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# Acid site densities and reactivity of oxygen-modified transition metal carbide catalysts

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ABSTRACT

Acidic properties of β-$Mo_2C$, α-$Mo_2C$, $W_2C$, and WC were quantified by assessing the kinetics of isopropanol (IPA) dehydration at 415 K either (i) under inert He/Ar atmosphere or (ii) with 13 kPa $O_2$ co-feed. Dehydration kinetics were zero-order with respect to IPA for all catalysts and under all reaction conditions. Intrinsic activation energies were similar across all catalysts (89–104 kJ $mol^{-1}$). Acid site densities calculated via in situ 2,6-di-tert-butylpyridine (DTBP) titration were used to normalize dehydration turnover frequencies (TOF). $O_2$ co-feed increased dehydration rates per gram by an order of magnitude for all catalysts tested, but TOF remained invariant within a factor of ~2. Mo- and W-based carbides showed similar dehydration kinetics regardless of $O_2$ co-feed, and $O_2$ co-feed did not alter bulk carbidic structure as noted by X-ray diffraction. Brønsted acid site provenance results from the oxophilicity of Mo and W carbides.

## 1. Introduction

Multifunctional interstitial transition metal carbide catalysts have been shown to catalyze hydrogenolysis [1–3], hydrogenation [2,4–7], isomerization [8–12], and hydrodeoxygenation (HDO) [13–17] reactions. The diverse functionalities of transition metal carbide bulk formulations arise from different catalytically active sites generated by modification of the catalyst surface. Ribeiro et al. [18,19] reported a bifunctional metal-acid surface of an oxygen-modified tungsten carbide formulation that catalyzed isomerization of $C_5$-$C_7$ alkanes at atmospheric pressure and 430–630 K via sequential dehydrogenation/methyl shift/hydrogenation pathways as evinced by terminal isotopic enrichment in n-heptane-1-$^{13}C$ isomerization reactions in contrast to the $C_5$ hydrogenolysis mechanism prevalent over noble metals that would also yield isotopic enrichment of interior carbon atoms. WC and $W_2C$ catalysts were oxygen-modified via slow $O_2$ introduction (0.1 μmol $s^{-1}$ $g^{-1}$) at room temperature followed by heating under 20 kPa $O_2$ to 300–800 K, and catalysts were finally pretreated under $H_2$ flow at 673 K for 1–2 h prior to exposure to reaction conditions (95 kPa $H_2$). The presence of Brønsted acid sites on $O^*$-$WC_x$ catalysts was implicated by the methyl shift isomerization mechanism in addition to ex situ $NH_3$ temperature programmed desorption (TPD) studies; these acid sites were shown to be similar to acid sites on $WO_x$ catalysts because comparable product distributions of 3,3-dimethylpentane isomerization over $O^*$-WC and $Al_2O_3$-supported $Pt/WO_3$ catalysts were observed. Isomerization site time yields, normalized by ex situ irreversible CO chemisorption uptakes, were similar over 700-K oxygen-modified WC and $W_2C$ catalysts ($244 \times 10^{-3}$ vs. $125 \times 10^{-3}$ $s^{-1}$) [8,18,19]. Lamic and coworkers [20] also demonstrated isomerization of n-heptane over both bifunctional $WC_x$ and mixed $Mo_2C/WO_2$ catalysts, hypothesizing that the carbidic $Mo_2C$ or $WC_x$ acts as the de/hydrogenation catalyst and the $WO_2$ provides the Brønsted acid site necessary for the isomerization of n-heptene via a carbenium ion intermediate.

Iglesia and coworkers [21,22] demonstrated the presence of both Brønsted and Lewis acid sites on supported $WO_x$ catalysts that were active for both isomerization and dehydration through the use of in situ pyridine and 2,6-di-tert-butylpyridine (DTBP) titrations. Ruddy and coworkers [23,24] demonstrated the presence of acid sites on bulk β-$Mo_2C$ and on SBA-15-supported α-$MoC_{1-x}$ nanoparticles via both $NH_3$ temperature programmed desorption (TPD) studies and density functional theory (DFT) calculations that showed comparable $NH_3$ binding energies between $O^*$-$MoC_x$ and proton-form zeolites. Although acid sites have been reported to exist across transition metal oxides and oxygen-modified

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transition metal carbides, quantification and comparison of acid site densities and strengths are lacking, and similarities between oxidic and carbidic acid sites have yet to be characterized.

We have previously investigated the acidic and metallic characteristics of molybdenum carbide catalytic formulations during HDO of biomass-derived oxygen-containing molecules including anisole, furfural, m-cresol, and acetone [25–31]. Metallic sites responsible for anisole, furfural, and m-cresol HDO can be selectively titrated using CO, and Brønsted acid sites responsible for the rate-determining isopropanol (IPA) dehydration during the sequential hydrogenation/dehydration of acetone could be selectively titrated using DTBP. These in situ titrations allow for site density and TOF measurements of the catalytically active sites without ex situ methods, yielding both the identity and quantity of active sites.

In this work, we use IPA dehydration activation energy, TOF, and site density measurements as probes of acid sites on freshly synthesized as well as oxygen-modified ($O^*$) transition metal carbide catalysts of molybdenum and tungsten ($\alpha$-$Mo_2C$, $\beta$-$Mo_2C$, $W_2C$, and WC). Catalysts demonstrated extreme oxophilicity as noted by zero-order kinetics with respect to IPA pressure, indicative of a catalyst surface saturated with oxygenate. Intrinsic activation energies and dehydration turnover frequencies (TOF) were calculated using acid site densities measured via in situ DTBP titration. Selective DTBP titration both directly demonstrates the presence of Brønsted acid sites on $O^*$-modified carbides and allows for calculation of intrinsic dehydration TOF values. Acid site densities increased with $O_2$ co-feed-induced surface oxidation, but the nature of the active sites, as quantified via intrinsic activation energies and TOF, was similar across all measured catalysts regardless of bulk carbide structure, the presence of $O_2$ co-feed, or bulk transition metal (Mo or W). The nature of the acid sites on TPR-synthesized transition metal carbides is uniform across formulations oxidized by both reactant alcohol $O^*$ incorporation and direct $O_2$ co-feed at reaction conditions. The persistent and consistent nature of acid site identity with $O^*$ source, site density, transition metal, and bulk crystal structure serves to further the understanding of catalytic applications of oxophilic transition metal carbides or other oxophilic catalytic materials from both a fundamental perspective and for any potential acid catalysis/HDO applications.

## 2. Experimental

### 2.1. Catalyst synthesis and passivation

All catalysts were prepared in a quartz tubular reactor (I.D. 10 mm). Catalyst precursors were heated either in a three-zone or in a one-zone split tube furnace (Applied Test Systems) under gas flows including $CH_4$ (Matheson, 99.97%), $H_2$ (Matheson, 99.999%), or He (Minneapolis Oxygen, 99.997%).

Synthesis of orthorhombic $\beta$-$Mo_2C$ was carried out using a temperature-programmed reaction method reported previously [25,32,33]. Batches of catalyst were synthesized using 0.03–1.0 g ammonium paramolybdate (sieved, 177–400 μm, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Sigma, 99.98%, trace metal basis). The paramolybdate was heated at 0.06 K $s^{-1}$ to 623 K and held at 623 K for 12 h under total flow of 3.0 $cm^3\ s^{-1}$ of 15 vol% $CH_4/H_2$, followed by a temperature ramp at 0.046 K $s^{-1}$ from 623 K to 873 K and a temperature hold at 873 K for 2 h. The reactor was then cooled under the same gas flow to reaction temperature (415 K) to begin reaction.

Cubic $\alpha$-$Mo_2C$ (also labeled as $\alpha$-$MoC_{1-x}$) [24] was synthesized according to a modified method of Vitale and coworkers [34]. Sucrose (5 g) and ammonium paramolybdate (5 g) were dissolved in 40 mL deionized $H_2O$, and the mixture was homogenized and magnetically stirred at ambient temperature for 0.25 h. The mixture was then placed in an oven at 393 K for 24 h. A dark gray porous solid mass was formed; the resulting solid was crushed and used as a precursor. Approximately 2 g of this precursor was treated under flowing He, heated at 0.25 K $s^{-1}$ to 1073 K, held at 1073 K for 0.5 h, and then cooled to ambient temperature under the same flow. This product was shown to have bulk $\alpha$-$Mo_2C$ crystal structure (see discussion in Section 3 below). Approximately 0.2 g of this precursor was then heated under flowing He to 415 K for IPA dehydration measurements and was subsequently treated with 13 kPa $O_2$ co-feed under reaction conditions as dehydration rates rose until they reached a stable value.

WC and $W_2C$ catalysts were synthesized according to a modified method of Delannoy and coworkers [35]. Both catalysts were synthesized with 0.03–0.1 g $WO_3$ precursor (Sigma Aldrich, 99.995% trace metal basis) using the quartz tube flow system described above under 1.82 $cm^3\ s^{-1}$ total flow of 20% $CH_4/H_2$ and heated at 0.0167 K $s^{-1}$ until their final synthesis temperature (1073 K for WC, 903 K for $W_2C$), and finally held isothermally for 8 h. $CH_4$ gas flow was then removed, and the catalyst was allowed to cool to 415 K under $H_2$ flow.

Catalysts were passivated after reaction by treatment in flowing 1% $O_2$/He (Matheson, Certified Standard Purity) at 1.0 $cm^3\ s^{-1}$ at ambient temperature for at least 0.75 h in an effort to avoid violent bulk oxidation with atmospheric $O_2$ [36,37]. Samples were passivated even if treated with $O_2$ co-feed during reaction.

### 2.2. Catalyst characterization

The mass fraction of molybdenum in the $\alpha$-$Mo_2C$ was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES); experimental details are provided in Section S.1 of Supplementary Information.

X-ray diffraction (XRD) was performed with a Bruker D8 Discover 2D X-ray diffractometer equipped with a 2-D VÅNTEC-500 detector and a 0.8-mm collimator. Cu $K_{\alpha1}$ and $K_{\alpha2}$ radiation was used in conjunction with a graphite monochromator. Scans were performed in two or three frames for 300 s per frame. Total scan range was typically $2\theta = 20$–$80°$ with the scan frames being adjusted so as to center the primary intensity peaks in each frame. The 2D scans were converted to 1D intensity vs. $2\theta$ with a step size of 0.04° $2\theta$ and merged for analysis. A zero background holder was used with a small amount of vacuum grease for sample support.

Surface area and porosity of the passivated catalyst samples were measured using an ASAP Micromeritics 2020 analyzer. BET surface area and porosity measurements using $N_2$ were performed at liquid nitrogen boiling temperature. Prior to $N_2$ physisorption measurements, samples were degassed to <6 μm Hg and heated to 523 K at 0.17 K $s^{-1}$ and held for 2–4 h. BET Surface areas of oxygen-modified carbide samples were typically <5 $m^2\ g^{-1}$, and surface areas of post-reaction samples without $O_2$ co-feed were typically ~20–60 $m^2\ g^{-1}$; surface areas were not used for quantitative comparison due to their evolution with $O_2$ exposure [27] or aging time [28].

### 2.3. Reaction and titration methods

Reactions were carried out in an apparatus described previously [32]. Briefly, reactants were fed to stainless steel reactor lines via either an M6 Valco syringe-free liquid handling pump or a KD Scientific syringe pump (KDS120). Reactant lines were heated by resistive heating tape to prevent condensation. 2-Propanol (ACS 99.97%), argon (Matheson, 99.999%), and helium (Minneapolis Oxygen, 99.997%) were used as received. Products and reactants at the reactor effluent were quantified using a flame ionization