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Control of the Catalytic Activity of Tungsten Carbides

III. Activity for Ethylene Hydrogenation and Cyclohexane Dehydrogenation

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The catalytic activity of tungsten carbide samples for ethylene hydrogenation and cyclohexane dehydrogenation is described and discussed in the light of their physicochemical characteristics (phase composition, presence of free carbon or superficial oxygen) and correlated with the parameters of their preparation. A lack of activity presented by samples prepared in pure CO can be ascribed to their surface being extensively covered by pregraphitic carbon. The activity of samples prepared in CO–CO_2 mixtures has been found to depend on their conversion to WC, and to increase markedly after being heated at 300°C in H_2; this treatment was necessary to eliminate the oxygen fixed on the samples as a result of a previous passivation treatment. A kinetic model based on a previously proposed mechanism on the W_2C-WC transformation has enabled the variation of the catalytic activity versus the conversion to WC to be simulated. According to the model, the active sites of the carbide catalysts can be poisoned by the atomic carbon deposited on their surface as a result of the dismutation of CO. At this stage, the samples can still be reactivated on being heated in H_2 at 500°C. Higher levels of contamination of free carbon can result in the progressive and irreversible formation of a pregraphitic layer which will prevent the gaseous reactants from being adsorbed on the surface of the carbide samples, thereby depressing their catalytic activity. © 1986 Academic Press, Inc.

INTRODUCTION

In Part I (1) it was shown that the preparation of highly dispersed tungsten carbides free of excess carbon was possible by reducing appropriate precursors in hydrogen and carburizing the resulting metallic tungsten samples in CO–CO_2 mixtures. In Part II (2), some physicochemical characteristics (pseudometallic surface area, lattice constants, and surface chemical composition) have been tentatively correlated with the phase composition of the samples and with the preparation variables (carburization time and atmosphere, nature of the precursor).

The aim of this final part is to demonstrate and interpret in the light of the previous findings how the preparation parameters of the tungsten carbide samples can influence their catalytic activity. Ethylene hydrogenation will be used as a first test reaction because it has been the object of numerous studies as a prototype of catalyzed hydrogenation on metals, especially on Ni (3). Dehydrogenation of cyclohexane has been chosen as a second test reaction in view of its industrial interest in catalytic reforming (4). The results will be tentatively correlated with the phase composition of the samples in the system W-W_2C-WC. A theoretical model of the transformation of W_2C to WC will be proposed, which allows us to simulate how the catalytic activity of carbide samples will vary as a function of their conversion to WC. Finally, the discrepancies observed between some experimental results and the theoretical predictions will be discussed in the light of the previous knowledge concerning the prepa-

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ration and the surface characteristics of the samples.

EXPERIMENTAL

Preparation and Characterization of the Samples

The tungsten carbide samples have been prepared as described in Part I of this series (*1*). The preparation conditions, phase compositions, specific surface areas, and pseudometallic surface areas (as defined in Part II) (*2*) of the samples selected for the present study are summarized in Table 1.

Catalytic Testing

Hydrogenation of ethylene. The exothermic character of ethylene hydrogenation made it necessary to dilute the catalysts with an inert material, in order to prevent temperature runaway. Thus, 0.15 g of tungsten carbide was mixed with 0.75 g of SiO_2 (S_{BET} = 3 m^2/g), previously calcined overnight in air at 1000°C. The diluted samples were homogenized by shaking them gently in a flask, until a uniform gray color was observed. The mixture was placed in a flow-through, fixed bed reactor (i.d. = 10 mm) around which a heating tape was wrapped. The control thermocouple was held against the wall of the reactor by the heating tape, its tip being placed halfway up the catalyst bed. The measuring thermocouple was placed in a thermowell which entered the center of the bed.

Before starting catalytic runs, the reactor was purged with N_2 at room temperature. The sample was then activated by flowing H_2 for 3 h at 300°C (temperature rise at 10°C/min) according to the procedure described previously (*2*). At the end of the activation treatment, the sample was cooled to room temperature. The reaction mixture (10% C_2H_4 in H_2) was then admitted to the reactor. The catalytic reaction was monitored by injecting 1-ml pulses of the effluent gas into a gas chromatograph (Intersmat IGC 10C, column Porapak Q 80/100, 2 m × $\frac{1}{8}$ in.).

Dehydrogenation of cyclohexane. The catalyst (0.2 g) was placed on a sintered glass disk in a dynamic reactor with continuous flow (the experimental device is outlined in Fig. 1). Before each run, oxygen was eliminated from the reactor by purging with N_2 at room temperature. Next, a flow

TABLE 1

Carburization Conditions and Characteristics of Tungsten Carbide Catalysts

Sample[a]	Carburizing conditions		Composition[b] WC/(W2C + WC)	S_{BET} (m^2/g)	Pseudometallic surface area (m^2/g)
	Gas CO_2/CO	Time (h)			
Wh-WC-CO	0.0	24	1.0	47	0
Wh-W_2C-wc[c]	0.5	24	0.0	33	30
Wh-W_2C-ic[c]	0.5	0.0	36	33	
Wh-WC-14	0.1	1	0.14	32	31
Wh-WC-24	0.1	3	0.24	34	—
Wh-WC-37	0.1	4.5	0.37	34	—
Wh-WC-55	0.1	6	0.55	30	21
Wh-WC-72	0.1	10	0.72	29	12.8
Wh-WC-76	0.1	10.5	0.76	31	12.5
Wh-WC-100	0.1	13	1.00	28	18

[a] The samples were first reduced in hydrogen (15 liters/h) at 500°C for 5 h.

[b] As deduced from X-ray diffraction data (for details, see Ref. (*1*)).

[c] wc, Well-crystallized, ic, ill-crystallized.

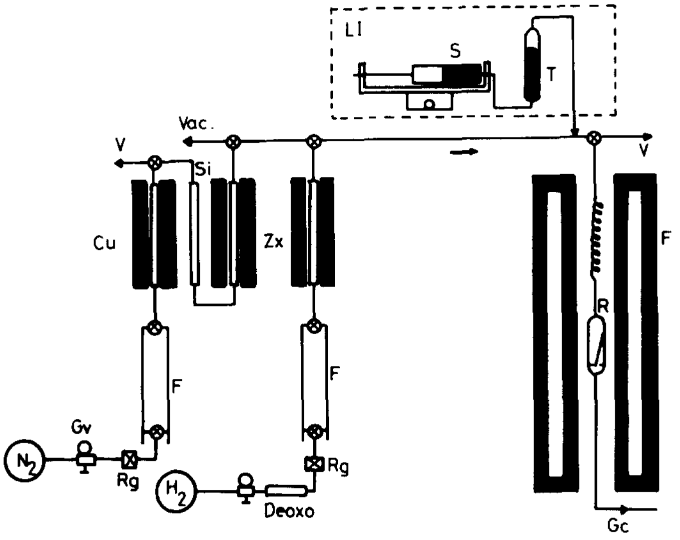

FIG. 1. Experimental setup for the study of cyclohexane dehydrogenation. Gv, gas valve; Rg, flow regulator; F, soap bubble flow meter; Cu, copper catalyst held at 400°C; Zx, molecular sieve 13X; Si, silica gel: R, reactor; Gc, chromatograph; Fu, furnace; V, vent; Vac, vacuum; S, syringe; T, mercury reservoir; LI: device for the injection of liquid hydrocarbon.

of hydrogen was begun and the temperature was raised to the value selected for the activation treatment (300 or 500°C). The temperature selected for the catalytic test was then established, with hydrogen still flowing in the reactor. The reaction was started by injecting cyclohexane ($v = 1.85 \times 10^{-2}$ mol/h, $P_C = 0.1$ atm, $P_H = 0.9$ atm) and the reaction products were analyzed by gas chromatography (column Reoplex 400, 2 m × $\frac{1}{8}$ in.).

RESULTS

Hydrogenation of Ethylene

Preliminary results. A constant gas flow of 28 liters/h was used throughout the experiments, after having checked that the reaction rates were not controlled by extragranular diffusion when flows beyond 20 liters/h were used.

No detectable conversion occurred in the 20-to-400°C temperature range when the reactor was filled only with silica and quartz wool. In all cases, the selectivity for ethane production was 100%.

When freshly activated catalysts were contacted with the ethylene-hydrogen mixture at 120°C, a high initial activity was observed together with a transient increase in the temperature of the catalyst bed (see Fig. 2, curve A). This phenomenon did not occur (Fig. 2, curve B) if the catalysts were kept overnight at room temperature in flowing hydrogen after the activation treatment. The figure shows that the same stationary activity is in any case reached after 50 min exposure to the reacting mixture. There-

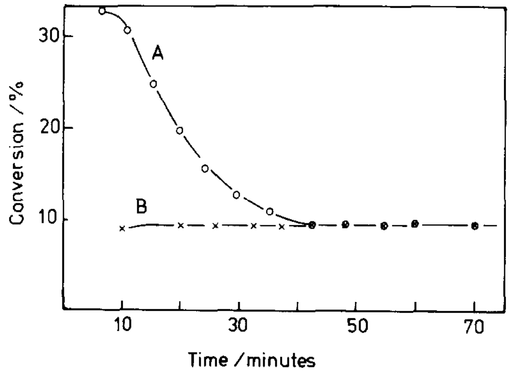

FIG. 2. Initial activity: influence of the pretreatment conditions on the activity of Wh-WC-100 for ethylene hydrogenation ($T = 120$°C). Curve A: freshly activated sample; curve B: activated sample left for 16 h at room temperature.

fore, the activity values reported below were those measured after 90 min stabilization. This transient behavior was exhibited by all the samples tested in this work. Sample Wh-WC-100 reproduced the same behavior, and the same steady-state activity as before was reached, within experimental error, when it was subjected to a second test cycle including the following steps: purging the reactor with Ar at the end of the first test cycle, passivating the sample *in situ*, under the same conditions as before and storing in air for a few days.

The Arrhenius plots corresponding to passivated and activated sample Wh-WC-100 are presented in Fig. 3. The corresponding activation energies, as deduced from the plots, were 20 and 13 kcal/mol, respectively.

Definitive results. All the metallic samples, together with the carbide samples prepared in pure CO, showed no measurable activity, despite the activation treatment in H_2 at 300°C. Table 2 shows that increasing conversions to WC of samples prepared in CO–CO_2 mixtures resulted in a significant increase of the activation energy for ethylene hydrogenation. Figure 4A shows that the activity of the samples prepared in CO–CO_2 mixture depends strongly on their composition. Comparison with the activities corresponding to the semicarbides (samples Wh-W_2-C-ic and Wh-W_2C-wc)

TABLE 2

Activation Energies Observed for Some Intermediate Tungsten Carbides

Sample[a]	Activation energies (kcal/mol)	
	Hydrogenation	Dehydrogenation
Wh-W_2C-wc	10	34
Wh-W_2C-ic	10	—
Wh-WC-14	11	26
Wh-WC-55	12	27
Wh-WC-100	13	29

[a] The samples were activated in hydrogen (15 liters/h) at 300°C for 3 h before the hydrogenation test, and at 500°C for 12 h before the dehydrogenation test.

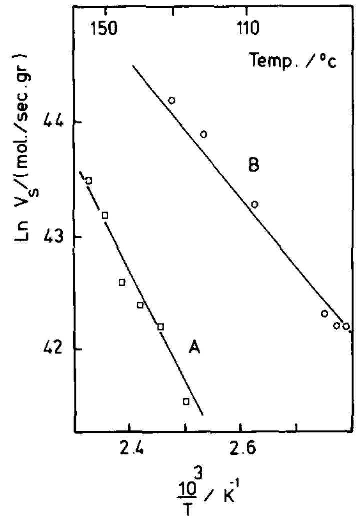

FIG. 3. Arrhenius plot for ethylene hydrogenation on sample Wh-WC-100. Curve A, passivated and curve B, activated catalyst.

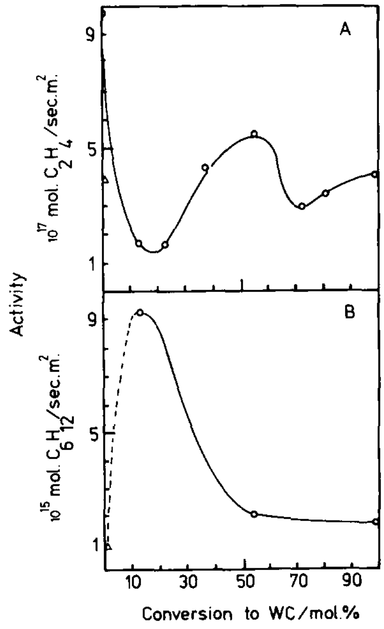

FIG. 4. Influence of the conversion to WC of carbides prepared in CO–CO_2 mixtures, on their catalytic activity for ethylene hydrogenation (A) and cyclohexane dehydrogenation (B). Open circles: samples Wh-W_2C-ic and Wh-WC-x; open triangle: sample Wh-W_2C-wc.

stresses that not only the phase composition but also the exact conditions of preparation (see Table 1) will affect strongly the final activity of the samples.

Dehydrogenation of Cyclohexane

Preliminary results. Table 3 shows that sample Wh-WC-100 exhibits only a low dehydrogenation activity after an activation treatment in H_2 at 300°C. A tenfold activity increase is observed when the activation temperature is raised to 500°C. The selectivity of the reaction, expressed as moles of benzene produced per mole of cyclohexane converted, was better than 0.92 for all the samples tested.

Definitive results. Sample Wh-WC-CO exhibited no measurable activity for cyclohexane dehydrogenation, whatever the activation temperature used. Table 2 shows that the activation energy of the reaction is significantly higher for sample Wh-W_2C-wc, as compared with the samples converted wholly or partially to WC. The influence of the phase composition of the samples prepared in CO–CO_2 mixtures on their dehydrogenation activity is presented in Fig. 4B. The least active hydrogenation catalyst appears to be the most active for cyclohexane dehydrogenation (compare the points corresponding to 14% conversion to WC on curves A and B).

TABLE 3

Influence of the Activation Conditions on the Activity of Sample Wh-WC-100 for Cyclohexane Dehydrogenation

Conditions		Reaction rate[a] (mol/h/g)
Temp. (°C)	Time (h)	
300	12	3.60×10^{-4}
500	12	3.75×10^{-3}
500	16	3.65×10^{-3}

[a] Conditions of reaction: $p_H/p_C = 42.5$, $T = 350°C$.

DISCUSSION

Effects of the Passivation and Activation Treatments

The authors realize that the results presented above are not exhaustive and that a more systematic study of the activation conditions of tungsten carbide catalysts would be desirable for elucidating more deeply the mechanisms of their catalytic activity. For instance, it would be interesting to measure the production of ethane by freshly activated samples brought into contact with pure ethylene, and to test the effect of activation treatments in hydrogen above 300°C. The authors hope that such complementary experiments, which were not possible to perform by the time of completion of this work, will be attempted in the future. Nevertheless, tentative interpretations of the data presently available will be proposed, in the hope of stimulating future work in the field of tungsten carbide catalysts.

The Arrhenius plots presented in Fig. 3 show that the activation treatment in hydrogen of the samples results in a marked increase of their activity. According to previous XPS results (*2*), this treatment eliminates the oxygen which had been fixed on the surface of the carbides during the passivation step and the storage of the samples in air. The lower activity of the passivated samples can thus be ascribed to the existence of a superficial oxide layer, in agreement with the previous observation of Kojima *et al.* (*5*) who found that a thermal treatment at 1100°C *in vacuo*, resulting in the desorption of oxygen, was effective in activating WC catalysts.

The higher initial activity for ethylene hydrogenation, together with the pyrophoric character of the freshly activated samples, suggest that their surface would be saturated with active hydrogen species which could react with ethylene or oxygen, as the case may be. As a result of the exothermicity of ethylene hydrogenation ($\Delta H° = -32.7$ kcal/mol), the temperature of the cat-

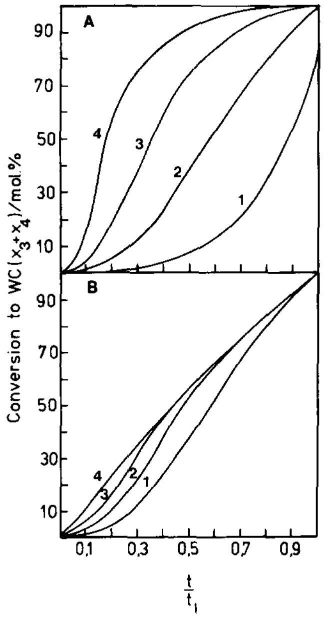

FIG. 5. Theoretical changes in the conversion to WC and WC* ($x_3 + x_4$), versus the reduced reaction time (carburization in CO–CO_2 mixtures).

Curve	k_1 (h^{-1})	k_2 (h^{-1})	k_3 (h^{-1})
	Graph A		
1	0.030	0.030	0.075
2	0.075	0.075	0.075
3	0.150	0.150	0.075
4	0.300	0.300	0.075
	Graph B		
1	0.075	0.075	0.075
2	0.150	0.075	0.075
3	0.300	0.075	0.075
4	0.600	0.075	0.075

alyst will rise, thus increasing further the reaction rate and causing the observed initial surging in activity and temperature runaway. After complete consumption of the excess adsorbed hydrogen, the reaction will reach a lower stationary rate. This explanation involves the hypothesis that the controlling step of the stationary rate is hydrogen adsorption, in agreement with the mechanism proposed by Horiuti and Miyahara (*3*) when the orders of the reaction are zero and one, respectively, with respect to ethylene and hydrogen.

No clear explanation of the effect of the activation temperature on the catalytic activity of tungsten carbides for cyclohexane hydrogenation is possible on the basis of the present data. Nevertheless, the fact that higher activation temperatures are needed to activate the samples in that case suggests that the active sites for dehydrogenation are distinct from the hydrogenation sites, and more strongly poisoned than the latter. Once can also speculate that the last traces of poisoning substance (either carbon or oxygen) would be eliminated by an activation treatment at higher temperatures.

Influence of Preparation Factors of the Activity of Tungsten Carbides

General considerations. Previous results (*1*) have shown that, during the preparation of tungsten carbides in CO–CO_2 atmospheres, the formation of a free carbon layer on the surface of the samples takes place along with the transformation of W_2C to WC. This carbon layer has been found to alter the pseudometallic surface area of the carbides, i.e., the fraction of their surface actually exposed to gaseous molecules (*2*). The following discussion will try to elucidate the respective contributions of the WC/W_2C ratio of the samples and the amount and state of free carbon deposited on their surface, to the variation of their catalytic activity.

To understand better the relationship between the catalytic activity of tungsten carbides and their carburization treatment, we first develop a kinetic model of the reactions which occur during the transformation of W_2C to WC. The model presented below will take into account the existence of carbide species poisoned with excess carbon, in agreement with the results of Parts I and II of this series (*1, 2*). In a second step, an attempt will be made to simulate the main features of the experimental curve of Fig. 4A, by ascribing appropriate values to the catalytic activities of the separate carbide species involved in the model. Finally, the validity of the model will be evaluated by comparing the observed catalytic activities with the theoretical predictions.

Kinetic model of the carburization reaction. According to the reaction pattern presented in Part I of this study (*1*), and taking into account the existence of carbide species contaminated with excess carbon, the following scheme can be proposed for the transformation of W_2C to WC:

$$W_2C^\circ \xrightarrow{k_1} W_2C^* \qquad (1)$$

$$W_2C^* \xrightarrow{k_2} WC^\circ \qquad (2)$$

$$WC^\circ \xrightarrow{k_3} WC^* \qquad (3)$$

where k_i is the rate constant of the *i*th reaction. The solid reactant is assumed to consist of particles of uniform shape and size. W_2C^* and WC^* stand for carbide species covered with excess carbon, in contrast with W_2C° and WC°. Note that X-ray diffraction cannot distinguish between the contaminated and uncontaminated species; however, they must be distinguished one from another in order to account for the catalytic activities of carbide mixtures, since the contaminated species are presumably less active as a result of their coverage with free carbon.

According to Part I (*1*), the rate of free carbon formation resulting from the dismutation of CO depends only on the reaction conditions (temperature and partial pressures of CO and CO_2). Consequently, Reactions (1) and (3) can reasonably be assumed to be zero order with respect to the concentrations of W_2C° and WC°, respectively. The change of the C/W ratio of carbide samples, as deduced from XPS results (2), together with the reaction pattern proposed in Part I (*1*) support the hypothesis that W_2C^* particles would convert to WC° by consuming primarily the excess carbon deposited on them. Considering the very small size of the carbide particles (*1*), the rate-controlling step for Reaction (2) is likely to be the nucleation of WC° in the W_2C particles. Assuming this to a first approximation to be a uniform nucleation process (i.e., the probability for a nucleus to appear within a given time is the same for each particle in the sample), it can be demonstrated (*6*) that the pseudoorder of Reaction (2) will be unity with respect to the concentration of W_2C^*. Summarizing, the respective molar fractions of W_2C°, W_2C^*, WC°, and WC^*, x_1, x_2, x_3, and x_4 are related to the time t of Reaction (2) by the following set of differential equations:

$$\frac{d}{dt}\left(\frac{x_2}{x_1 + x_2}\right) = k_1 \qquad (4)$$

$$\frac{d}{dt}\left(\frac{x_3}{x_2 + x_3}\right) = k_2\left(\frac{x_2}{x_2 + x_3}\right) \qquad (5)$$

$$\frac{d}{dt}\left(\frac{x_4}{x_3 + x_4}\right) = k_3 \qquad (6)$$

$$x_1 + x_2 + x_3 + x_4 = 1 \qquad (7)$$

It is easy to solve this system of equations and hence to calculate the variations with time of the molar fractions, for known values of the rate constants k_i. Typical results are presented in Fig. 5, where theoretical values of $(x_3 + x_4)$, corresponding to the total conversion to WC, are plotted versus the reduced time t/t_1 for different values of the k_i's (t_1 corresponds to the time necessary to reach $x_3 + x_4 = 1$). A trial and error procedure can be used to select the k_i values corresponding to a theoretical variation of $(x_3 + x_4)$ vs time fitting at best the kinetic data of the W_2C-WC transformation, extracted from Table 1. Figure 6A shows the very good fit obtained using appropriate values of the rate constants (see the legend of Fig. 6). Figure 6B presents the separate changes with time of the various carbide species corresponding to this set of rate constants. It has been confirmed that other combinations of the constants could not produce the theoretical curve of Fig. 7A.

Catalysts prepared in CO–CO_2 mixtures: (i) Hydrogenation of ethylene. In order to see whether the proposed model can predict the relationship between the catalytic activity and the composition of the carbide

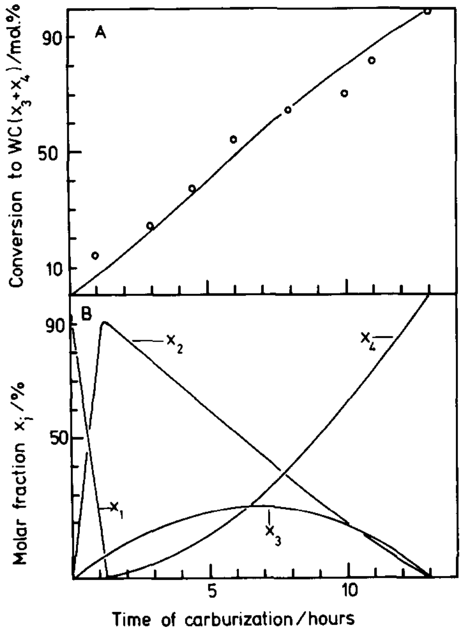

FIG. 6. Graph A: theoretical changes in the conversion to WC and WC* (x_3 + x_4), versus the reaction time (h) corresponding to k_1 = 0.8, k_2 = 0.065, and k_3 = 0.075 (h^{-1}). Open circles correspond to the experimental data taken from Table 1. Graph B: theoretical changes in the carbide species versus carburization time, under the same conditions as above. x_1: $W_2C°$, x_2: W_2C*, x_3: WC°, and x_4: WC*.

samples illustrated in Fig. 4A, specific activities must be ascribed to the carbide species considered in the model. Considering that W_2C* and WC* are, by definition, covered by free carbon and that the carbide samples prepared in pure CO (and therefore extensively covered by free carbon) proved to be totally inactive, the specific activities of these species can be reasonably assumed to be zero. The activity experimentally observed for the sample Wh-W_2C-ic (10^{18} mol ethylene/s/m^2) will be ascribed to $W_2C°$. Finally, a value for the specific activity of WC° has been chosen by trial and error so as to achieve the best fit between the theoretical curve and the experimental data. The choice of two distinct intrinsic activities for $W_2C°$ and WC° is supported by the fact that two significantly different values of the activation energies were observed for samples Wh-W_2C-ic and Wh-WC-14 on the one hand (10 kcal/mol) and for samples Wh-WC-55 and Wh-WC-100 on the other (12–13 kcal/mol, see Table 2). Figure 7 shows the fit obtained when a value of 2 × 10^{18} mol/s/m^2 is assumed for the specific activity of WC°.

The agreement between the experimental data and the theory is very good in view of the approximation involved in the model. Only the activity of sample Wh-WC-100 departs markedly from the predicted value. According to the model, this sample should be completely inactive, since it is supposed to be extensively covered with free carbon. However, this hypothesis is questionable for carbide samples submitted to very long carburization times, as shown by the pseudometallic surface area determinations presented previously (*2*) and summarized in the last column of Table 1. The fact that the pseudometallic surface area of carbide samples went through a minimum at 80% conversion to WC was tentatively ascribed to a larger fraction of the carbide surface being exposed to the gas phase, probably as a consequence of the sintering of the free carbon layer to discrete carbon aggregates.

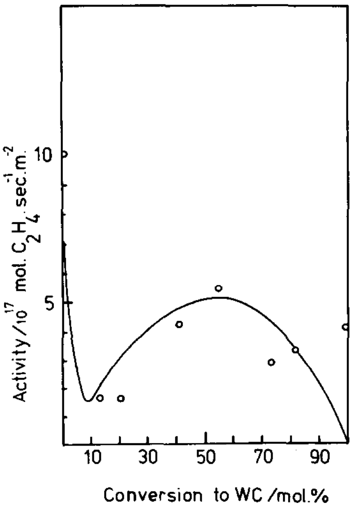

FIG. 7. Theoretical variation and experimental data (open circles) of the activity of samples Wh-WC-*x* for ethylene hydrogenation. The specific activities of the different carbide species were (in μmol/m^2/s) 17 for $W_2C°$, 34 for WC°, and 0 for W_2C* and WC*.

This interpretation is supported by the change in the catalytic activity of the samples containing more than 80% WC. The fact that the minimum catalytic activity observed at about 20% WC does not correspond to a minimum of pseudometallic surface area (see Table 1, samples Wh-WC-14 and Wh-WC-23) would, at first sight, cast a doubt on a possible correlation between the pseudometallic surface area, as deduced from H_2–O_2 titration data, and the active surface revealed by catalytic testing. This apparent discrepancy indicates that the free carbon species involved in the transformation of W_2C° to W_2C^* differs from that making WC* inactive. As the former does not prevent oxygen from adsorbing on the carbide surface during the titration experiment, we can imagine it to consist of atomic carbon which would poison the active hydrogenation sites. This picture agrees well with the reaction mechanism suggested in Part I (*1*), according to which W_2C would convert to WC by reacting with atomic carbon produced by the dismutation of CO.

(ii) Dehydrogenation of cyclohexane. The maximum activity observed at 14% conversion to WC for cyclohexane dehydrogenation (Fig. 4B), corresponding to a minimum in hydrogenation activity (compare with Fig. 4A) suggests various interpretations. A presumably higher affinity of WC for unsaturated bonds would result in a stronger adsorption of ethylene and benzene on the WC surface, and hence to a faster formation of saturated hydrocarbons. However, no experimental or literature data are available to support this interpretation. Furthermore, it does not take into account the differences of contamination by free carbon between carbide samples corresponding to different degrees of carburization. Thus, we could assume that dehydrogenation would take place on specific sites not poisoned by free atomic carbon; however, this latter interpretation is not substantiated by other experimental evidence. Literature data (*7*) have shown that free atomic carbon could be removed from metallic surfaces by exposing them to hydrogen at temperatures above 400–500°C, while pregraphitic carbon was completely inert in hydrogen below 600°C. Assuming that carbides would behave in the same way, free carbon would have been completely eliminated from the catalysts tested for cyclohexane dehydrogenation, as a result of their activation in hydrogen at 500°C, in contrast with those tested for ethylene hydrogenation which were activated at 300°C only. Consequently, the change in the catalytic activity illustrated in Fig. 4B would reflect mainly the change in the pseudometallic surface area of the samples, i.e., the fraction of their surface free of pregraphitic carbon.

Catalysts prepared in pure CO. The lack of activity of the samples prepared in pure CO, whatever the test reaction considered, is clearly correlated to their very low pseudometallic surface area (see Table 1). According to the XPS data presented in Part II (*2*), the surface of these samples becomes extensively covered with pregraphitic carbon as a result of the Boudouard reaction ($2\ CO \rightarrow C + CO_2$) (*1*). The so formed carbon layer has been found, in Part II of this work (*2*), to prevent any O_2 or H_2 from being adsorbed during the titration experiments, resulting in very low estimates of the pseudometallic surface area of these samples. This carbon layer is also likely to impede the access of all the reactants to the surface of the samples, thereby explaining their lack of activity.

CONCLUSIONS

The present work has enabled us to elucidate the effects of various physicochemical characteristics (e.g., surface and phase composition, presence of surface oxygen or free carbon) on the catalytic activity of tungsten carbides for ethylene hydrogenation and cyclohexane dehydrogenation.

This low hydrogenation activity of passivated tungsten carbides can be ascribed to their surface oxidation as a result of the passivation treatment. The complete removal of the surface oxide brought about by a treatment in H_2 at 300°C results in a marked increase of the catalytic activity of the samples.

The carburizing atmosphere appears to be a crucial factor for the preparation of active tungsten carbide catalysts. Thus, the lack of activity of samples carburized in pure CO is clearly correlated to their very low pseudometallic surface area and can be explained by the coverage of their surface by a carbon layer which prevents it from being contacted with gaseous reactants. Conversely, the catalysts prepared in appropriate $CO-CO_2$ atmospheres exhibit an appreciable activity, which is markedly influenced by their phase composition (W_2C/WC/C). The relationship between the activity and the phase composition of tungsten carbides can be accounted for in the frame of a kinetic model which has been developed in accordance with the most recent knowledge about the W_2C-WC transformation in $CO-CO_2$ atmospheres. The results show that the active sites for ethylene hydrogenation and cyclohexane dehydrogenation were poisoned by free atomic carbon deposited during the first hours of the carburization treatment; the removal of this carbon species upon reaction with hydrogen probably explains the considerable increases in dehydrogenation activity of some carbide samples after their treatment in hydrogen at 500°C. The catalytic activity of the samples carburized for longer times is affected primarily by the formation of a pregraphitic carbon layer. This pregraphitic layer is not removed by the activation treatments used in this work, and results in a lesser fraction of the carbide surface being accessible to gaseous molecules. A good agreement has been found between the catalytic activity of tungsten carbides samples and the extent of their pseudometallic surface, as derived from H_2-O_2 titration.

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