implying decreased W 5d electronic density in the W₁₀Nb₁-KIT-6 catalyst, which is consistent with Nb L-edge XANES. This further corroborates possible interaction between W and Nb elements in the W₁₀Nb₁-KIT-6 catalyst.^[47] This conclusion is in agreement with the Nb L₃-edge XANES results (Figure 8).

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Figure 8. Normalized tungsten L₃-edge XANES spectra for W_{10} -KIT-6, W_{10} Nb₁-KIT-6 catalysts, and the reference WO₃ at ambient condition.

To further confirm the proposed hypothesis, molecular specificity and surface sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS)^[6,48-52] was deployed to determine the surface composition. In the negative ToF-SIMS spectra (Figure 9), two interesting clusters were detected for W10-KIT-6 and $W_{10}Nb_1$ -KIT-6 catalysts: the SiWO₆⁻ (m/z = 308) ion demonstrates the presence of W-O-Si bonds on both catalysts, while the NbWO₆⁻ (m/z = 373) ion confirms the presence of W-O-Nb bond on W10Nb1-KIT-6 catalyst. Similar findings were also reported to confirm the formation of Ti-O-V bond on V2O5/TiO2 catalyst^[53] and W-O-V bond on V₂O₅-WO₃/TiO₂ catalyst^[54]. Even though the population of the species involving W-O-Nb bonds (Scheme 1b) on the W10Nb1-KIT-6 is low, we hypothesize that they are significantly more active than the conventional active site without Nb (Scheme 1a), resulting in a net enhancement of the metathesis activity.



Figure 9. Partial negative ToF-SIMS spectra of W_{10} -KIT-6 and $W_{10}Nb_1$ -KIT-6 catalysts in the mass range m/z = 300-420.

Discussion

A new possible active site precursor on W₁₀Nb₁-KIT-6 is proposed in Scheme 1b (M = Nb) based on the evidence from H₂-TPR, XPS, EXAFS, and ToF-SIMS experiments. The dominant active site precursor on the WO₃/SiO₂ catalyst is (O=)₂W(O-Si)₂ species, as shown in Scheme 1a,^[8] created by grafting a W precursor on the SiO₂ framework. As shown in Scheme 1b, the new proposed active site precursor on W10Nb1-KIT-6 is (O=)2W(O-Si)(O-Nb), in which one Si atom is replaced by an Nb atom, when a Nb precursor is also grafted on the SiO₂ framework. The electronegativity (Pauling scale) of Nb atom is 1.60, while that of the Si atom is 1.90.^[55] The -O-Nb and -O-Si structures coordinate to the tungsten atoms and tune their activity. This hypothesis was confirmed by the Nb L3-edge XANES and W L3-edge XANES results (Figures 7 and 8). Similar electronic effects have been reported in the case of homogeneous Ru-based olefin-metathesis catalysis based on ligand design.[56,57]

To further understand the relationship between structure and catalytic activity, we synthesized and evaluated a series of W10M1-KIT-6 (M = Zr, Hf, and Ta) catalysts (Figure S15 and Table S2). Since all the W atoms are coordinated by two different OM groups (M = Si, Zr, Hf, Ta, and Nb), the question arises whether the O=W=O bond angles in the bimetallic catalysts may influence the metathesis activity similar to how the dihedral angle dictates the performance of Ru-P based catalysts in homogenous catalysis.[57] To compute the O=W=O bond angles, ten models for each of the bimetallic W₁₀M₁-KIT-6 (M = Zr, Hf, Ta, and Nb) catalyst were considered. One of the proposed active site precursor for W₁₀Nb₁-KIT-6 used in the computation is shown in Figure 10, while those for the other bimetallic catalysts are shown in Figure S16. Interestingly, a linear correlation is apparent for the calculated O=W=O bond angle and the initial propene yield on W10-KIT-6 and $W_{10}M_1$ -KIT-6 (M = Zr, Hf, Ta, and Nb) catalysts (Figure 11 and Scheme 2). Experimental evidence of active site precursors similar to those on W10Nb1-KIT-6 catalyst are shown in Figure S17. The foregoing results suggest that if the dopant and W form active site precursors as shown in Scheme 2, the O=W=O bond angle in such W-based bimetallic catalyst can be used to predict the relative metathesis activity of the doped catalysts. Given that the metathesis activity follows the same trend as acidity,[15,17,39] establishing a definitive link between bond angle and acidity in future investigations will shed further fundamental insights into the underlying mechanism and guide the rational design of metathesis catalysts.



Figure 10. Modelled active site precursor on $W_{10}Nb_1$ -KIT-6 catalysts. The metal structure is shown by the ball-and-stick-frame, the silica within the 6 Å sphere

is shown by the tube-frame region and the frozen silica by the wire-frame. O, Si, H, W, and Nb is labeled as red, gray, white, blue, and purple colors, respectively.



Figure 11. Enhancement of metathesis activity with increasing O=W=O bond angle for W_{10} -KIT-6 and $W_{10}M_1$ -KIT-6 (M = Zr, Hf, Ta, and Nb) catalysts.



Scheme 2. Apparent correlation between O=W=O bond angle and propene yield in W₁₀-KIT-6 and W₁₀M₁-KIT-6 (M = Zr, Hf, Ta, and Nb) catalysts.

Conclusion

We demonstrate a one-pot synthesis technique to prepare W-KIT-6 catalysts doped with Nb (WNb-KIT-6). At a certain combination of relatively high W loading and low Nb loading, the propene yield is maximized during ethylene + 2-butene metathesis reaction in a fixed bed reactor. The best performing catalyst W10Nb1-KIT-6 catalyst (W/Si = ~10 mol% and Nb/Si = ~1 mol%) displayed ~70% propene yield at steady state, which is significantly higher than values previously reported with W-KIT-6 and W-EISA catalysts (~60%) under identical reaction conditions. Nb incorporation enhances the dispersion of W species on the catalyst surface and produces new active sites. Based on the H2-TPD, XPS, EXAFS and ToF-SIMS results, the (O=)₂W(O-Si)(O-Nb) moiety is proposed as the possible active site precursor. In contrast, transition elements such as Ta, Hf, and Zr perform less effectively when doped into W-KIT-6. DFT computations predict that the O=W=O bond angle is increased upon dopant (M) introduction in the bimetallic WM-KIT-6 catalysts as follows: Nb>Ta>Hf>Zr. This increase in O=W=O bond angle correlates with enhanced metathesis activity on these catalysts compared to W-KIT-6. We therefore hypothesize that the -O-Nb moeity tunes the electronic environment around the W atom to increase the metathesis activity.

Methods

1.1 Materials

Ammonium metatungstate hydrate (H₂₆N₆O₄₀W₁₂·H₂O, \ge 85% WO₃ basis, gravimetric), Triblock copolymer Pluronic P123 (EO20-PO70-EO20, average MW = 5800), and tetraethyl orthosilicate (TEOS, 98%), Pluronic F127 were purchased from Sigma-Aldrich. Sodium tungstate (99.0-101.0%, Na₂WO₄·2H₂O) and WCl₆ (99%) were purchased from Alfa Aesar. Niobium (V) chloride (99+%-Nb) was purchased from Strem Chemicals. 1-Butanol (HPLC grade), hydrochloric acid (certified ACS plus) and ethanol were purchased from Fisher Scientific. 2-Butene (\ge 95 wt%, 39% *cis*-2-butene and 61% *trans*-2-butene) and ethylene (\ge 99.5%) were purchased from Matheson Tri-Gas Inc. All the reagents were used as received without further purification.

1.2 Catalyst preparation

1.2.1 W₁₀-KIT-6 catalysts

Following the protocols described in our earlier publication^[15], W10-KIT-6 and W10-KIT-6 (Na) were synthesized by using ammonium metatungstate hydrate and Na₂WO₄·2H₂O as tungsten source, respectively (Na represents Na₂WO₄·H₂O). The number 10 represents the W/Si mole percentage in the synthesis gel. In a typical synthesis procedure of W10-KIT-6 catalyst, a mixture of 4 g of P123, 140 mL of H_2O and 6.1 g of 37.1 wt% HCl was stirred at 38 ± 2°C overnight for dissolution. Then, 4.0 g of 1butanol were added and the mixture was stirred for 2.5 h. Following this step, 8.7 g of TEOS was added and the stirring was continued for 24 h. After that, 1.13 g of ammonium metatungstate hydrate (dissolved in 5 ml of H₂O) was added. After stirring for another 24 h, the resulting mixture was transferred into a Teflonlined autoclave and heated to 100°C for 24 h. The solid product was filtrated, then dried at 100°C overnight. The resulting sample was calcined in flowing air at 550°C for 5 h at a ramp rate of 1 °C/min. The W10-KIT-6 (Na) catalyst synthesis was using Na₂WO₄·2H₂O as W source, TEOS and Na₂WO₄·H₂O reagents were added at the same time. Other procedures are same as W10-KIT-6 synthesis.

1.2.2 Nb1-KIT-6 catalyst

The Nb₁-KIT-6 catalyst with Nb/Si mole ratio percentage of 1 was synthesized by hydrothermal method according to previously reported procedure.^[38] 0.112 g of NbCl₅ and 8.7 g of TEOS were simultaneously added to a mixture of P123, H₂O, HCl, and 1-butanol. Other steps are identical to those used for synthesizing W₁₀-KIT-6 catalyst, with Nb source replacing the W source.

1.2.3 W_xNb_y-KIT-6 catalysts

In a typical synthesis of W_xNb_y-KIT-6 catalysts, 4 g of P123 were dissolved in 140 mL of H₂O and 6.1 g of 37.1 wt% HCl by stirring at 38 ± 2°C overnight. Then, 4.0 g of 1-butanol were added and the mixture was stirred for 2.5 h. Following this step, 8.7 g of TEOS and the required amounts of NbCl₅ (to yield 0.25 – 10 Nb/Si mol%) were added and the stirring was continued for 24 h. Following this step, required amounts of ammonium metatungstate hydrate (to yield 1 – 10 W/Si mol%) dissolved in 5 ml of H₂O was added and the mixture was stirred for another 24 h. The resulting mixture was transferred into a Teflon-lined autoclave and heated to 100°C for 24 h. The solid product was

filtrated, then dried at 100°C overnight. The resulting sample was calcined in flowing air at 550°C for 5 h at a ramp rate of 1°C/min. The catalysts are denoted as W_xNb_y -KIT-6 where *x* and *y* represents the W/Si and Nb/Si mole percentages in the synthesis gel, respectively.

1.2.4 $W_{10}Hf_1$ -KIT-6, $W_{10}Ta_1$ -KIT-6, and $W_{10}Zr_1$ -KIT-6 catalysts

The synthesis of $W_{10}Hf_1$ -KIT-6, $W_{10}Ta_1$ -KIT-6, and $W_{10}Sn_1$ -KIT-6 catalysts are similar to the synthesis of $W_{10}Nb_1$ -KIT-6 catalyst, with the NbCl₅ reagent being substituted with HfBr₄, TaCl₅ and ZrOCl₂, respectively.

1.2.5 WO₃/Nb₂O₅ catalyst

The Nb₂O₅ is synthesized based on reported method^[58] with slight modification. The calcination of the as-synthesized Nb₂O₅ was carried out at 500°C. After calcination, Nb₂O₅ is impregnated with required amounts of WCl₆ solution in ethanol. The samples were dried overnight at 100°C and calcined again at 500°C.

1.3 Catalyst characterization

Small angle X-ray scattering and wide angle XRD patterns of W-KIT-6, Nb-KIT-6, WNb-KIT-6 catalysts were analyzed in a PANalytical Empyrean instrument, operating at 45 kV and 40 mA. The samples prepared for TEM analysis were suspended in ethanol solution and ultrasonically treated for 1 hour. Approximately 5 μ L of this mixture were dropped onto the copper grid and dried in air, which was then transferred into the TEM chamber for analysis. The catalyst morphology, particle size and active sites were analyzed by bright-field and dark-field transmission electron microscopy (TEM and STEM) using a FEI Technai G2 transmission electron microscope, operating at an electron acceleration voltage of 200 kV.

The W, Nb, and Si contents of the catalysts were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis on a Horiba Jobin Yvon JY 2000 instrument. The nitrogen adsorption-desorption isotherms were obtained on a Quantachrome NOVA 2000e instrument. The temperature-programmed desorption of ammonia (NH₃-TPD), and the temperature-programmed reduction (H₂-TPR) analysis were performed on the Micromeritics Autochem 2910 instrument. The diffuse reflectance UV/Vis (DR UV/Vis) spectra were obtained on a PerkinElmer Lambda 850 spectrometer, using Spectralon as the reference under ambient conditions. Detailed procedures for the various techniques (ICP-OES analysis, N₂ adsorption-desorption isotherms, NH₃-TPD, H₂-TPR and UV/Vis) are described elsewhere.^[15,33,59]

X-ray photoelectron spectroscopy (XPS) was measured on a PHI 5000 Versa Probe II instrument. Monochromated Al Ka (50 W. 15 kV) X-ray and a beam diameter of 200 µm was used for the measurement. The charging effect was eliminated by a dualbeam charge neutralizer. The spherical capacitance analyzer was operated with a pass energy of 46.95 eV for detailed scan. Prior to the analysis, the surface of the catalyst was sputtered with Ar⁺ ions (2.0 keV) for 5 min to expose the elements that reside deep in the pores of the catalyst. The following spectra were recorded: survey spectrum, Si 2p, Nb 3d, and W 4f. The resulting spectral data were processed with MultiPak software. All XPS peaks were referenced to the Si_{2p} peak at 103.3 eV. For solid-state NMR experiment, the fresh catalyst was treated with the dry N2 (high purity 99.99%, purified with a moisture trap) in a reactor at 550°C for 24 h with ramping rate of 2°C/min. The sealed reactor was transferred into an Ar glove-box and the sample was packed into a 4 mm Bruker rotor. Then, the sample was investigated by ¹H MAS NMR spectroscopy on a Bruker Avance III WB 400 MHz

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NMR instrument at a spinning rate of 10.0 kHz. The ¹H chemical shifts were referenced to tetramethylsilane (TMS) and the precision of the ¹H chemical shift is ± 0.1 ppm.

The mass spectra were collected on an OmniStar GSD 320 O mass spectrometer (Pfeiffer Vacuum). The range for the detection range is 1 to 300 aum. The temperature for the transfer line is set at 120°C to prevent condensation.

The time-of-flight secondary ion mass spectroscopy (ToF-SIMS) results were collected on a ToF-SIMS V instrument (ION-TOF GmbH Germany). The samples with 1×1 cm² area were mounted on a suitable sample holder and directly introduced into the instrument. The Bi3⁺ primary ion was used for the analysis with a primary ion energy of 30 keV and an analysis current of 0.75 pA. The analysis area is 50 \times 50 μ m² and the measurement time is 100 s. During the measurement, the flood gun was used for charge compensation.

X-ray absorption spectroscopy (XAS) measurements were used to identify the oxidation state, local symmetry, coordination of tungsten and niobium. W L3-edge spectra were collected at the IDEAS beamline of Canadian Light Source (CLS), using Ge (220) double crystal monochrometer for an energy range of 3.4-13.4 keV. Nb L3-edge XAS spectra were collected at the SXRMB beamline at the CLS. W L-edge spectra were recorded in both the transmission and fluorescence modes and transmission spectra were used for comparison. For Nb L-edge at the SXRMB, spectra were recorded in fluorescence mode using an SDD detector, and in total electron yield (TEY) by measuring the sample drain current For high concentration samples, e.g., Nb₂O₅, the TEY spectrum is used while the fluorescence spectrum was used for catalysts with low Nb loading. All measurements were performed at room temperature using pelleted powders with appropriate thickness for W L-edge or with powders spread thinly on the conducting carbon tape in a vacuum chamber for Nb L-edge. All the XAS data were analyzed by using Athena® software.

The Aspen Plus® 8.6 software was used to simulate the equilibrium conversion of 2-butene and ethylene to propene at different temperatures. The RCSTR reactor and Peng-Robinson equation of state were selected for the calculation. The following reactions were used for the calculation.

- (1) ethylene + *cis*-2-butene ≒ propene
- (3) cis-2-butene ≒ 1-butene
- (4) *trans*-2-butene ≒ 1-butene

The software uses Gibbs free energy minimization technique to compute the results [i.e., equilibrium conversions when the ΔG of reactions (1-4) equal 0]. The predictions are unaltered as long as the total molar amount of butenes (mixture of cis-2-butene, trans-2-butene and 1-butene) is constant. As 2-butene is a mixture of cis-2-butene and trans-2-butene, we simply use 1butene and ethylene as reagents for ease of computation.

1.4 Metathesis activity

Detailed procedures for the measurement of the metathesis activity has been previously reported. [15, 17] Briefly, 1.0 g of catalyst (0.425-0.850 mm) was loaded into the center of the stainless steel tube reactor (i.d. = 9.4 mm). A thermocouple was used to detect

the temperature of the catalyst bed. The catalyst was activated in flow N₂ (50 std cm³/min) at 550°C for 1 h, following which the reactor was cooled down to desired reaction temperature. Then, a mixture of 2-butene and ethylene gas was introduced into the reactor. The metathesis reaction was performed at $T = 450^{\circ}$ C, P = 1 atm, WHSV (ethylene and 2-butene) = 2.0 h⁻¹, n(ethylene)/n(2butene) in feed = 3/1. At these operating conditions, the reaction rate was confirmed to be not limited by either internal or external transport limitations.^[15] The products were analyzed by an on-line Varian CP-3800 gas chromatograph, equipped with an Agilent GS-gaspro[®] column (30 m x 0.320 mm) and a flame ionization detector (FID). The transfer-line between the reactor and the sixway valve was heated to 200°C to prevent product condensation. A typical gas chromatograph based on sampling and analysis of the reactor effluent stream is given in Figure S8. The various catalyst assessment metrics are as follows^[17]. The apparent activity is defined as the number of moles of 2-butene converted to propene per gram of catalyst per hour.[52]

$$X_{2-butene} = \frac{[2-butene]_{in} - [2-butene]_{out}}{[2-butene]_{in}} \times 100\%$$

 $[propene]_{out}$ $- \times 100\%$ $S_{propene} = \frac{1}{[2-butene]_{in} - [2-butene]_{out}}$

 $Y_{propene} = X_{2-butene} \times S_{propene} \times 100\%$

Mass balance closure = [Total carbon in products] [Total carbon in feed components] - × 100%

where $X_{2-butene}$, $S_{propene}$ and $Y_{propene}$ represent the steady state values of 2-butene conversion, propene selectivity and propene yield, respectively; WHSV, M_{2-butene} and m_{catalyst} represent weight hourly space velocity, molar mass of 2-butene and the mass of catalyst, respectively.

1.5 DFT Calculations

The bimetallic amorphous silica clusters are built on the basis of the monometallic clusters from METASIL, METal-doped Amorphous Silicate Library, which was previously used to reproduced experimental trends of acidity and NMR spectra.^[60, 61] The methodology for generating METASIL clusters is reported elsewhere^[60]. Twenty clusters have been taken from METASIL, ten doped with Zr(IV) and ten with Nb(V), both including one hydroxyl group on the metal. The bimetallic clusters are created by adding a WO₃ group between a metal hydroxyl and a nearby silanol of a monometallic cluster (Schemes S1 and S2). Examples of the active sites precursor of W10Nb1-KIT-6, W10Hf1-KIT-6, W10Zr1-KIT-6, and W10Ta1-KIT-6 catalysts are shown in Figures 10 and S16. An additional ten monometallic W(VI) clusters are taken directly from METASIL with no alterations to the structure to compare with the bimetallic clusters. To maintain the amorphous character of the silica, only a sphere with a radius of 6 Å centered at the non-tungsten metal is allowed to relax during the geometry optimization. The structure is treated with the B3LYP functional and D3 dispersion correction.[62] The basis sets used are Def2TZVP and Stuttgart pseudopotentials for W, Nb, Ta, Hf and Zr, 6-31++g(2d,p) for hydroxyl groups within the 6 Å sphere, 6-31g(d) for the Si and O within the sphere, and 3-21g for the surrounding frozen silica.^[63] All calculations were performed with a development version of the GAUSSIAN suite of programs.[64]

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- Plotkin, J. S. The Propylene Gap: How Can It Be Filled? [1] www.acs.org (accessed Oct. 12, 2016).
- [2] N. Popoff, E. Mazoyer, J. Pelletier, R. M. Gauvin, M. Taoufik, Chem. Soc. Rev. 2013, 42, 9035-9054.
- S. Lwin, I. E. Wachs, ACS Catal. 2014, 4, 2505-2520. [3]
- [4] N. Gholampour, M. Yusubov, F. Verpoort, Catal. Rev.: Sci. Eng. 2016, 58, 113-156.
- D. P. Debecker, M. Stoyanova, F. Colbeau-Justin, U. Rodemerck, C. Boissiere, E. M. Gaigneaux, C. Sanchez, *Angew. Chem.* **2012**, [5] 124, 2171-2173; Angew. Chem. Int. Ed. 2012, 51, 2129-2131.
- K. Bouchmella, P. H. Mutin, M. Stoyanova, C. Poleunis, P. Eloy, U. [6] Rodemerck, E. M. Gaigneaux, D. P. Debecker, J. Catal. 2013, 301, 233-241
- H. Liu, K. Tao, P. P. Zhang, W. Xu, S. H. Zhou, New J. Chem. 2015, [7] 39, 7971-7978.
- S. Lwin, Y. Li, A. I. Frenkel, I. E. Wachs, ACS Catal. 2016, 6, 3061-[8] 3071
- [9] Y. Bouhoute, D. Grekov, K. C. Szeto, N. Merle, A. De Mallmann, F. Lefebvre, G. Raffa, I. Del Rosal, L. Maron, R. M. Gauvin, L. Delevoye, M. Taoufik, ACS Catal. 2016, 6, 1-18.
- [10] M. Pucino, V. Mougel, R. Schowner, A. Fedorov, M. R. Buchmeiser, C. Copéret, Angew. Chem. 2019, 128, 4372-4374; Angew. Chem. Int. Ed. 2016, 55, 4300-4302.
- K. L. Ding, A. Gulec, A. M. Johnson, T. L. Drake, W. Q. Wu, Y. Y. [11] Lin, E. Weitz, L. D. Marks, P. C. Stair, ACS Catal. 2016, 6, 5740-5746
- J. G. Howell, Y.-P. Li, A. T. Bell, ACS Catal. 2016, 6, 7728-7738. [12]
- [13] W. L. Jiang, R. L. Huang, P. D. Li, S. O. Feng, G. L. Zhou, C. C. Yu,
- H. J. Zhou, C. M. Xu, Q. Xu, *Appl. Catal., A* **2016**, *517*, 227-235. G. Chen, M. Dong, J. F. Li, Z. W. Wu, G. F. Wang, Z. F. Qin, J. G. Wanga, W. B. Fan, *Catal. Sci. Technol.* **2016**, *6*, 5515-5525. [14]
- J.-F. Wu, A. Ramanathan, W. K. Snavely, H. Zhu, A. Rokicki, B. [15] Subramaniam, Appl. Catal., A 2016, 528, 142-149
- A. Gallo, A. Fong, K. C. Szeto, J. Rieb, L. Delevoye, R. M. Gauvin, [16] M. Taoufik, B. Peters, S. L. Scott, J. Am. Chem. Soc. 2016, 138, 12935-12947
- J.-F. Wu, A. Ramanathan, B. Subramaniam, J. Catal. 2017, 350, [17] 182-188.
- F. Zhang, K. C. Szeto, M. Taoufik, L. Delevoye, R. M. Gauvin, S. L. [18] Scott, J. Am. Chem. Soc. 2018, 140, 13854-13868.
- P. Zhao, L. Ye, Z. Sun, B. T. W. Lo, H. Woodcock, C. Huang, C. [19] Tang, A. I. Kirkland, D. Mei, S. C. Edman Tsang, J. Am. Chem. Soc.
- **2018**, *14*0, 6661-6667. N. Maity, S. Barman, Y. Minenkov, S. Ould-Chikh, E. Abou-Hamad, T. Ma, Z. S. Qureshi, L. Cavallo, V. D'Elia, B. C. Gates, J. M. Basset, *ACS Catal.* **2018**, *8*, 2715-2729. [20]
- K. Yanamoto, K. W. Chan, V. Mougel, H. Nagae, H. Tsurugi, O. V. Safonova, K. Mashima, C. Coperet, *Chem. Commun.* **2018**, *54*, [21] 3989-3992
- [22] G. Z. Zuo, Y. B. Xu, J. Zheng, F. Jiang, X. H. Liu, RSC Adv. 2018, 8, 8372-8384.
- M. Pucino, F. Zhai, C. P. Gordon, D. Mance, A. H. Hoveyda, R. R. [23] Schrock, C. Copéret, Angew. Chem. 2019, 131, 11942-11945; Angew. Chem. Int. Ed. 2019, 58, 11816-11819.

- S. Zhang, D. F. Consoli, S. K. Shaikh, Y. Román-Leshkov, Appl. [24] Catal., A 2019, 580, 53-58.
- S. Lwin, I. E. Wachs, ACS Catal. 2017, 7, 573-580. [25]
- [26] J.-F. Wu, A. Ramanathan, A. Biancardi, A. M. Jystad, M. Caricato, Y. Hu, B. Subramaniam, ACS Catal. 2018, 8, 10437-10445.
- W. Li, Y. Wang, Z. Xie, Q. Chen, W. Yang, CN 1618515 A [27]
- [28] F. Verpoort, A. Bossuyt, L. Verdonck, Chem. Commun. 1996, 417-418 [29] A. Ceccon, S. Santi, L. Orian, A. Bisello, Coord. Chem. Rev. 2004,
- 248, 683-724 [30]
- L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, J. Organomet. Chem. 2005, 690, 5407-5413. [31]
 - H. Clavier, S. P. Nolan, Chem. Commun. 2010, 46, 841-861.
- R. Clavier, S. F. Nolari, *Chem. Commun.* 2010, 40, 641-661.
 T. I. Bhuiyan, P. Arudra, M. N. Akhtar, A. M. Aitani, R. H. Abudawoud, M. A. Al-Yami, S. S. Al-Khattaf, *Appl. Catal.*, A 2013, 467, 224-234.
 A. Ramanathan, B. Subramaniam, D. Badloe, U. Hanefeld, R. Maheswari, *J. Porous Mater.* 2012, *19*, 961-968. [32]
- [33]
- [34] Q. Zhao, S.-L. Chen, J. Gao, C. Xu, Transition Met. Chem. 2009, 34, 621-627.
- [35] E. Briot, J. Y. Piquemal, M. Vennat, J. M. Bregeault, G. A. Chottard,
- J. M. Manoli, *J. Mater. Chem.* **2000**, *10*, 953-958. Y. S. Ko, H. T. Jang, W. S. Ahn, *J. Ind. Eng. Chem.* **2007**, *13*, 764-[36] 771
- P. Srinivasu, C. Anand, S. Alam, K. Ariga, S. B. Halligudi, V. V. [37] Balasubramanian, A. Vinu, J. Phys. Chem. C 2008, 112, 10130-10140.
- A. Ramanathan, R. Maheswari, D. H. Barich, B. Subramaniam, [38] Microporous Mesoporous Mater. 2014, 190, 240-247
- [39] S. Maksasithorn, P. Praserthdam, K. Suriye, M. Devillers, D. P. Debecker, Appl. Catal., A 2014, 488, 200-207.
- [40] D. P. Debecker, M. Stoyanova, U. Rodemerck, F. Colbeau-Justin, Boissere, A. Chaumonnot, A. Bonduelle, C. Sanchez, Appl. C Catal., A 2014, 470, 458-466.
- [41] D. C. Vermaire, P. C. Vanberge, J. Catal. 1989, 116, 309-317.
- [42] B. Q. Wang, Y. Zhao, M. N. Banis, Q. Sun, K. R. Adair, R. Y. Li, T.
- K. Sham, X. L. Sun, ACS Appl. Mater. Inter. 2018, 10, 1654-1661. [43] C. Sugiura, M. Kitamura, S. Muramatsu, J. Phys. Chem. Solids 1988, 49. 1095-1099.
- J. Cao, B. Poumellec, L. Mazerolles, F. Brisset, A. L. Helbert, S. Surble, X. He, M. Lancry, *J. Am. Ceram. Soc.* 2017, 100, 115-124.
 Y. Kubouchi, S. Hayakawa, H. Namatame, T. Hirokawa, *X-Ray* [44]
- [45] Spectrom. 2012, 41, 259-263.
- [46] S. Yamazoe, Y. Hitomi, T. Shishido, T. Tanaka, J. Phys. Chem. C 2008, 112, 6869-6879.
- M. Fernandez-Garcia, A. Martinez-Arias, A. Fuerte, J. C. Conesa, *J. Phys. Chem. B* **2005**, *109*, 6075-6083. [47]
- J. Grams, Eur. J. Mass Spectrom. 2010, 16, 453-461. [48]
- J. P. Hofmann, M. Rohnke, B. M. Weckhuysen, *Phys. Chem. Chem.* [49] Phys. 2014, 16, 5465-5474. [50]
 - L. T. Weng, Appl. Catal., A 2014, 474, 203-210.
- [51] D. P. Debecker, K. Bouchmella, C. Poleunis, P. Eloy, P. Bertrand, E. M. Gaigneaux, P. H. Mutin, *Chem. Mater.* **2009**, *21*, 2817-2824. D. P. Debecker, B. Schimmoeller, M. Stoyanova, C. Poleunis, P. [52] Bertrand, U. Rodemerck, E. M. Gaigneaux, J. Catal. 2011, 277, 154-163
- D. P. Debecker, K. Bouchmella, R. Delaigle, P. Eloy, C. Poleunis, P. [53] Bertrand, E. M. Gaigneaux, P. H. Mutin, Appl. Catal., B 2010, 94, 38-45.
 - M. A. Reiche, P. Hug, A. Baiker, J. Catal. 2000, 192, 400-411.
- [55]
- https://en.wikipedia.org/wiki/Electronegativity. E. Tzur, A. Szadkowska, A. Ben-Asuly , A. Makal, I. Goldberg, K. [56] Woźniak, K. Grela , N. G. Lemcoff, Chem. - Eur. J. 2010, 16, 8726-8737.
- [57] S. Monfette, K. D. Camm, S. I. Gorelsky, D. E. Fogg, Organometallics 2009, 28, 944-946.
- J. Fan, S. W. Boettcher, G. D. Stucky, Chem. Mater. 2006, 18, 6391-[58] 6396
- H. D. Zhu, A. Ramanathan, J. F. Wu, R. V. Chaudhari, B. [59] Subramaniam, AIChE J. 2017, 63, 2888-2899.
- A. M. Jystad, A. Biancardi, M. Caricato, J. Phys. Chem. C 2017, 121, [60] 22258-22267. [61]
 - A. Jystad, M. Caricato, Chem. Mater. 2018, 30, 7813-7822
- [62] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104-154119
- F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-[63] 3305
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. L. Nakatsuji, X., M. Caricato, A. Marenich, J. Bloino, B. G. [64] Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. D. Williams-Young, F., F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D.

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Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. H. Liang, M. , M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. K. Millam, M., C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 09, Revision A. 02*; Gaussian, Inc: Wallingford, CT, 2015.

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RESEARCH ARTICLE

Synergistic Metal Doping Effects: Niobium incorporation into W- KIT-6 materials significantly enhances propene yield during 2-butene + ethylene metathesis reaction.



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Enhanced Olefin Metathesis Performance of Tungsten and Niobium Incorporated Bimetallic Silicates: Evidence of Synergistic Effects Accepted Manuscrip