Cumene hydrogenation turnover rates on Mo_2C: CO and O_2 as probes of the active site

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The use of CO and O_2 chemisorption to titrate surface sites on β-Mo_2C was examined using cumene (isopropylbenzene) hydrogenation as a test reaction. The tests were carried out using β-Mo_2C samples prepared at two different temperatures so as to deposit different amounts of pyrolytic carbon on their surfaces. Synthesis at 961 K produced a surface that was substantially free of pyrolytic carbon (90% clean), while synthesis at 981 K produced a surface that was contaminated with carbon (25% clean). It was found that O_2 uptakes were about six times higher than CO uptakes, but both gave consistent turnover rates for the reaction.

Keywords: molybdenum carbide, turnover rates, cumene hydrogenation, CO and O_2 chemisorption, active site density

The turnover rate (TOR) is defined as the number of catalytic cycles per surface site and provides a means by which catalysts can be compared between different studies. But to calculate a TOR, one must be able to quantify the number of active sites exposed on a given catalyst, i.e., a site density must be known. Site densities are typically determined using probe molecules such as CO, H_2, or O_2. However, the choice of probe molecule is critical to obtaining meaningful turnover rates. Transition metal carbides and nitrides, which are the focus of this study, are typically characterized by either CO or O_2 chemisorption [1–5].

The purpose of this note is twofold. First, to compare CO and O_2 chemisorption as a basis for calculating cumene (isopropylbenzene) hydrogenation TORs on β-Mo_2C. Second, to report the effect of temperature on the synthesis of β-Mo_2C, in particular with respect to the cleanliness of the surfaces produced.

β-Mo_2C was synthesized via a temperature-programmed reaction between MoO_3 and 20% CH_4/H_2 (v/v). Typically, 4 g of MoO_3 were loaded onto a plug of quartz wool in a quartz straight tube reactor. The CH_4/H_2 carburizing gas was delivered at a flow rate of 2000 $\mu mol\,s^{-1}$ (3000 $cm^3(NTP)\,min^{-1}$). The temperature program consisted of two parts: room temperature to 646 K at 0.17 $K\,s^{-1}$, and then 646 K to a variable final temperature ($T_f = 961$ for Mo_2C-I and 981 K for Mo_2C-II) at 0.03 $K\,s^{-1}$. Following a 20 min soak period at T_f, the sample was purged in 69 $\mu mol\,s^{-1}$ (100 $cm^3(NTP)\,min^{-1}$) He before being rapidly cooled to room temperature. Finally, the material was passivated in 34 $\mu mol\,s^{-1}$ (50 $cm^3(NTP)\,min^{-1}$) 0.5% O_2/He for 6 h to prevent pyrophoric oxidation upon exposure to air.

The synthesized catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), N_2 physisorption, and CO chemisorption. XRD was carried out on a Scintag XDS2000 using Mg K_α radiation operated at 30 kV and 40 mA. A scan rate of 2° min^{-1} was employed over the 20–90° 2θ range. Physisorption and chemisorption measurements were performed with a Micromeritics ASAP 2010 Chemi system. Prior to chemisorption measurements, samples were reduced in 34 $\mu mol\,s^{-1}$ (50 $cm^3(NTP)\,min^{-1}$) of H_2 at 723 K for 2 h, evacuated at 723 K for 0.5 h, and subsequently cooled to 307 K. CO and oxygen chemisorption amounts were calculated assuming a stoichiometry of one CO per surface site and two oxygen atoms per surface site. The error in these values is estimated to be about 5% based on the reproducibility of the measurements on different samples. The N_2 physisorption measurements were performed at 77 K after degassing the sample at 473 K for 2 h. XPS was done using a Perkin–Elmer model 5600 ci XPS/Auger system with Mg K_α radiation. Prior to XPS analysis of the fresh catalysts, the samples were reduced in H_2 for 2 h at 723 K and transferred to the vacuum chamber without exposure to air.

Cumene hydrogenation over Mo_2C was measured in a three-phase trickle bed reactor. The catalysts were loaded into baskets between plugs of quartz wool in 316 SS reactors. Importantly, the amounts of catalysts used in the tests were chosen to correspond to 70 μmol irreversible CO uptake, so that rates were compared using equal amounts of surface sites. The total amounts of catalyst used were 0.69 g for Mo_2C-I and 2.59 g for Mo_2C-II. The packed beds were made of equal volume by dilution with screened quartz chips so that the pressure drop in the reactors was the same. Pretreatment consisted of reduction in 102 $\mu mol\,s^{-1}$ (150 $cm^3(NTP)\,min^{-1}$) of H_2 at 723 K and 1 atm for 2 h to remove the protective oxide layer. Upon cooling to 523 K,

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the reactors were pressurized to 5.1 MPa with H_2. Liquid feeds consisted of 5 wt% cumene and 95 wt% tetradecane delivered at a flow rate of 5 $cm^3\,h^{-1}$ using high pressure liquid pumps. Samples were collected in sealed septum vials and analyzed offline with a gas chromatograph using a fused silica capillary column and a flame ionization detector. Samples were collected until steady-state reactivity (approximately 60 h) was achieved. Following reaction, the system was flushed for 24 h with hexane to remove residual organics. The spent catalysts were then washed in hexane and air-dried. Post-reaction characterization included XRD and XPS.

Figure 1 shows the equilibrium curve for CH_4 decomposition to C(s). It can be seen that at 20% CH_4/H_2 the thermodynamic equilibrium lies at 971 K. The synthesis temperatures for Mo_2C were tailored to lie slightly above ($T_f = 981$ K) and slightly below ($T_f = 961$ K) the equilibrium line at 20% CH_4/H_2. Following synthesis and passivation, XRD results indicated that the bulk structure of the materials synthesized at both 961 and 981 K was β-Mo_2C (hcp).

Table 1 summarizes the surface characterization results of the Mo_2C catalysts. The choice of soak temperature had little effect on the surface areas, indicating that the surface morphological properties of the two materials were similar. However, the soak temperature did have an effect on the CO and oxygen uptakes. Mo_2C-I, which was synthesized at 961 K, had higher CO and oxygen uptakes than Mo_2C-II, which was synthesized at 981 K (table 1). Furthermore, XPS analysis of the fresh Mo_2C samples showed a carbon content of 51 mol% for Mo_2C-I and 70 mol% for Mo_2C-II. These results indicate that carbon deposition from methane decomposition is significant enough at the higher synthesis temperature to decrease the site density. This is understandable by examining the equilibrium curve which indicates that methane will decompose to form carbon above 971 K. This carbon is likely to be in the form of pyrolytic carbon [6]. These results are important because most studies of Mo_2C synthesis employ a T_f of 973 K or higher [2,7].

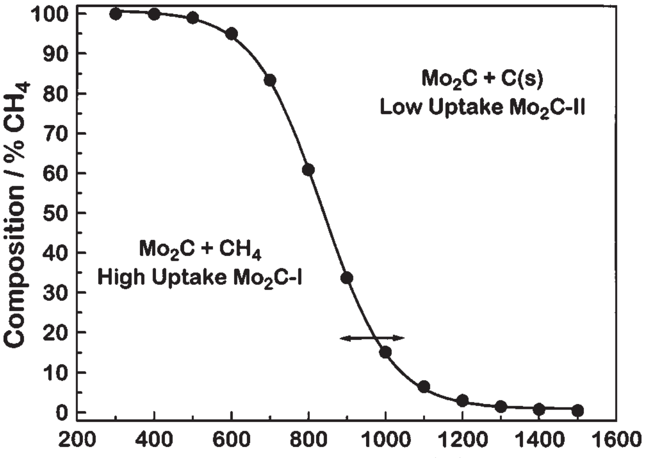

Figure 1. Equilibrium curve for CH_4 decomposition to C(s).

In addition, the ratio of oxygen uptake to CO uptake was seen to be relatively constant for both samples (~6). This finding suggests that the sites that are probed by CO and oxygen are in approximately the same proportion on both Mo_2C-I and Mo_2C-II. The CO site density for Mo_2C-I reported in table 2 is low, but is consistent with previous studies [2,3,8]. However, the oxygen site density for Mo_2C-I reported in table 2 is higher than a previous study of supported Mo_2C [5], and this is likely due to the synthesis conditions employed here which yield a surface that is relatively free of graphite. The oxygen site density is actually closer to the expected surface molybdenum density (1.0×10^{15} cm^{-2}) and, therefore, may be a better probe of these surface atoms. From the site density, it can be estimated that synthesis at 961 K produces a surface that is 90% clean while synthesis at 981 K produces a surface that is 25% clean. The site density in the samples was also affected by small amounts of oxygen left over from the synthesis, which were estimated by XPS to be 21 mol% for Mo_2C-I and 9 mol% for Mo_2C-II in the near-surface region. The lower CO uptake compared to O_2 uptake may be an intrinsic property of the molybdenum carbide surface resulting from blockage of CO chemisorption sites by surface carbidic carbon. Evidence of such blocking is provided by the low CO uptakes observed on single-crystal Mo_2C [9].

Table 2 summarizes the cumene hydrogenation activity results for the two types of Mo_2C. Aromatic hydrogenation is a structure insensitive reaction [10] and, hence, a proper probe to determine whether sites are properly counted on a catalyst surface. The steady-state cumene conversions for catalyst amounts corresponding to equal CO uptake were nearly identical for both catalysts. As expected then, the TORs based on CO uptake were also nearly identical (table 2), indicating that CO is a good probe molecule for cumene hydrogenation. Furthermore, since the ratio of oxygen uptake to CO uptake was approximately the same for both catalysts, then the comparison basis of equal CO uptake was essentially also a comparison basis of equal oxygen uptake. This result is evidenced by the fact that the

Table 1
Comparison of Mo_2C surface characterization for the two different synthesis temperatures.

Catalyst	T_f (K)	S_g ($m^2\,g^{-1}$)	CO uptake (μmol g^{-1})	CO surface concentration (cm^{-2})	Oxygen uptake (μmol g^{-1})	Oxygen surface concentration (cm^{-2})	Ratio of oxygen uptake to CO uptake
Mo_2C-I	961	39	102	1.5×10^{14}	579	8.8×10^{14}	5.7
Mo_2C-II	981	39	27	0.4×10^{14}	165	2.5×10^{14}	6.1

Table 2
Comparison of Mo_2C cumene hydrogenation activities. Amounts of catalysts loaded corresponded to 70 μmol CO uptake.

Catalyst	T_f (K)	Steady-state cumene conversion (%)	TOR (s^{-1})	
			CO uptake basis	Oxygen uptake basis
Mo_2C-I	961	87	5.4×10^{-3}	9.5×10^{-4}
Mo_2C-II	981	83	5.2×10^{-3}	8.5×10^{-4}

cumene hydrogenation TORs were also nearly equal on the basis of oxygen uptake (table 2). This finding indicates that O_2 is also a good probe of the sites that are active for cumene hydrogenation.

The results reported here indicate that synthesis temperature is critical for preparing a molybdenum carbide sample that has a surface substantially free of graphite. It is also found that both oxygen and CO can be used as probes of surface sites that are active for cumene hydrogenation.

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