Structure and site evolution of molybdenum carbide catalysts upon exposure to oxygen

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Acid site densities could be reversibly tuned by a factor of ∼30 using an O_2 co-feed, which reversibly creates Brønsted acid sites on the carbide surface without altering the bulk crystal structure of 2–5 nm Mo_2C crystallites. Unimolecular isopropanol (IPA) dehydration at 415 K, a probe reaction, occurred on Brønsted acid sites of these oxygen-modified carbides with an intrinsic activation energy of 93 ± 1.3 kJ mole^{-1} via an E_2 elimination mechanism with a kinetically-relevant step of β-hydrogen scission. Site densities were estimated via in situ 2,6-di-*tert*-butylpyridine (DTBP) titration and used to calculate a turnover frequency (TOF) of 0.1 s^{-1}, which was independent of site density. Oxygen co-processing allows for facile in situ tunability of acidic and metallic sites on highly oxophilic metal carbides.

1. Introduction

Catalytically active interstitial carbides first rose to scientific prominence through the early work of Yates [1], Boudart [2], and Madey [3], demonstrating the catalytic variation of molybdenum and tungsten formulations as a function of both surface and bulk composition as evinced by development of metallic hydrogenolysis or acidic isomerization functionalities with concurrent carburization. Liu and Rodriguez [4] investigated Mo_2C as a water gas shift (WGS) catalyst using periodic density functional theory (DFT), demonstrating the variation in catalyst activity based on surface termination as Mo, C, or O. Subsurface diffusion and development of an oxycarbide phase led to decreased WGS reactivity, and deposition of surface oxygen atoms (O*) from reaction products was shown to suppress WGS reactions due to thermodynamically favorable binding and dissociation of product H_2O that did not allow for facile O* removal.

Leary and coworkers [5] experimentally demonstrated the role of surface O* on Mo_2C as a poison for metal-catalyzed ethylene hydrogenation at 298 K. Leary and coworkers used online gas chromatographic and mass spectroscopic (GC and MS) analysis to observe the complication of bulk carbon removal concurrent with

O* removal with temperature ramps under H_2 and He flow. Posada-Pérez et al. [6] used X-ray photoelectron spectroscopy (XPS) to monitor the O 1s region (528–533 eV) during sequential CO_2 dosing of the β-Mo_2C surface at 300 K. Both O* and adsorbed CO were observed with the relative ratio of CO/O* increasing with CO_2 dosage, demonstrating the ability of O* on the Mo_2C surface to inhibit cleavage of the second C≡O bond and sequential hydrogenation reactions to CH_3OH and CH_4. Flaherty et al. [7] used reflection absorption infrared spectroscopy under ultra-high vacuum (UHV) conditions (1×10^{-10} torr) to monitor formic acid decomposition via dehydrogenation to produce CO_2 or dehydration to produce CO. Clean Mo(1 1 0) performed predominantly dehydration; C-modification of the surface decreased the rate of dehydration without altering the activation energy for dehydration while formation of a carbidic layer on the Mo(1 1 0) surface decreased the activation energy of dehydrogenation from 34 to 13 kJ mole^{-1}. Activation energies were calculated using kinetic measurements of reactive molecular beam scattering.

Chen and coworkers [8,9] used DFT calculations and temperature-programmed desorption/high-resolution electron energy loss spectroscopy (TPD/HREELS) to demonstrate the tunability of the carbide surface with Ni and Cu adatoms to break C—C, C—O, or C—H bonds of oxygenates including ethanol, propanal, propanol, and furfural. The pure carbide surface under UHV conditions could dehydrate and dehydrogenate/hydrogenate oxygenates, but complete atomic decomposition of reactant oxygenates to surface

adatoms typically accounted for nearly 50% of reactivity. Total reactant conversion was less than 0.2 molecules reacted per surface metal atom in the reported studies, implying that the Mo_2C reactivity reported might be stoichiometric. These results stress the variation in Mo_2C reactivity as a function of both surface adatoms and time-on-stream.

Ledoux and coworkers [10] synthesized a MoO_xH_y phase that formed an isostructural oxycarbohydride phase while simultaneously developing n-butane isomerization activity, demonstrating in situ catalytic modification via structure alteration. In situ temperature-programmed oxidation (TPO) of the oxycarbohydride phase with intermittent ex situ X-ray diffraction (XRD) showed the concurrent loss of lattice carbon as CO_2 and structural oxidation to MoO_2 and MoO_3. Lattice carbon loss observed during TPO was distinct from a higher temperature coke oxidation; a separate MoO_2 sample that was inactive for isomerization exhibited similar CO_2 TPO characteristics for coke removal. Iglesia et al. [11] also manipulated catalytic isomerization activity via oxygen exposure of tungsten carbide catalysts, using transient and isotopic kinetic measurements to evince bifunctional isomerization via rapid dehydrogenation on WC_x sites and sequential WO_x Brønsted acid-catalyzed methyl shifts in contrast to Pt/SiO_2-catalyzed sequential cyclization/hydrogenolysis. Matsuda [12] used both n-heptane isomerization and 2-propanol (IPA) dehydration as probe reactions to investigate high-surface area MoO_xH_y species and correlated acidic activity to both catalyst Brunauer–Emmett–Teller (BET) surface area and ex situ NH_3 TPD site density estimates. The reports outlined above demonstrate that reactive characteristics of metal carbide catalysts are strongly influenced by heteroatom adsorption on the catalyst surface and subsurface domains. In this study, we probe the identity and number of active centers created by heteroatom addition to molybdenum carbide formulations.

In this work, we use rigorous kinetic analysis of IPA dehydration over oxygen-treated Mo_2C formulations to investigate in situ catalytic site modification and report both the identity and number of sites generated by such treatments. As-synthesized Mo_2C with no exposure to oxygen exhibits strong alkaline and metallic functionalities, catalyzing carbon chain growth to C_6^+ products via carbonyl condensation pathways and IPA dehydrogenation to near-equilibrium values under IPA/Ar flow. Catalysts were composed of 2–5 nm orthorhombic Mo_2C domains. Concurring XRD and transmission electron microscopy (TEM) analysis showed that bulk crystalline Mo oxides or oxycarbides were not formed with passivation or reaction under O_2 flow. Oxygen modification of the surface over time via (i) O^* deposition from IPA dehydration or H_2O co-feed, or (ii) O_2 co-feed, greatly suppresses carbon chain growth and dehydrogenation rates and concurrently bolsters acid reactivity, forming dehydration products propylene and diisopropylether (DIPE) with ∼90% carbon selectivity. Carbon chain growth pathways and substantial dehydrogenation activity are irreversibly eliminated after O_2 exposure, but acid-catalyzed product rates can be reversibly altered by a factor of ∼30 via acid site density modification with an O_2 co-feed. Acid site densities were measured with in situ 2,6-di-tert-butylpyridine (DTBP) titration experiments, and turnover frequencies (normalized with acid site density by assuming a 1:1 stoichiometry of DTBP:acid site) are invariant with site density. Kinetic experiments, including partial pressure variation, activation energy measurements, and kinetic isotope experiments, lead to the conclusion that IPA dehydration occurs on oxygen-modified molybdenum carbide catalysts via E_2 β-hydrogen elimination on Brønsted acid sites. We propose that the oxygen modification of highly oxophilic transition metal carbides can be used as a regenerable and tunable source of catalytic Brønsted acidity [13].

2. Experimental

2.1. Catalyst synthesis

Catalyst synthesis was carried out using a temperature-programmed reaction method reported previously [14–16]. Catalysts were prepared in a quartz tubular reactor (I.D. 10 mm). Batches of catalyst were synthesized using 0.025–1.5 g ammonium paramolybdate (sieved, 177–400 μm, $(NH_4)_6Mo_7O_{24}·4H_2O$, Sigma, 99.98%, trace metal basis). The paramolybdate was heated in a three-zone split tube furnace (Applied Test Systems) 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 (Matheson, 99.97%) in H_2 (Minneapolis Oxygen, 99.999%). The temperature was then ramped at 0.046 K s^{-1} from 623 K to 873 K and held at 873 K for 2 h. The reactor was then cooled under the same gas flow to either reaction temperature or ambient temperature, to begin reaction or passivation, respectively.

The product was then treated in flowing 1% O_2/He (Matheson, Certified Standard Purity) at 1.0 cm^3 s^{-1} for at least 1 h in an effort to passivate the carbide surface and avoid violent bulk oxidation with atmospheric O_2 [17,18]. Passivated samples were used for ex situ characterization methods.

2.2. Catalyst characterization

Mo_2C samples were characterized using an ASAP Micrometrics 2020 analyzer to determine surface area, porosity, and CO chemisorption values. 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.

CO chemisorption measurements were performed at 323 K. Before measurement, passivated samples were evacuated to <2 μm Hg at 383 K for 0.5 h, followed by treatment in flowing H_2 at 723 K for 2 h, degassing at 723 K for 2 h, followed by the first adsorption measurement at 323 K. Weakly adsorbed CO was removed with degassing at 2 μm Hg, then the CO adsorption isotherm was repeated. The difference between the first and second isotherms was plotted, and this curve was extrapolated to zero pressure to calculate the amount of irreversibly adsorbed CO [18].

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$_{\alpha 1}$ and K$_{\alpha 2}$ radiation was used in conjunction with a graphite monochromator. Scans were performed in three frames during 900 s centered at $2\theta = 35°$, $60°$, and $85°$, for a total range of $2\theta = 17.5°$ to $102.5°$. The three 2D scans were converted to 1D intensity vs. 2θ with a step size of $0.04°$ 2θ and merged for analysis. A zero background holder was used with a small amount of vacuum grease for sample support.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an SSX-100 system (Surface Science Laboratories, Inc.) equipped with a monochromated Al K$_\alpha$ X-ray source, a hemispherical sector analyzer (HSA), and a resistive anode detector. The base pressure was 1.0×10^{-9} Torr. During data collection, the pressure was ∼2.0×10^{-8} Torr. An area of approximately 1 mm × 1 mm was illuminated with 200 W X-rays. The survey spectra were collected using 150 eV pass energy and 1 eV step^{-1}. The high-resolution spectra were collected using 50 eV pass energy and 0.1 eV step^{-1}.

The atomic percentages were calculated from the survey spectrum using the ESCA Hawk software provided with the XPS system. The adventitious carbon 1s peak was set at 285.0 eV and used as the reference for all of the other elements. A combination of