

Basic properties of molybdenum and tungsten nitride catalysts

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Abstract

The basic and related properties of high surface area Mo₂N and W₂N catalysts were characterized using CO₂-temperature programmed desorption (TPD), the decomposition and dehydration of 2-methyl-3-butyn-2-ol (MBOH), and changes in the reaction rates on the addition of CO₂, a base site poison. The Mo₂N and W₂N catalysts were prepared using the temperature programmed reaction method and had surface areas of 135 and 45 m²/g, respectively. The CO₂-TPD and MBOH decomposition rates to acetone and acetylene indicated significant densities of base sites. The CO₂ poisoning study implicated the involvement of weak sites in MBOH decomposition. The density of base sites and the rate of acetone formation were functions of the reduction temperature. Results for the nitride catalysts were compared to those for MgO and ZnO, known base catalysts. Base sites on the nitrides were of similar strength and density as those on the ZnO catalyst, but were weaker and less dense than those on MgO. Estimated turnover frequencies for the Mo₂N and W₂N catalysts were $(6.0 \pm 1.0) \times 10^{-3}$ and $(1.8 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$, respectively at 180 °C, and were slightly lower than those for the MgO and ZnO catalysts.

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1. Introduction

Early transition metal nitrides have received considerable attention for use as possible replacements for Pt-group metal catalysts. Like the Pt-group metals, nitride based catalysts are capable of catalyzing isomerization, dehydrogenation, hydrogenation, water gas shift, and amination reactions with competitive rates [1–11]. As a consequence of the significant difference between electronegativities for the metal and nitrogen atoms, there is charge transfer in the nitrides [12]. This charge transfer is expected to result in the creation of base and/or acid sites. Acid sites have been reported for alumina supported Mo₂N catalysts by Nagai et al. [13] based on Fourier Transform-infrared spectroscopy of chemisorbed pyridine and for high surface area Mo₂N catalysts by Chang et al. [14] based on NH₃-temperature programmed desorption (TPD), although the presence of acid sites has been reported to be the consequence of oxygen impurities

[15]. Keller et al. [16] used 2-methyl-3-butyn-2-ol (MBOH) dehydration and isomerization to characterize the acidic properties of Mo₂N and W₂N. They reported high rates for the production of 3-methyl-3-butene-1-yne (MByne) and methyl-2-butene-1-al (prenal) over these catalysts. MBOH can also be decomposed into acetone and acetylene over base sites [17]. The formation of these products was not reported by Keller and co-workers however, we recently concluded, based primarily on the results of CO₂-TPD, that early transition metal nitrides can possess base sites on the surface [18]. Solid base catalysts are an attractive alternative to the use of liquid bases. They are non-corrosive, thus presenting fewer disposal problems. Solid bases also allow for easier separation and recovery.

The primary objective of work reported in this paper was to follow-up our investigation of the basic properties of high surface area Mo₂N and W₂N using MBOH decomposition as the test reaction. The decomposition of MBOH appears to be more selective for base sites than other reactions that we have evaluated including acetone condensation into mesityl oxide ((CH₃)₂C=CHCOCH₃) [18]. In fact, the literature

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indicates that MBOH decomposes exclusively over weak base sites into acetone and acetylene [16]. We also characterized the Mo₂N and W₂N catalysts using CO₂-TPD, and monitored changes in the MBOH consumption rates while selectively poisoning the base sites with CO₂. The reaction rates and sorption properties were compared to those for ZnO and MgO. While nitride catalysts can possess acidic properties [13–15,18], this issue will not be addressed in this paper.

2. Experimental

2.1. Catalyst preparation

The temperature programmed reaction method was used to prepare the high surface area nitrides in a vertical quartz reactor. Approximately, 1.5 g of the oxide precursor was placed on quartz wool supported on a quartz frit. A thermocouple was situated just above the oxide bed, and the reactor was placed inside a furnace. Ammonia (Scott) was passed through the reactor at a rate of 300 ml/min. Note that, as appropriate, gases used in this research were ultrahigh purity (UHP) and/or purified using commercial moisture and oxygen traps. For the synthesis of Mo₂N, the reactor was heated from ambient temperature to 350 °C in 30 min, then to 450 °C in 2.5 h, then to 700 °C in 2.5 h and held at this temperature for 1 h. For the synthesis of W₂N, the reactor was heated from ambient temperature to 270 °C in 1 h, then to 560 °C in 9.6 h and held at this temperature for 15 min. After completion of the reaction, the reactor was quenched to room temperature. To prevent pyrolysis on exposure to air, the product material was passivated using a mixture of 1% O₂ in He (Scott) flowing at 20 ml/min.

The MgO catalyst was prepared according to the procedure described by Di Cosimo et al. [19]. Approximately 250 ml of distilled water was added to 25 g of MgO (Baker) at room temperature. The mixture was stirred and the temperature was increased to 80 °C. The temperature was maintained for 4 h with constant stirring. The material was dried overnight at 85 °C, the dried mass was calcined at 350 °C for 2 h and 500 °C for 8 h in flowing air (30 ml/min). The calcined sample was stored in an airtight container. The ZnO (99%, min assay; Alfa Aesar), HZSM-5 (Zeolyst International) and Pt-black (Aldrich) catalysts were used as received.

2.2. Catalyst characterization

The BET surface areas were determined using a Micromeritics ASAP 2010 analyzer with N₂ (Cryogenics) as the adsorbate. The materials were degassed in vacuo at 400 °C until the static pressure remained less than 3 μm Hg. The BET surface areas of the catalysts are given in Table 1. The temperature programmed reduction (TPR) experiments were carried out using a Micromeritics ASAP 2910

Table 1

Surface areas and amounts of CO₂ that desorbed from Mo₂N and W₂N reduced in H₂ at 550 °C for 4 h and MgO and ZnO degassed at 500 °C for 5 h

Catalyst	BET surface area (m ² /g)	CO ₂ desorbed	
		(ml/g)	(molecules/m ²)
Mo ₂ N	135	8.1	1.6 × 10 ¹⁸
W ₂ N	47	2.4	1.3 × 10 ¹⁸
MgO	212	28.4	3.6 × 10 ¹⁴
ZnO	13	0.45	1.2 × 10 ¹⁸

characterization instrument. Approximately 150 mg of catalyst was used. A 5% H₂/Ar (Cryogenics) mixture flowing at 20 ml/min was contacted with the catalyst as the temperature was increased at 10 °C/min to 1000 °C. A moisture trap was used to collect water.

Before carrying out the TPD and catalytic activity measurements, the nitrides were reduced in H₂ (Matheson) flowing at 20 ml/min for 4 h at 300–650 °C. The MgO, ZnO and HZSM-5 catalysts were degassed at 500 °C for 4–6 h in He flowing at 20 ml/min, and the Pt-black catalyst was reduced at 200 °C for 4 h in H₂ flowing at 20 ml/min. Conditions used to activate the HZSM-5 and Pt-based catalysts were similar to those reported in the literature [20]. He- and CO₂-TPD experiments were performed using an Altamira AMI 100 characterization instrument. The He-TPD experiments were used to determine gases produced during thermal decomposition of the surfaces. After pre-treatment, the H₂ (Cryogenics) or He (Cryogenics) flow was replaced with Ar (Cryogenics) and the sample was cooled to ambient temperature. The adsorbate flowing at 30 ml/min was contacted with the catalyst for 30 min at 40 °C. The catalyst bed was then flushed with He for 30 min and the desorption experiment was initiated using a heating rate of 10 °C/min and maximum temperature of 1000 °C. Gases that desorbed were analyzed using a thermal conductivity detector (TCD).

2.3. Catalytic activity measurements

The MBOH consumption experiments were carried out in a 4 mm ID quartz reactor. Approximately 50 mg of the catalyst was placed on a bed of quartz wool inside the reactor then the reactor was placed inside the furnace. A thermocouple was placed above the catalyst bed to measure the temperature. The temperature of the furnace was controlled using an Omega CN2010 temperature controller.

The Mo₂N and W₂N catalysts were reduced at 300–650 °C in H₂ flowing at 20 ml/min prior to the activity measurements. Afterwards the H₂ flow was stopped and He flowing at 20 ml/min was introduced. Gas flow rates were controlled using a Tylan RO-28 mass flow controller. Helium was passed through a saturator containing MBOH at room temperature to produce a reactant stream containing 2.3% MBOH. Product analysis was initiated after approximately 20 min on stream. The reactor effluent was analyzed

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