



Single-phase mixed molybdenum-niobium carbides: Synthesis, characterization and multifunctional catalytic behavior in toluene conversion



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ABSTRACT

Single-phase mixed molybdenum-niobium carbides were synthesized to establish structure–activity relationships. Precursors for carburization were obtained by hydrothermal synthesis or, to achieve high molybdenum content (metal fraction $x_{\text{Mo}} = 0.86$), by flash-freezing of salt solutions and subsequent freeze-drying. Thermogravimetric and evolved gas analysis during carburization showed that bimetallic precursors were more easily reduced than monometallic ones; and as the niobium content increased, the removal of oxygen shifted to higher temperatures and from H_2O to CO formation (from H_2 or CH_4 , respectively), and the final carburization temperature rose from 650 to 950 °C. Carbides crystallized in cubic $\text{NbC}/\text{MoC}(cF8)$ structure for $x_{\text{Nb}} \geq 0.38$ and hexagonal $\text{Mo}_2\text{C}(hP3)$ structure for $x_{\text{Nb}} \leq 0.14$. After passivation, mixed metal carbides could be reduced at lower temperatures than Mo_2C . With increasing molybdenum content of the carbides, CO uptake per gram increased, and turnover frequencies for hydrogenation of toluene to methylcyclohexane increased from 0 to 3.1 s^{-1} (at a temperature of 250 °C, 21 bar pressure, and $\text{H}_2/\text{toluene} = 36$). At 400 °C, mixed carbides with $x_{\text{Nb}} \geq 0.38$ were more selective toward acid-catalyzed products and less selective toward hydrogenolysis products than carbides with lower niobium content.

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1. Introduction

Transition metal carbides exhibit catalytic behavior reminiscent of that of noble metals while being less expensive and more tolerant toward some poisons [1–4]. Carbides of molybdenum or tungsten have shown promise as catalysts for, among other reactions, hydrocarbon transformations [1,2], hydrotreating [5], hydrodeoxygenation of biomass-derived molecules [6,7], and electrode reactions in fuel cells [8]. To optimize the catalytic behavior and to expand the applications of carbides, it is desirable to be able to tune their properties. A strategy offering potential to control the properties of a particular transition metal carbide is the partial substitution of anions or cations in the carbide bulk or near the surface.

With respect to anion substitution, oxide is the most widely tested species, followed by nitride [9]. The effect of introducing oxygen to carbides has been investigated by several groups emphasizing different aspects, with experimental work including both surface modification [10–12] and the synthesis of bulk oxycarbides [13–15]. DFT calculations [16] show that oxygen adsorbs strongly on the surface of molybdenum carbide, consistent with the pyrophoric nature of Mo_2C with a clean surface. Tungsten carbide is also oxophilic [10,17]. The presence of oxygen on the surface generally reduces the surface affinity for carbon [16] and the catalytic behavior moves away from that of a typical noble metal [18]; for example, hydrogenolysis is suppressed [10,12]. In addition, the presence of oxygen may result in formation of acid sites, thus creating a bifunctional catalyst [11,12]. One problem with this type of catalyst is that oxygen may be removed in H_2 -containing atmosphere; this reduction occurs at 300 °C for Mo_2C and 400 °C for W_2C at atmospheric H_2 pressure [17]. The stability of the catalyst under reaction conditions for many of the transformations listed above is thus not necessarily a given.

Regarding cation substitution, a variety of attempts have been made to synthesize mixed metal carbides, and their catalytic behavior typically differs from that of the two respective

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monometallic carbides. Examples include mixed molybdenum-tungsten carbides, which Leclercq et al. [19] found to be enriched in molybdenum on the surface and to exhibit complex behavior in cyclohexane dehydrogenation, and butane isomerization and hydrogenolysis. Oyama and co-workers reported bulk mixed molybdenum–niobium carbides to have promising performance in the hydrodesulfurization (HDS) of dibenzothiophene [20] and alumina-supported molybdenum–niobium carbides to be better catalysts for HDS than $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ and to have higher HDS and hydrodenitrogenation (HDN) activities per active site compared to commercial sulfided Ni-Mo/ Al_2O_3 [21]. Green and co-workers published a series of papers [22–27] on combining tungsten or molybdenum with cobalt or nickel to give bimetallic carbides, which were mainly tested for hydrotreating but also for methane partial oxidation.

Anion and cation substitution have also been combined. Principally, synergy appears possible if, for example, a second cation of higher oxophilicity assists in retaining oxygen on the surface at high temperatures. For example, vanadium reportedly delays the reduction process during carburization of molybdenum oxide to molybdenum carbide [28]. In another report, mixed molybdenum–niobium oxycarbides showed better HDS and HDN activity compared to the monometallic compounds [29].

Synthesis of bimetallic carbides is generally a challenge. Metallurgical methods are excluded because they do not lead to high-surface-area materials. Like monometallic carbides, bimetallic carbides have also been made by temperature-programmed carburization of suitable precursor materials. Precursors have been generated in various ways, by physically mixing the individual oxides [20], by fusing the oxides in a high-temperature reaction [29,30], or by combining nitrates and oxides [23]. Attempts have been reported to obtain oxide solid solutions via calcination of precipitates [28,31] or reduction of calcined co-precipitates under mild conditions [32]. A variation of the oxide path is to first form a nitride and then a carbide. Sulfides have been used as precursors in carburizations to produce mixed molybdenum–tungsten carbides [33]. In sum, there are few reports of phase-pure materials over a wide range of compositions [32].

The goal of this paper is to develop methods for the synthesis of single-phase mixed metal carbides over a range of compositions such that structure–activity relationships can be established. To have an observable effect, molybdenum is combined with the more oxophilic niobium. The pure carbides obtained by temperature-programmed reduction, $\text{Mo}_2\text{C}(hP3)$ and $\text{NbC}(cF8)$, have different stoichiometries and structures. In hydrotreating and butane conversion, Mo_2C is more active than NbC [34,35]. A secondary effect of cation substitution is the change in affinity to oxygen, which can make oxycarbides stable under a wider range of conditions, and niobium reportedly should be prone to retain oxygen [29] and introduce acid sites. Hydrothermal synthesis [36] or flash-freezing followed by freeze-drying [37,38] is used to produce precursors with intimately mixed metals, which are subsequently carburized. Toluene is employed as the reactant, and the selectivity toward ring hydrogenation and hydrogenolysis is used to assess the metallic properties, while the selectivity toward ring contraction and isomerization is used to assess the acidic properties.

2. Experimental section

2.1. Carbide synthesis

2.1.1. Synthesis of precursors

Hydrothermal synthesis was one of two methods to obtain molybdenum–niobium precursors with intimately mixed metal

ions. The procedure described by Murayama et al. [36] was followed with some modifications. Ammonium heptamolybdate (AHM) (ACS reagent, 81–83% MoO_3 , Sigma Aldrich) was dissolved in 0.5 M oxalic acid (anhydrous, purity > 99%, Sigma-Aldrich), and ammonium niobate (V) oxalate hydrate (ANOH) (99.99%, Aldrich) was dissolved in water. The amount of salt in each solution was adjusted to give a total salt load of 4 g in 100 ml of the mixed solution while varying the metal ratios. Salt solutions were combined and mixed by stirring for 15 min. The following niobium mole fractions x_{Nb} (considering only the metals, i.e. $x_{\text{Nb}} = n_{\text{Nb}}/(n_{\text{Mo}} + n_{\text{Nb}})$) were prepared: 1.0 (ANOH-HT), 0.5, 0.33, 0.2, 0.14, 0.05 and 0 (AHM-HT). The clear solution was transferred to the 250 ml Teflon liner of a stainless-steel autoclave. The autoclave was heated to a temperature of 175 °C for 3 days under static conditions. After 3 days, the suspension was centrifuged to separate any solids from the mother liquor. The solid was washed three times with water, and then dried overnight at 80 °C in an oven.

To obtain stoichiometries that were not accessible by hydrothermal synthesis, mixed metal precursors were produced by flash-freezing and freeze-drying. Appropriate amounts of ammonium heptamolybdate and ammonium niobate oxalate hydrate were dissolved separately in water and mixed together to obtain various metal ratios with a final total metal concentration of 0.1 M. The solution was added dropwise to liquid N_2 . Globules of the frozen solution were recovered, and freeze-dried at a pressure of 110 μtorr in an ATR FD3.0 freeze drier.

2.1.2. Equipment for thermal treatments and gases

A Netzsch STA 449 F1 thermogravimetric analyzer (TGA) was connected to a mass spectrometer (QMS 403 C Aeolos) via a stainless-steel capillary. Temperature-programmed reaction runs with empty crucibles were used to correct for sample holder buoyancy and gas viscosity artifacts. MS signals were generally normalized to initial sample mass. Methane (UHP, Airgas) was used as received; other gases were further purified prior to use. Air (zero grade, Airgas) and H_2 (ultra-high purity, Airgas) were passed through a moisture trap (Agilent, MT400-2), and argon (ultra-high purity, Airgas) was passed through a dual moisture and oxygen trap (Z-Pure Dual Purifier). All flow rates are given at STP, all percentages by volume.

2.1.3. Calcination of freeze-dried samples

Freeze-dried samples (AHM-FD, ANOH-FD and a mixed metal sample with $x_{\text{Nb}} = 0.13$) were calcined in the TG apparatus in 80% air in argon at a total flow rate of 50 ml/min. The temperature was increased from 40 to 600 °C with a temperature ramp of 5 °C/min, and was held at the final temperature for 30 min.

2.1.4. Carburization and passivation

Precursors were carburized in the TG-MS apparatus, and mass-charge ratios of 2–78 were scanned during the treatments. The carburization gas was obtained by mixing 20 ml/min of methane, 70 ml/min of H_2 and 10 ml/min of argon. The synthesis of all metal carbides was carried out at atmospheric pressure by heating from 40 to 450 °C at 5 °C/min and from 450 °C to the final temperature at 2 °C/min. Samples were held at the final temperature until no weight change was observed by TG and formation of CO was terminated. All metal carbides were cooled down to room temperature under argon flow. Before exposure of the carbides to the ambient, they were passivated isothermally at 40 °C with air diluted in argon. The concentration of O_2 was increased from 0.1% (10 h) to 1% (9 h) and 16% (2 h) in argon [17], with the total flow rate between 60 and 402 ml/min.

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