

RESEARCH NOTE

Chloropentafluoroethane Hydrodechlorination over Tungsten Carbides: Influence of Surface Stoichiometry

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Tungsten carbides were prepared by temperature-programmed reaction of WO_3 with methane/hydrogen mixture and activated according to several thermal treatments by varying the temperature or the feed composition. Modification of these parameters was expected to change the surface composition (C/W). Such surface modifications have been related to acid–base properties observed in the decomposition of isopropanol. Finally, it was found that such acidic properties are probably involved in the dehydrohalogenation of chloropentafluoroethane responsible mainly for the formation of unsaturated compounds. © 2002 Elsevier Science (USA)

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Earlier studies showed that group VI transition metal carbides, in comparison to noble metals, exhibit interesting catalytic properties in C–Cl bond cleavage (1–3). Recently the hydrodechlorination of chloropentafluoroethane (CFC-115) into pentafluoroethane (HFC-125) was investigated on carbide catalysts MC (with $M = \text{W}$ or Mo) (4). This reaction is potentially interesting for practical applications, particularly to substitute hydrofluorocarbons (HFCs) for chlorofluorocarbons (CFCs), HFCs being less harmful to stratospheric ozone. Among the carbides studied, it was found that the activity of WC was lower than that of a reference Pd-based catalyst; on the other hand, their selectivities were comparable for the production of HFC-125. In fact additional by-products, mainly unsaturated compounds from dehydrofluorination reactions, have also been observed on WC compared with Pd which essentially yields products from hydrodefluorination reactions. Such an observation suggests a bifunctional catalysis on tungsten and molybdenum carbide catalysts. Indeed, hydrodehalogenation reactions are activated on metallic sites while dehydrofluorination reactions probably take place on acid–base

sites. Presently, the origin of such acid–base sites is not well understood. Several hypotheses can be considered: (i) their promotion could occur during the reaction by fluorine or oxygen accumulation at the catalyst surface; (ii) the carburization procedure could also develop such an acidity related to the partial ionicity of the $M^{\delta+}-C^{\delta-}$ bond in the bulk; (iii) more probably the presence of acid–base sites could be related to the surface carbide stoichiometry since we have shown that the proportion of dehydrohalogenation products increased when the ratio C/M decreased (4). Generally the activation step under pure hydrogen, which is always performed before catalytic experiments to remove excess polymeric carbon, which is frequently deposited at sample surfaces during the carburization step, results in partial decarburization of the carbide surface (5, 6), the extent of which depends on the temperature, the hydrogen flow rate, and the duration of the activation step. Consequently, changes in the activation conditions could be an interesting way to modify the surface carbide composition and then to study the relationship between this composition and reaction selectivity. To check whether acid–base sites are related to a surface substoichiometry, we prepared three samples of WC with various surface stoichiometries by changing the activation conditions.

All tungsten carbides were prepared using a similar conventional procedure (7, 8) by temperature-programmed carburization of WO_3 (99.95% Fluka) from room temperature to 800°C with a carbiding mixture composed of (20 vol%) CH_4 (99.995%) in H_2 (99.995%). The catalysts were further activated in pure hydrogen at 750 or 800°C or in a mixture composed of 1–2 vol% CH_4 in H_2 at 800°C for 5 h (9–11) according to the experimental conditions summarized in Table 1. Finally, the solids were cooled to room temperature before reaction. The samples are labeled WCX-Y, where X and Y represent respectively the temperature and the composition of the feed gas used during the activation step. WCX- H_2 and WCX- CH_4 stand for catalysts respectively activated in pure hydrogen and in 1 to 2% CH_4 in H_2 .

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TABLE 1

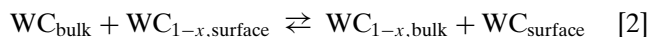
Parameters of the Activation Treatments of the Tungsten Carbide Samples

Catalyst	Feed composition	Total flow (L/h)	Temperature (°C)	Duration (h)	Specific area (m ² /g)
WC750-H ₂	H ₂	8	750	5	15
WC800-H ₂	H ₂	8	800	5	14.5
WC800-CH ₄	1–2%CH ₄ /H ₂	8	800	5	15

The carbidic carbon removal during the treatment in pure hydrogen, mentioned above, is the result of two successive steps: elimination of carbidic carbon at the surface,



followed by replenishment of the surface by carbon diffusion from the bulk,



At 800°C, the CH₄ partial pressure (P_{CH_4}) at steady state is slightly lower than that at equilibrium of step [1]. Consequently, both steps [1] and [2] are fast, and global decarburization of the surface is likely to be limited. At 750°C, P_{CH_4} at steady state is slightly higher than at 800°C but it is lower than that at equilibrium, probably because step [2] of carbon diffusion is slower than step [1]. In such a case, a more extensive decarburization is expected. In fact, estimation of the global (C/W) atomic ratios for WC800-H₂ and WC750-H₂, taking into account the amount of carbidic carbon removed during the decarburization step (considering the steady-state partial pressure of methane, the flow rate, and the duration of the treatment), led to 0.90 and 0.865, respectively, indicating global decarburization for both samples, but to a slightly greater extent for WC750-H₂. Of course it is likely that the surface decarburization involves the top surface layers more than the bulk of the sample. On the contrary, activation with a low CH₄ pressure in hydrogen (1 to 2%) was supposed to avoid together surface decarburization and polymeric carbon deposit at the surface, considering the equilibria corresponding to tungsten carburization by CH₄ and CH₄ decomposition (12). Summarizing the above considerations, the surface C/W ratio should decrease in the following sequence: WC800-CH₄ > WC800-H₂ > WC750-H₂.

X-Ray diffraction measurements show that no structural modification occurs due to changes in the decarburization procedure; the usual hexagonal close-packed compact structure is preserved for all WC samples. The surface properties were investigated by XPS analysis. Figure 1a illustrates the C 1s spectra obtained on tungsten carbides after passivation by exposure to 2 vol% O₂ in N₂. The main contribution at 283.3 ± 0.2 eV is characteristic

of carbidic carbon (13). An additional small shoulder is observed at 284.9 ± 0.2 eV which corresponds to polymeric carbon (14); its intensity decreases according to the sequence WC800-CH₄ > WC800-H₂ > WC750-H₂. The W 4f spectra (Fig. 1b) are similar for all the samples and show the contributions of oxidic and carbidic tungsten species. The major photopeaks at 32.3 and 34.4 ± 0.2 eV correspond respectively to W 4f_{7/2} and W 4f_{5/2} lines characteristic of WC (14) while the W 4f_{5/2} photopeak at 38.2 eV has been attributed to W⁶⁺ species (15). This assignment is also supported by the difference between the W 4f_{7/2} and W 4f_{5/2} binding energy levels, respectively, for the more reduced component and the oxidic phase. Indeed, a value of 5.9 eV seems to agree with the presence of WC in the layers probed by XPS while deviations from this value up to 6.4 eV are encountered when metal species are still present on the surface (16). A quantitative estimation of the surface composition reflected by the atomic ratio C/W has been achieved considering the total surface area of the photopic W 4f, while only the intensity signal related to the carbidic phase has been accounted for after decomposition of the C 1s photopeak. The values calculated for C/W, in Table 2, emphasize previous statements regarding the increase in carbon deficiency in the sequence WC800-CH₄ > WC800-H₂ > WC750-H₂. It is worth noting that XPS analysis involves about 10 monolayers. Consequently the atomic C/W ratios in Table 2 are average stoichiometries which do not reflect exactly the surface composition of the topmost layer involved in catalysis. The difference between the actual values of the C/W ratio of the three samples are probably much greater than those

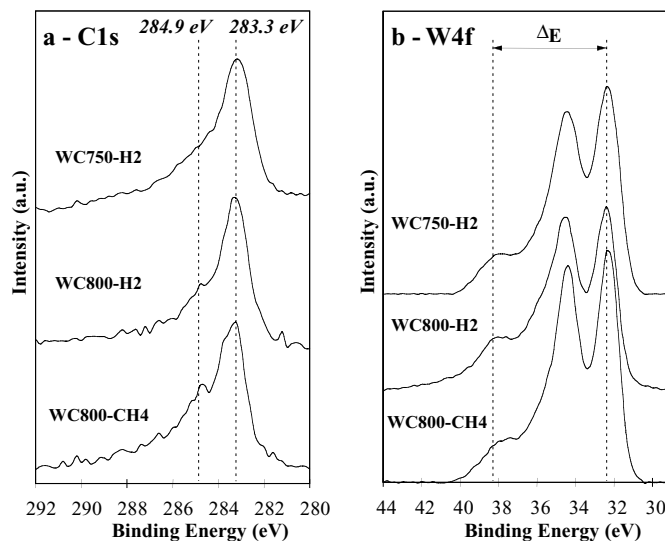


FIG. 1. (a) X-Ray photoelectron spectra of C 1s energy region for the fresh samples. Carbidic carbon is located at 283.3 eV and polymeric carbon at 284.9 eV. (b) X-Ray photoelectron spectra of W 4f_{7/2}–W 4f_{5/2} doublets for the fresh samples. ΔE represents the gap in binding energy between W 4f_{5/2} (W⁶⁺) and W 4f_{7/2} (reduced phase).

TABLE 2

Surface Composition and Binding Energy Gap from XPS Measurements

Catalyst	Intensity ratio (I_c/I_w)	Atomic (C/W) ratio	ΔE^a (eV)
WC750-H ₂	7.8×10^{-2}	0.74	5.9
WC800-H ₂	8.6×10^{-2}	0.80	5.8
WC800-CH ₄	10.3×10^{-2}	0.97	5.8

$$^a \Delta E = E_{b/W4f7/2(W+6)} - E_{b/W4f7/2(\text{reduced phase})}$$

measured in Table 2. Nevertheless, their comparison shows that thermal treatment at 750°C in pure hydrogen leads to partial carbon surface depletion, while treatment at 800°C in a mixture containing a low concentration of CH₄ prevents (or reduces) such surface decarburization.

On the three catalysts, we studied selectivity in the hydrogenolysis of chloropentafluoroethane (CFC-115) and in the conversion of isopropanol which is a good probe reaction for the study of metallic/acid–base behavior of supported metals (17–19); the dehydrogenation into acetone occurs on metal-like sites while the dehydration into propene or diisopropyl ether take place on acid–base sites. Consistently, this latter reaction quantifies the acid–base properties of the three carbides by the selectivity in dehydration versus dehydrogenation. Hydrogenolysis of chloropentafluoroethane (CFC-115) was studied under atmospheric pressure in temperature-programmed experiments performed in a stainless-steel fixed-bed flow reactor described earlier (4), from room temperature to 350°C with a constant heating rate of 1°C/min. The space velocity was 4000 h⁻¹ and the molar ratio H₂/CFC-115 was 2. Then the catalysts were maintained for a few hours at 350°C. Transformation of chloropentafluoroethane leads to a complex product distribution where CF₃CF₂H (HFC-125), the target molecule, CF₃CFH₂ (HFC-134a), and CF₃CH₃ (HFC-143a) are produced from hydrodehalogenation reactions, unsaturated compounds (C₂H₄, CF₂CH₂, C₂F₄) are produced from dehydrofluorination reactions, and alkanes such as CH₄, C₂H₆, and C₃H₈ are also formed in substantial proportions. As shown in Fig. 2 and Table 3, no significant changes in steady-state activities are observable with respect to the conditions of activation and to the surface composition related to the atomic C/W ratio. WC800-CH₄ seems to be slightly more active than the other two carbides. This relates to the very similar specific surface areas of the three samples. More relevant are the changes in selectivity at low temperature (Fig. 3, Table 3) with surface C/W ratio: selectivity in HFC-125 decreases while the ratio C/W decreases, whereas the formation of unsaturated compounds and alkanes (all resulting from dehydrofluorination of HFC125) follows the reverse trend. This suggests that the lower the surface C/W ratio, the higher the acid–

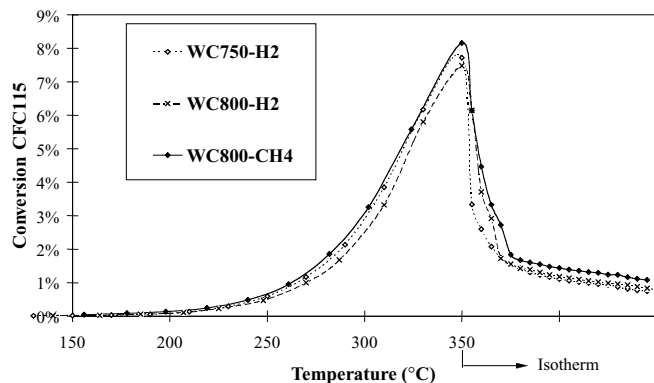


FIG. 2. Temperature-programmed and steady-state conversion curves in the hydrodechlorination of CF₃CF₂Cl (CFC-115) over WC750-H₂, WC800-H₂, and WC800-CH₄. The loading of catalyst was 1.5 g, the volumetric space velocity was 4000 h⁻¹, and the molar ratio H₂/CFC-115 was fixed at 2. The temperature was raised gradually from RT to 350°C at 1°C/min.

base properties. At first glance, it may seem surprising that such wide differences in selectivities were observed while there is almost no difference in activities. This can be very well accounted for by considering that the primary product is HFC-125, further leading to secondary elimination reactions which will govern the selectivity of the reaction. Consequently, overall conversion of CFC-115 probably depends essentially on the specific surface areas, which are quite similar for all samples, while selectivity depends on the proportion of acid–base sites.

As time-on-stream and temperature increase, selectivity in HFC-125 increases and ultimately the three catalysts exhibit similar selectivities in HFC-125, i.e., about 90% (Fig. 3). This suggests that during reaction, and probably at higher temperature, surface recarburization occurs and sample surfaces reach similar compositions. Such observations are in good agreement with earlier work showing that

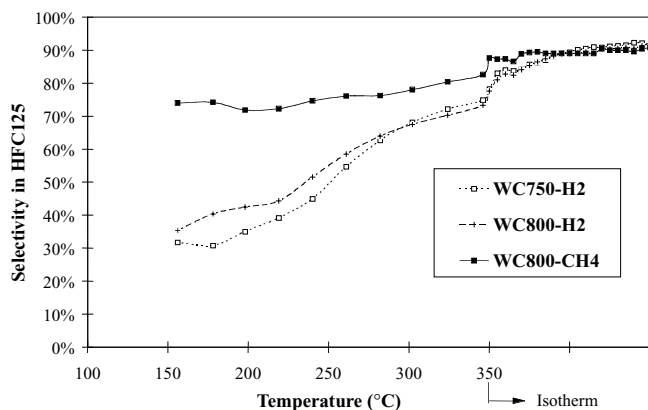


FIG. 3. Temperature-programmed and steady-state selectivity curves in the hydrodechlorination of CF₃CF₂Cl (CFC-115) over WC750-H₂, WC800-H₂, and WC800-CH₄.

TABLE 3
Conversion and Product Distribution (%) in the Hydrogenolysis of $\text{CF}_3\text{CF}_2\text{Cl}$

	WC750-H ₂			WC800-H ₂			WC800-CH ₄		
	200°C	240°C	350°C	200°C	240°C	350°C	200°C	240°C	350°C
Conversion	0.15	0.6	7.2	0.12	0.5	7.5	0.15	0.5	8
$\text{CF}_3\text{CF}_2\text{H}$ (HFC-125)	39	45	72	44	52	73	72	75	88
Alkanes (CH_4 , C_2H_6 , C_3H_8)	43	32	15	43	31	15	27	17	5
Unsaturated (C_2H_4 , CF_2CH_2 , C_2F_4)	17	22	13	12	16	11	1	8	6
Others (CF_3CFH_2 , CF_3CH_3)	<1	<1	1	<1	<1	1	<1	<1	1

during the exposure of metallic tungsten or molybdenum to a hydrocarbon/hydrogen mixture, partial carburization occurs (20, 21). Formation of a Pd–C solid solution has also been confirmed during the hydrogenolysis of chlorofluorocarbons on Pd-based catalyst (22, 23), suggesting that under our experimental reaction conditions recarburization is likely to occur on partially decarburized WC samples.

The results obtained in the conversion of isopropanol performed at 150°C ($P_{\text{isopropanol}} = 0.2$ atm, helium is the carrier gas) are reported in Fig. 4 and Table 4, where it can be seen that the product distribution is strongly dependent on the activation procedure. The proportion of acetone decreases while that of the dehydration products increases on the carbides in the following sequence: WC800-CH₄, WC800-H₂, WC750-H₂, that is, when the surface C/W ratio decreases. This shows very clearly that the acid–base character increases with surface carbon deficiency.

Acid–base properties could be a direct result of substoichiometry, the surface carbon vacancies being pair electron acceptors (i.e., Lewis acid sites) or W^{x+} carbide species

(here again potential Lewis acid sites) being predominantly exposed at the surface. Alternatively, the carbon-deficient carbides more sensitive to oxygen adsorption could lead to the formation of oxycarbide species, due to the presence of traces of O_2 in the reagents, which also exhibit acidic properties (24–26). This hypothesis is supported by the study of Kwon *et al.* (27), who observed stronger adsorption of oxygen on a carbon-deficient vanadium carbide than on a stoichiometric one. They concluded that imperfect carburization of the surface might enhance its affinity toward oxygen adsorption. This is emphasized by various studies reporting that changes in the surface compositions of transition metal carbides and nitrides might affect both activity and selectivity (28–31). For instance, Choi (31) suggested that geometrical defects such as kinks, dislocations, and vacancies in deficient carbon tantalum carbides might affect their activity in the decomposition of ammonia. However, this author did not rule out the contribution of surface electronic modifications to the catalytic properties of these materials. Recently, Choi *et al.* (32) studied the influence of the degree of carburization of molybdenum carbides on their density of sites and hydrogenation activity. They found that an increase in the activity per site in the hydrogenation of benzene occurs when the degree of carburization, which is related to the ability of the catalyst to selectively chemisorb CO, increases. They concluded that the higher the carbidic carbon content and the lower the residual oxygen content in the Mo lattice, the higher “the noble metal-like” behavior. The trends observed in our experiments agree well with this hypothesis.

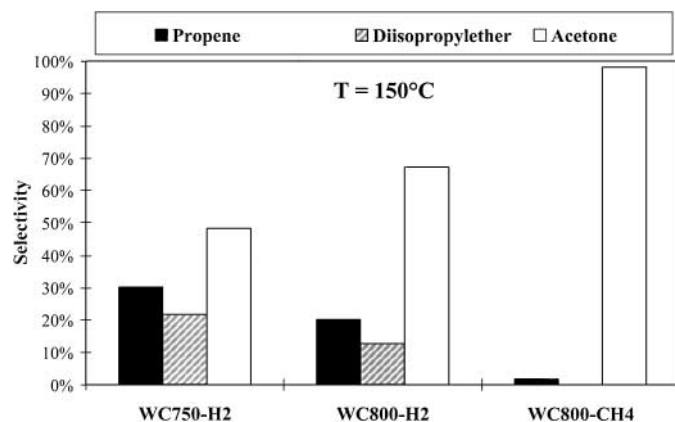


FIG. 4. Product distribution at steady state in the decomposition of isopropanol over WC750-H₂, WC800-H₂, and WC800-CH₄ at 150°C. The loading of catalyst was 500 mg; the flow of isopropanol was diluted in helium (40 cm³/min) corresponding to a partial pressure of isopropanol of 0.2 atm.

TABLE 4
Selectivity Ratio for the Decomposition of Isopropanol

Catalyst	Sel. dehydration products/Sel. acetone (S_D/S_A)		
	150°C	165°C	180°C
WC750-H ₂	1.1	2.8	4.9
WC800-H ₂	0.5	1.2	1.9
WC800-CH ₄	0.02	0.03	0.08

In conclusion, it seems obvious that modifying the activation of tungsten carbide by changing the surface carbide stoichiometry converts the catalytic properties of WC into either metallic or acid–base ones and subsequently its selectivity toward the formation of pentafluoroethane or alkanes and unsaturated by-products. More generally, this work provides evidence of a relationship between the mode of activation and the catalytic properties of tungsten carbides; the acid–base character seems to increase with the extent of decarburization of the surface. It is obvious that the surface properties of WC could be adjusted toward the formation of unsaturated compounds or alternatively toward hydrogenolysis compounds, according to the practical application considered. Such flexibility in the preparation procedure could be of practical interest. However, the convergence observed in the temperature-programmed selectivity curves, whatever the initial C/W ratio, probably shows that the sample surfaces reach similar compositions by recarburization during reaction.

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