Cumene hydrogenation turnover rates on Mo$_2$C: 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$_2$C was examined using cumene (isopropylbenzene) hydrogenation as a test reaction. The tests were carried out using β-Mo$_2$C 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 characterized by either CO or O$_2$ chemisorption. 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$_2$C. Second, to report the effect of temperature on the synthesis of β-Mo$_2$C, in particular with respect to the cleanliness of the surfaces produced.

β-Mo$_2$C 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 μmol 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 K for Mo$_2$C-I and 981 K for Mo$_2$C-II) at 0.03 K s$^{-1}$. Following a 20 min soak period at $T_f$, the sample was purged in 69 μmol s$^{-1}$ (100 cm$^3$(NTP) min$^{-1}$) He before being rapidly cooled to room temperature. Finally, the material was passivated in 34 μmol 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$_\alpha$ 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 μmol 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$_\alpha$ 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$_2$C 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$_2$C-I and 2.59 g for Mo$_2$C-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 μmol 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,
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$_2$C were tailored to lie slightly above ($T_i = 981$ K) and slightly below ($T_i = 961$ 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 $\beta$-Mo$_2$C (hcp).

Table 1 summarizes the surface characterization results of the Mo$_2$C 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$_2$C-I, which was synthesized at 961 K, had higher CO and oxygen uptakes than Mo$_2$C-II, which was synthesized at 981 K (table 1). Furthermore, XPS analysis of the fresh Mo$_2$C samples showed a carbon content of 51 mol% for Mo$_2$C-I and 70 mol% for Mo$_2$C-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$_2$C synthesis employ a $T_i$ of 973 K or higher [2,7].

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$_2$C-I and Mo$_2$C-II. The CO site density for Mo$_2$C-I reported in table 2 is low, but is consistent with previous studies [2,3,8]. However, the oxygen site density for Mo$_2$C-I reported in table 2 is higher than a previous study of supported Mo$_2$C [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 $\times$ 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$_2$C-I and 9 mol% for Mo$_2$C-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 carbide carbon. Evidence of such blocking is provided by the low CO uptakes observed on single-crystal Mo$_2$C [9].

Table 2 summarizes the cumene hydrogenation activity results for the two types of Mo$_2$C. 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

![Equilibrium curve for CH₄ decomposition to C(s).](image-url)