

Carbon–hydrogen bond activation over tungsten carbide catalysts

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Abstract

Tungsten carbides with surface areas ranging from 4 to 39 m²/g were prepared by the temperature-programmed carburization of tungsten oxide and nitride powders with pure CH₄ or a 48.9% CH₄ in H₂ mixture. Oxygen uptakes on the carbides were low most likely because of the presence of graphitic carbon at the surface. Nevertheless, the carbides were active and selective for the dehydrogenation of butane at temperatures between 623 and 723 K and atmospheric pressure with and without H₂ in the reactant feed. With H₂ in the feed, the higher surface area carbides (≥ 36 m²/g) were as active as a Pt–Sn/ γ -Al₂O₃ catalyst, but their selectivities were different. Without H₂ in the feed, the selectivities of the carbides were similar to those of the Pt–Sn/ γ -Al₂O₃ catalyst, but their reaction rates were 1–3 orders of magnitude lower. The high surface area materials were also active for the hydrogenolysis of butane. Because the catalytic properties of the carbides varied with the average particle size, we concluded that butane dehydrogenation was structure-sensitive over these materials, and suspected that this behavior was due to variations in the surface stoichiometry as well as the particle faceting.

1. Introduction

Striking similarities have been reported between the catalytic properties of W carbides and Pt group metals for hydrocarbon conversion reactions including dehydrogenation [1–3], isomerization [3–8] and hydrogenolysis [2,3,5–8]. Early studies indicated that the selectivities over low surface area carbides were similar to those over supported Pt group metals for the reactions of neopentane, n-hexane, n-heptane and cyclohexane, but the reaction rates were 1–4 orders of magnitude lower [2–4]. Recent advances in the synthesis of high surface area materials have led to the preparation of carbides with reaction rates comparable to those of Pt group metals for the aforementioned reactions [5–8]; however, their selectivities are

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typically different. There is evidence that the preparation conditions affect the surface composition [2,8]. The carbon stoichiometry in the carbide lattice in turn influences the catalytic and electronic properties [9–11]. Nonstoichiometric carbides have been reported to be active for the dehydrogenation of cyclohexane and hydrogenation of propene [2,12]. We believe that both the stoichiometry and structure control catalytic function. While some structure-function information is available, detailed relationships between the structure, stoichiometry and catalytic properties of W carbides have not been presented.

In this paper, we describe the structural, compositional and functional properties of W carbide catalysts with a range of surface areas. These catalysts were prepared by the temperature-programmed carburization (TPC) of W oxide and nitride precursors. This is an effective technique for manipulating solid state reaction events like particle nucleation and growth. Butane dehydrogenation was used as the test reaction. This reaction is of importance in the petroleum refining and synthetic rubber industries. Characterization techniques including X-ray diffraction and O₂ chemisorption were employed to evaluate the structural and sorptive properties of these catalysts.

2. Experimental

2.1. Synthesis

A series of W carbides was prepared via the TPC of W oxide and nitride precursors. Different heating rates (β), H₂ to CH₄ ratios (H₂/CH₄), and CH₄ (99.99%, Scott) weight hourly space velocities (SV) were used in an effort to vary the carbide structural and compositional properties. The CH₄ weight hourly space velocity is defined as the mass flow-rate of CH₄ divided by the mass of catalyst precursor.

Typically, a plug of quartz wool was packed onto a frit inside a quartz reactor (15.88 mm OD) fitted with a cooling water jacket. Between 1 and 5 g of WO₃ (99.7%, Alfa), H₂WO₃ (99%, Aldrich), or (NH₄)₁₀W₁₂O₄₁·5H₂O (99.999%, Johnson Matthey) was spread over the plug in the form of a thin bed. The reactor bed was then placed in a furnace (Thermcraft Model 132) connected to a temperature controller (Omega CN-2010). The flow-rates of CH₄ or CH₄ in H₂ were set so that CH₄ space velocities of 1.27 to 7.77 h⁻¹ were obtained. The gas flow-rates were measured using calibrated rotameters and controlled using needle valves. After establishing the flow-rates, a chromel–alumel (K type) thermocouple was secured against the outside wall of the reactor, and the furnace was closed.

Two temperature programs were employed for preparation of the catalysts. In the first program, the temperature was increased from room temperature to 943 K in 0.5 hours then from 943 K to 1153 K at 60 or 120 K/h. In the second program, the temperature was increased from room temperature to 973 K at 60 or 120 K/h.

In both cases, the reactant mixture was held at the final temperature for 1 hour. These synthesis conditions bracketed those employed previously [13,14]. After synthesis, the furnace was opened and the bed was rapidly cooled to room temperature in He (99.99%, Air Products). Before exposure to air, the materials were passivated with a mixture of 0.996% O₂ in He (Scott).

A tungsten carbide catalyst was prepared also via the topotactic carburization of tungsten nitride [15]. The nitride was prepared in a fashion similar to that used to produce the carbides from WO₃. About 4 g of WO₃ was reacted with anhydrous ammonia (99.998%, Scott) flowing at a space velocity of 1.08 h⁻¹. The temperature was increased from room temperature to 673 K in 0.5 hours, then to 873 K at 67 K/h and finally to 1023 K at 75 K/h. After completion of the nitridation, the bed was rapidly cooled to room temperature in flowing He. The material was exposed to flowing CH₄ at room temperature so that a space velocity of 1.01 h⁻¹ was obtained. The temperature was increased to 828 K in 0.5 hours and finally to 1128 K at 75 K/h. After completion of the temperature program, the bed was quenched to room temperature in He, and the product was passivated. Carbides with surface areas as high as 100 m²/g have been prepared via the TPC of W nitrides [14,15].

2.2. Characterization

The bulk properties of the materials were characterized using a computer controlled Rigaku Rotaflex DMAX-B rotating anode X-ray diffractometer with a Cu K α radiation source. The structure of the material was determined by comparing the patterns to those found in the Powder Diffraction Files (ICDD) [16]. We used line broadening analysis based on the most intense peak in the diffraction pattern to determine the average crystallite size. The crystallite size, D_c , was estimated using the Scherrer equation [17]. The ratio of the intensities of the two most intense peaks in the patterns were used to assess preferential orientation of the crystallites.

The bulk compositions of the materials were estimated using a Perkin-Elmer 2400 CHN analyzer equipped with an autosampler. Between 2–5 mg of sample was placed in a Sn sample holder. After running several blanks and acetanilide standards, the sample was combusted in the analyzer at 1198 K. The effluent gases were separated using a frontal chromatographic method and the percentages of C, H, and N were recorded. Each sample was analyzed at least twice, and the values obtained were used to estimate the carbon to tungsten atomic ratios (C/W). These ratios were determined assuming that whatever was not carbon, nitrogen or hydrogen was tungsten.

Nitrogen BET surface area and O₂ chemisorption measurements were performed using a Quantasorb model QS-17 sorption analyzer. Approximately 100–200 mg of material was placed in a quartz sample holder. After reduction in H₂ at 753 K for 3 hours, single point BET measurements were performed using a 28.9% N₂ in He mixture (Scott) at 77 K. Pulses of prepurified N₂ (99.998%, Air Products) were used to calibrate the volume adsorbed. This volume was then used to determine

the surface area (S_g). The particle size, a semi-quantitative measure of the surface structure, was estimated from the surface area using the equation $D_p = 6/\rho S_g$ where ρ is the density of the primary bulk phase of the material ($\rho = 15.63 \text{ g/cm}^3$ for WC and 17.15 g/cm^3 for W_2C). For the chemisorption measurements, calibrated volumes of 9.98% O_2 in He (Scott) were pulsed over the catalyst at room temperature until the surface was saturated. The volume of O_2 that was not adsorbed, was measured and used to determine the chemisorbed volume. The chemisorbed volumes and the surface areas were reproducible over several runs. Averaged values were reported for all measurements.

2.3. Activity and selectivity measurements

Butane dehydrogenation activity and selectivity measurements were carried out using a 6 mm OD quartz U-tube reactor. Approximately 300–400 mg of catalyst was spread over a plug of quartz wool packed into the U-tube, and a chromel–alumel (K type) thermocouple was inserted directly into the catalyst bed. After H_2 pretreatment at 753 for 3 hours, activity and selectivity measurements were carried out using 4% C_4H_{10} (99.998%, AGA) with a He balance or 4% C_4H_{10} , 36% He with a H_2 balance. The activity measurements were made at temperatures between 623 and 723 K after 4 to 6 hours on stream. The activities were reproducible to within $\pm 15\%$. The reactions were run so that differential conditions prevailed; butane conversions during activity measurements were $\leq 5\%$. We compared the catalytic properties of the carbides to those of a Pt–Sn/ γ - Al_2O_3 catalyst (1.8% Na, 1.2% Sn, and 0.3% Pt) that was pretreated under similar conditions. Hereafter, Pt–Sn/ γ - Al_2O_3 is referred to as the Pt–Sn catalyst.

The products were separated and analyzed using an HP 5890 Series II gas chromatograph (GC) equipped with a 3.05 m n-Octane/Porasil C packed column connected to a flame ionization detector. The HP ChemStation software was used to estimate product peak areas and retention times. The retention times and response factors were determined using standard alkane and alkene mixtures (Scott, ± 2 –5%).

3. Results

3.1. Characterization

The primary bulk phases, as revealed by XRD, were WC (hex) and W_2C (hcp) (Table 1). The phase constituents did not change on use in butane dehydrogenation. All of the lower surface area materials contained WC, while the higher surface area materials contained primarily W_2C with a small amount of WC in the bulk. The crystallite sizes of the carbides were independent of the synthesis conditions and precursor. A comparison of the crystallite and particle sizes suggested that the lower

surface area materials contained polycrystalline aggregates. The higher surface area materials, on the other hand, contained small single crystallites. Preliminary transmission electron microscopy (TEM) verified that the lower surface area materials were polycrystalline and that the higher surface area materials were single crystallites. In both cases, the domain sizes from TEM were similar to the average crystallite sizes obtained from XRD. There was no simple correlation between the crystallite and particle sizes, and the materials did not show any texturing or preferred orientation.

The surface areas of the W carbides, which ranged from 4 to 39 m²/g, depended on the synthesis conditions employed (Table 1). In general, the surface areas increased with increasing space velocity. This is consistent with previous studies which indicated that high space velocities were necessary for the synthesis of high surface area carbides and nitrides [13,18]. The addition of H₂ to the feed mixture also resulted in an increased surface area. Hydrogen probably prohibited the deposition of graphitic carbon on the carbide surfaces. Lower C/W ratios for carbides prepared with H₂ in the feed support this proposition. The heating rate employed during carburization had only a modest effect on the resulting surface areas. This was quite surprising since one would expect the heating rate to influence the solid-state reaction selectivity and surface area [19]. The oxide precursor employed did not affect the resulting surface area. For similar conditions the TPC of tungsten trioxide (TO), tungstic acid (TA) and ammonium tungstate (AT) led to materials with similar surface areas and bulk structures. The carbide prepared via carburization of W nitride had a higher surface area than the carbides synthesized directly from the oxides under similar conditions.

Table 1
Summary of tungsten carbide synthesis conditions and bulk structural properties

Catalyst code	β (K/h)	H ₂ /CH ₄	CH ₄ SV (h ⁻¹)	S_g (m ² /g)	Particle size (nm)	Phase (s) present	Crystallite size (nm)	C/W
WC-1	60	0	1.27	4.0	96	WC	12	1.85
WC-2	60	0	2.54	4.7	79	WC	12	1.75
WC-3	60	1.04	1.27	6.8	55	WC	16	1.41
WC-4	60	1.04	2.54	10.7	35	WC	12	1.45
WC-5	120	0	1.27	3.9	98	WC	13	1.72
WC-6	120	0	2.54	6.1	63	WC	12	1.72
WC-7	120	1.04	1.27	9.3	43	WC	16	1.40
WC-8	120	1.04	2.54	6.0	64	WC	14	1.57
T ^a	75	0	1.01	19.5	20	WC	11	1.65
TO	60	1.04	7.77	37.3	10	W ₂ C	13	0.97
TA ^{b,d}	60	1.04	7.77	38.7	10	W ₂ C + WC	17	1.0
AT ^{c,d}	60	1.04	7.77	36.6	10	W ₂ C + WC	15	1.03

^a Carbide prepared from WN.

^b Carbide prepared from H₂WO₄.

^c Carbide prepared from (NH₄)₁₀W₁₂O₄₁ · 5H₂O.

^d Particle and crystallite sizes calculated assuming W₂C bulk phase.

Table 2
Chemisorptive properties of tungsten carbide catalysts

Catalyst code	Oxygen uptake ($\mu\text{mol O}_2/\text{g}$)	N_{oxygen} ($10^{12} \text{ O}/\text{cm}^2$)
TO	2.9	9.4
TA	2.7	8.4
AT	4.3	14.2
Pt-Sn/ $\gamma\text{-Al}_2\text{O}_3$	3.3	–

Chemisorption was attempted on all of the materials, but only the higher surface area catalysts chemisorbed oxygen (Table 2). These materials had site densities that corresponded to oxygen surface coverages of ca. 1%. Either the surfaces were blocked by graphitic carbon, ineffective in chemisorbing oxygen at room temperature, or residual oxygen at the surface after reduction prohibited chemisorption. Graphitic carbon has been reported to suppress the chemisorption of O_2 , H_2 and CO on W carbides [13,20]. Oxygen has been reported to dissociate and strongly chemisorb onto W carbides at room temperature [14,21,22]. In fact, oxygen coverages in excess of 100% have been observed for bulk W carbides [14]. While the amount of oxygen in the material after reduction was not quantified, results from elemental analysis indicated that the C/W ratios were in excess of unity for the lower surface area materials and near unity for the higher surface area materials (Table 1). The C/W ratios expected for the stoichiometric equilibrium phases, WC and W_2C , are 1.0 and 0.5, respectively. We have therefore concluded that the low uptake values on our W carbides were due primarily to the presence of graphitic carbon at the surface. Nevertheless, chemisorption does quantify the number of available sites so we used this value, when available, to normalize the reaction rates.

3.2. Butane dehydrogenation over tungsten carbides

3.2.1. Dehydrogenation

The tungsten carbides were active and selective for the dehydrogenation of butane. The Arrhenius plots in Fig. 1 show that, in general, the activities increased with increasing surface area. In Table 3, the kinetic properties of the carbides are compared to those of the Pt-Sn catalyst. Activities of the higher surface area W carbides (on an O_2 uptake basis) were about an order of magnitude less than that of the Pt-Sn catalyst. The average carbide activation energy of 21 ± 4 kcal/mol compared favorably with the value of 18 ± 1 kcal/mol for the Pt-Sn catalyst. The butane conversion activation energies for all the catalysts were similar to those reported in the literature for dehydrogenation reactions [2,23].

Examples of the selectivities are given in Fig. 2. The selectivities over the carbide catalysts depended on the surface area and bulk structure. The primary products produced over the carbides were butenes. The higher surface area carbides produced small quantities of hydrogenolysis products. Selectivities over these materials were

similar to those of the Pt–Sn catalyst. While the lower surface area carbides also produced primarily butenes, the distribution among these was different from those for the higher surface area carbides and the Pt–Sn catalyst. The higher surface area carbides and the Pt–Sn catalyst produced significant amounts of 2-butenes which probably resulted from the isomerization of 1-butenes. These catalysts appeared to have sites capable of catalyzing skeletal isomerization reactions.

3.2.2. Dehydrogenation with H_2

The activities were generally higher in the presence of H_2 compared to those in the absence of H_2 . This may have been due to prohibition of coke deposition, a common problem for dehydrogenation catalysts. Again, the activities over the

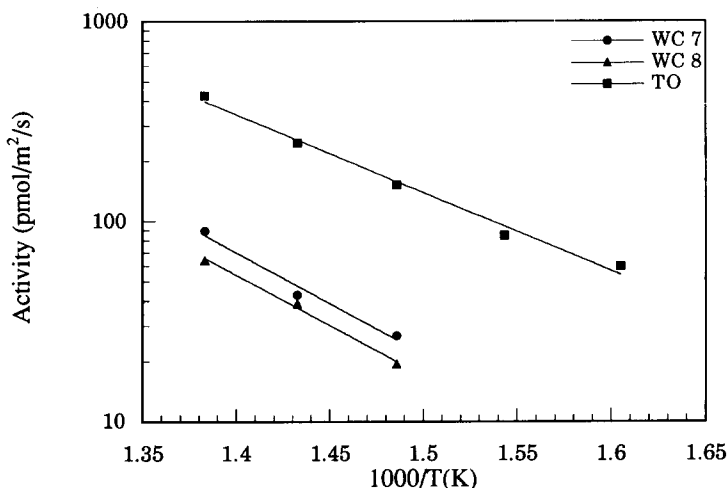


Fig. 1. Arrhenius plots of butane reaction activities over catalysts TO, WC-7 and WC-8. The surface areas of TO, WC-7 and WC-8 were 37.3, 9.3 and 6.0 m^2/g , respectively.

Table 3

Summary of butane dehydrogenation results

Catalyst code	Reaction rate (pmol/g/s)	Activity at 723 K		ΔE_{act} (kcal/mol)
		(pmol/m²/s)	(mmol/mol O_2 /s)	
WC-1	461	115	–	17
WC-2	568	121	–	22
WC-3	481	71	–	14
WC-4	3123	292	–	27
WC-5	469	120	–	22
WC-6	602	99	–	21
WC-7	836	90	–	23
WC-8	440	73	–	23
T	410	21	–	26
TO	15999	429	5.5	21
TA	4541	117	1.7	25
AT	12269	335	2.9	16
Pt–Sn/ γ - Al_2O_3	2.75×10^5	–	83.5	18

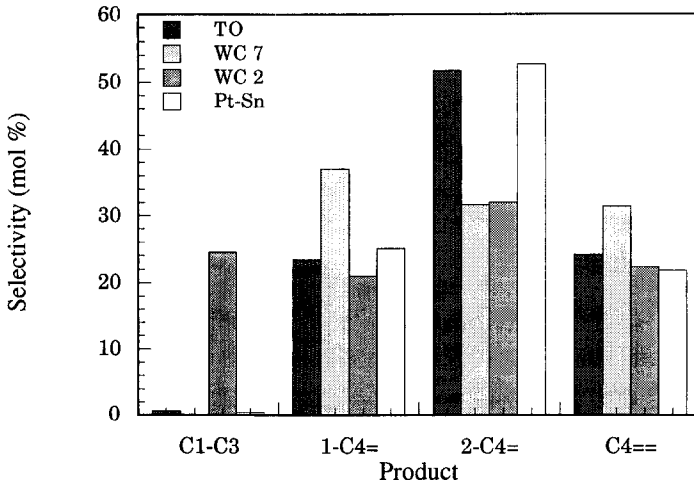


Fig. 2. Examples of selectivities from butane reactions at 723 K. C_n denotes an n carbon hydrocarbon. The = sign denotes a double bond. The surface areas of TO, WC-7 and WC-2 were 37.3, 9.3 and 4.7 m^2/g , respectively.

carbides increased with increasing surface area (Fig. 3). The activities of the carbides are compared to those of the Pt–Sn catalyst in Table 4. The low surface area materials were 1 to 2 orders of magnitude less active than the Pt–Sn catalyst, while the higher surface area carbides had activities (on an O_2 uptake basis) that were comparable or superior to that of the Pt–Sn catalyst. These results suggested that the characteristics of active sites in the tungsten carbides were similar to those in the Pt based catalyst, as have been previously reported [1–8]. The average apparent activation energy of 23 ± 5 kcal/mol was within experimental error of the value for the Pt–Sn catalyst (28 ± 2 kcal/mol).

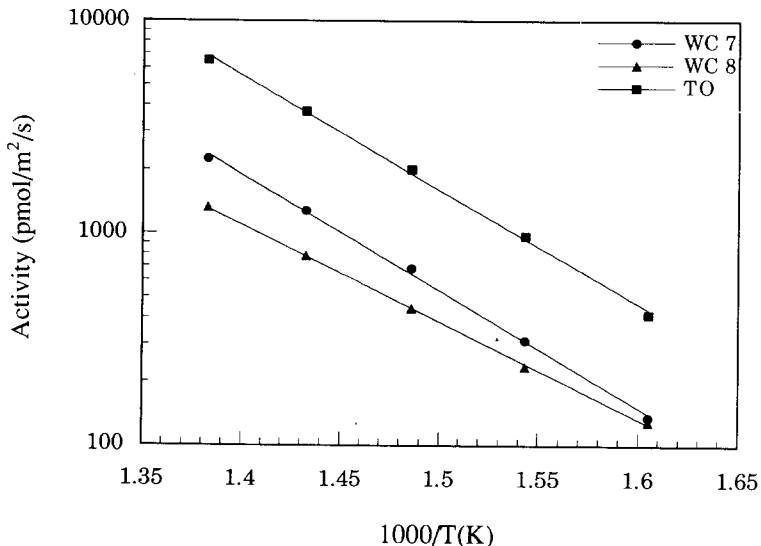


Fig. 3. Arrhenius plots of butane reaction activities in H_2 over catalysts TO, WC-7 and WC-8. The surface areas of TO, WC-7 and WC-8 were 37.3, 9.3 and 6.0 m^2/g , respectively.

Table 4
Summary of butane dehydrogenation in H₂ results

Catalyst code	Reaction rate (nmol/g/s)	Activity at 723 K		ΔE_{act} (kcal/mol)
		(nmol/m ² /s)	(mmol/mol O ₂ /s)	
WC-1	10	2.5	–	22
WC-2	44	9.4	–	24
WC-3	3	0.4	–	28
WC-4	52	4.9	–	22
WC-5	43	11.1	–	28
WC-6	14	2.3	–	24
WC-7	21	2.2	–	25
WC-8	8	1.3	–	21
T	10	0.5	–	18
TO	244	6.5	84.1	25
TA	170	4.4	63.0	18
AT	188	5.1	43.7	25
Pt–Sn/ γ -Al ₂ O ₃	194	–	58.8	28

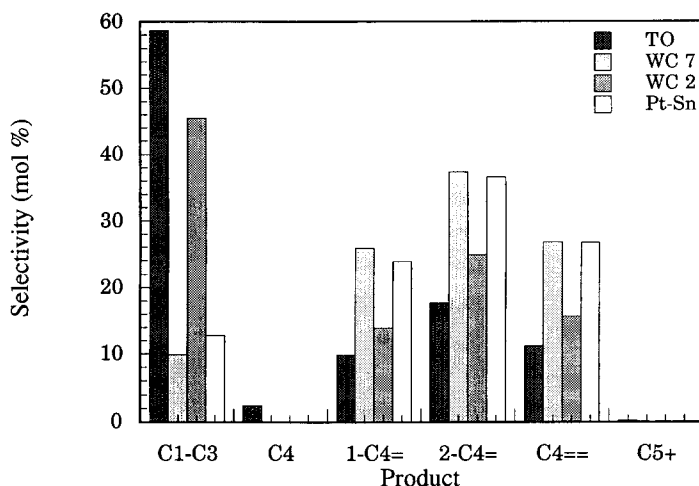


Fig. 4. Examples of selectivities during butane reactions in H₂ at 723 K. C_n denotes an *n* carbon hydrocarbon. The = sign denotes a double bond. The surface areas of TO, WC-7 and WC-2 were 37.3, 9.3 and 4.7 m²/g, respectively.

The selectivities in the presence of H₂ were different than those in the absence of H₂, although in both cases, the selectivities depended on the surface area and bulk structure (Fig. 4). The higher surface area materials were very active for hydrogenolysis. Small quantities of isomerization products, *i*-C₄H₁₀ and *i*-C₅H₁₂, were also detected over these materials. Selectivities over the higher surface area materials were also different from those over the Pt–Sn catalyst. With the exception of WC-2, the lower surface area carbides were not very active for hydrogenolysis.

4. Discussion

Of the synthesis variables studied, the space velocity and feed composition (namely the H_2 content) had the most significant effects on the carbide surface areas and structures. These variables can regulate the solid-state reaction pathways [24]. Increasing the space velocity led to an increase in the surface area. Oyama et al. [13] reported similar behavior during the preparation of Mo_2C . The increase in surface area may have been caused by changes in the composition of the gas at the reaction interface. A plausible explanation is that high space velocities removed H_2O vapor from the reaction interface. Water vapor, even in small concentrations, can cause hydrothermal sintering [25,26]. Water might also inhibit the solid-state reactions leading to higher surface area carbides. In either case, high space velocities would minimize the amount of H_2O and other volatile reaction products near the surface [18]. The similarity between the surface areas and bulk structures of the TO, TA and AT carbides suggested that there was no effect of precursor structure and their solid-state reaction intermediates were similar. This intermediate did not appear to be WO_2 . High temperature X-ray diffraction results showed that carburization of WO_3 through a WO_2 intermediate led to materials with low surface areas. It has been reported that the nitridation of MoO_3 through MoO_2 also results in low surface area nitrides [9,23,27]. The primary function of H_2 in the CH_4 feed appeared to be inhibition of the growth of graphitic carbon at the surface [15]. While the exact amount of H_2 necessary to prepare materials without carbon at the surface is unknown, it is clear that H_2 facilitated the evolution of high surface areas.

The catalytic properties of the W carbides were different from those reported in the literature [2,5,6,8]. We found that the low surface area W carbides were selective for butane dehydrogenation, while the higher surface area materials were selective for hydrogenolysis. Leclercq et al. [2] reported that a series of low surface area W carbides were active primarily for butane hydrogenolysis (at 623 K using a H_2/C_4H_{10} partial pressure ratio of 9). These materials, which were prepared isothermally from reduced tungstic acid and acetylene black, also catalyzed the isomerization of butane. Ribeiro et al. [5,6] prepared WC ($30\text{ m}^2/\text{g}$) and $\beta\text{-W}_2\text{C}$ ($100\text{ m}^2/\text{g}$) via the TPC of WO_3 and reported that these materials catalyzed neopentane and hexane hydrogenolysis. For the neopentane reactions (at 490 K using a H_2/C_5H_{10} ratio of 9), there was a 30 fold difference between the activities over these catalysts. Activities for hexane hydrogenolysis (at 430 K using a H_2/C_6H_{14} ratio of 16) were similar for the two materials. Ledoux et al. [8] reacted WO_2 vapors with activated carbon under vacuum at high temperatures to prepare high surface area carbides. They reported that these materials were active for hexane hydrogenolysis and isomerization (at 723 K using a H_2/C_6H_{14} ratio of 151). Our results and those in the literature suggest that the character of the active sites is a strong function of the synthesis conditions. The ratio of hydrogen to hydrocarbon in the feed also appears to affect the catalytic properties as evidenced by the wide variation in catalytic activities and selectivities.

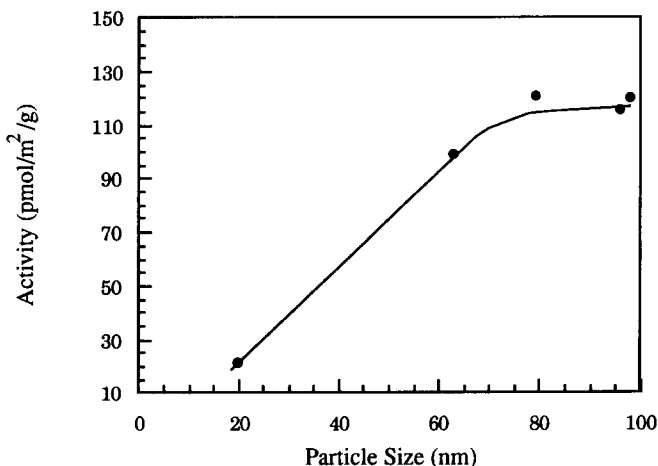


Fig. 5. Schematic showing the relationship between the butane dehydrogenation activity and particle size. These W carbides were prepared using pure CH_4 .

Very clear trends between the catalytic and structural properties were observed when the W carbides were grouped based on the conditions used to prepare the materials. Fig. 5 shows the dehydrogenation activities over the catalysts prepared using pure CH_4 . The C_4H_{10} dehydrogenation activities in the absence of H_2 increased with particle size up to ca. 80 nm, then leveled off. No clear trends for the activity in C_4H_{10} - H_2 mixtures with particle size were apparent for these catalysts. Nevertheless, the results suggested that the catalytic properties of W carbides varied with the surface structure and stoichiometry.

Dehydrogenation activities over the carbides prepared using CH_4 - H_2 mixtures are shown in Fig. 6 and Fig. 7. The materials with particle sizes greater than 30 nm

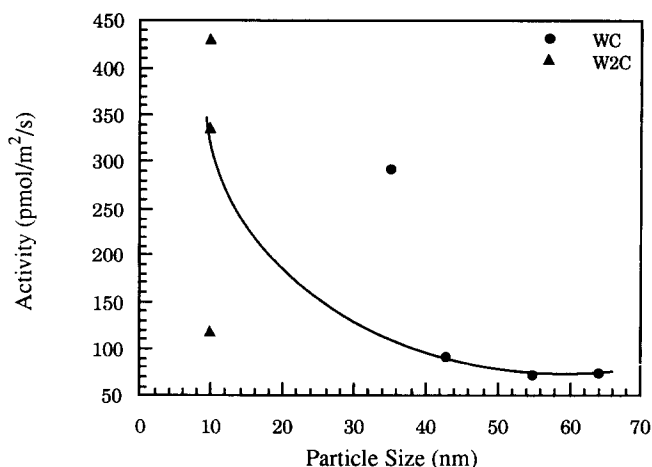


Fig. 6. Schematic showing the relationship between the butane dehydrogenation activity and particle size. These W carbides were prepared using CH_4 - H_2 mixtures.

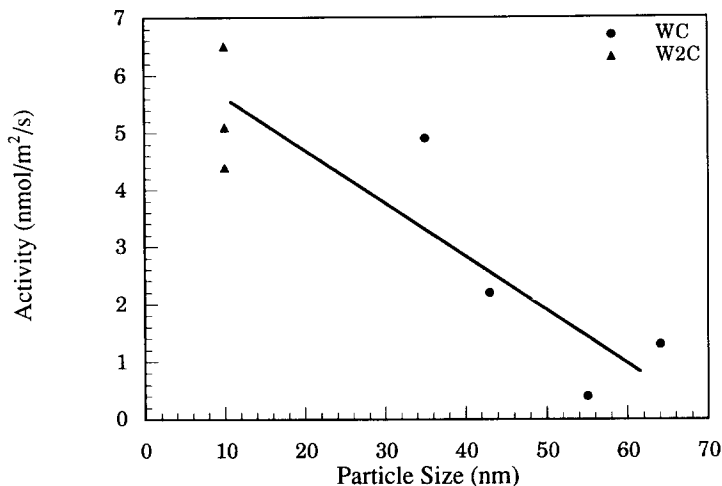


Fig. 7. Schematic showing the relationship between the butane dehydrogenation activity in the presence of H₂ and particle size. These W carbides were prepared using CH₄-H₂ mixtures.

contained only WC in the bulk, while those with particle sizes less than 30 nm contained either W₂C or mixtures of W₂C and WC. The butane dehydrogenation activities, without and with H₂ in the reactant feed, increased with decreasing particle size. Despite the different bulk structures, a single line adequately described all of the data including that for the W₂C containing catalysts. The reasons why W₂C and WC follow similar trends with particle size are not clear, however, it is noteworthy that W₂C and WC are hexagonal structures.

The apparent structure-sensitivity of butane dehydrogenation over the W carbides was not expected. Structure-sensitivity is typically manifested for particles smaller than ca. 10 nm [28]. For metals it is usually associated with variations in the reaction rates with the crystallographic faceting of the surface. However, for W carbides, one must also consider the influence of surface stoichiometry and the presence of more than one phase. Given the observed variations in the phase constituents with surface area, it is plausible that the near surface C/W stoichiometry was a function of the particle size, even for the relatively large particles in the W carbides. The carbides also appeared to contain significant amounts of graphitic carbon at the surface although one would not expect the catalysis to occur on carbon. It is possible that the character of the unblocked surface is affected by the size of the carbide particles. Structure-sensitivity is more common for hydrogenolysis than for dehydrogenation reactions [28]. Lee et al. [29] reported that the butane hydrogenolysis activity over Mo₂C/Al₂O₃ increased with increasing loading. They also found that the hydrogenolysis activity over hexagonal Mo₂C was greater than that over cubic α -MoC_{1-x}. The smaller α -MoC_{1-x} particles had higher turnover frequencies than the larger ones. These results implied the structure-sensitivity of hydrogenolysis over Mo carbides. Dehydrogenation has typically been found to be structure-insensitive over noble metals like Pt [28,30].

5. Conclusions

The properties of a series of W carbides prepared by the temperature-programmed carburization method were strong functions of the synthesis conditions employed. The most influential synthesis parameters were the space velocity and the H_2/CH_4 ratio. Higher space velocities resulted in materials with high surface areas presumably because of the removal of H_2O and other volatiles from the reaction interface. While the mechanisms for inhibition of graphitic carbon deposition or its removal are unclear, the presence of H_2 in the feed mixture reduced the amount of carbon in the materials and increased their surface areas. The higher surface area materials contained W_2C or a mixture of W_2C and WC , while the lower surface area materials contained WC . The lower surface area carbides contained particles that appeared to be polycrystalline aggregates with no apparent preferential orientation. Oxygen chemisorption was only achieved on the higher surface area materials. We believe that chemisorption was inhibited by the presence of graphitic carbon at the surface.

The W carbides were active for the dehydrogenation of butane in the presence and absence of H_2 . The higher surface area materials were as active as a Pt–Sn catalyst in the presence of H_2 . The selectivities of the lower surface area materials were similar to those of the Pt–Sn catalyst. In the absence of H_2 , the carbides were 2 to 4 orders of magnitude less active than the Pt–Sn catalyst. While the primary reaction products were alkenes, the product distributions over the carbides varied with surface area. The higher surface area carbides also catalyzed butane hydrogenolysis in addition to butane dehydrogenation.

Dehydrogenation over the W carbides appeared to be structure-sensitive since the activity varied with changes in the surface area and particle size. We believe that these responses were due to variations in the surface stoichiometry/composition. We are currently investigating the influences of surface structure using TEM.

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