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Resumen-Abstract

An investigation of bulk and cobalt or ruthenium supported tungsten carbide was carried out for their use in the Fischer-Tropsch reaction. Two types of WC were studied : tungsten carbide protected by free carbon and clean tungsten carbide, respectively noticed WC(A) and WC(B). XPS analysis shows that after air exposure, the WC(A) carbide surface is protected from the excess carbon whereas a surface W^{6+} phase is induced during the passivation step for WC(B). However WC(A) is inert towards aqueous impregnation, whereas WC(B) starts to corrode. A reduction in hydrogen at 673 K for Ru and 773K for Co supported catalysts allows obtaining Co^0 and Ru^0 dispersed on layers of free carbon covering the WC core for WC(A) and on a surface free of oxygen for WC(B). All the catalysts were active for the FT reaction. WC(A) produces mainly light alkanes (78%) and alcohols (22%), whereas no alcohol production is observed for WC(B). Co/WC(B) has a better activity than Co/WC(A), due to a better dispersion of cobalt on WC(B). The addition of Ru on WC(A) allow to obtain an high active catalyst with production of heavy hydrocarbons. On the contrary, formation of a Ru-W alloy could be consider to explain the low activity of Ru/WC(B) catalyst.

Introduction

The Fischer-Tropsch synthesis leads to a broad range of products, i.e. hydrocarbons, alcohols, acids ans esters, etc. The increasingly stringent regulations on the sulfur and aromatics content in fuels are reasons for new interest in this reaction [(1)]. Moreover FT reaction is one of the major route for the valorization of large reserves of natural gas.

Conventionnal FT catalysts are prepared via aqueous impregnation of an oxide support as Al_2O_3 or SiO_2 with solutions of metal salts, generally, Co, Fe, Ru, etc. Active species, that is metal atoms, is obtained by catalysts reduction in hydrogen at middle temperature (300-500°C), after calcination in air. The major drawback of silica or alumina catalysts is the formation of aluminate or silicate that can occur during the calcination step. These species are not active for the reaction. Thus use of another support, avoiding the lost of metal available for the FT reaction, is an interesting alternative. Indeed, WC is a remarkable material in the sense that it combines physical and catalytic properties suitable for exothermic FT reaction. It has good mechanical properties, high density and a high thermal conductivity. Moreover tungten and molybdenum carbides have been previously reported as active for FT reaction, producing mainly light alkanes and alcohols [(2-5)].

The aim of the work is to study the performances of 1wt% Co/WC(X) and Ru/WC(X) (X = A or B), where A is a tungsten carbide protected by free carbon and B is a clean tungsten carbide, in order to discriminate physical and catalytic properties. The catalysts have been characterized by elemental analysis, nitrogen adsorption,

XRD, and XPS. Evaluation of catalytic activity has been realized in a fixed bed reactor.

Experimental

Bulk tungsten carbides were prepared by a Temperature Programmed experiment [6].

WO_3 (Fluka, 99.9% purity was first heated at 823K for 10 h in flowing N_2 (10 l.h^{-1}) and reduced and carburized in a mixture of 20% CH_4-H_2 (10 l.h^{-1}) from room temperature to 1073 K (β = 60 K.h^{-1}). The isotherm was maintained for about 8 h. After cooling down to room temperature, the mixture of CH_4-H_2 was replaced by a N_2 flow (10 l.h^{-1}) for one hour. By this procedure a tungsten carbide protected by free carbon on the surface was obtained.

The experimental procedure described above was completed by a cleaning step in order to remove free carbon from the tungsten carbide surface. Carbon removal was analyzed on line by the detection of methane with gas chromatography analysis. After carburization, the sample was submitted to a flow of pure H_2 (8 l.h^{-1}) from ambient temperature to 1073 K (100 K.h^{-1}). The final temperature was kept for one hour. The sample was then submitted to a flow of N_2 (10 l.h^{-1}) for one hour before to be passivated at room temperature in a 2 % O_2-N_2 mixture for 2h (3l.h^{-1}) to protect the catalyst against a deep oxidation.

Hereafter the solids will be denoted WC(A) for tungsten carbide protected by free carbon on the surface and WC(B) for clean tungsten carbide.

The supported catalysts were obtained by wet impregnation of the tungsten carbide with an aqueous solution of $RuCl_3$, $2H_2O$ (Fluka, purum, $\approx$ 38-40% Ru) or $Co(NO_3)_2$, 6 H_2O (Fluka, $\geq$ 98 % purity), to obtain 1wt% Ru or Co. After slow evaporation of the solvent, the solids were dried at 393K overnight.

The chemical analysis of the supported catalysts was determined by atomic absorption for Co, W and Ru and by coulometry for C, by the Central Service of Chemical Analysis of the CNRS (Vernaison, France).

The B.E.T. surface areas were measured by a single point BET method using a QUANTASORB J.R. apparatus.

X-ray diffraction patterns were recorded at room temperature by a SIEMENS D5000 diffractometer using Cu K$_\alpha$ radiation.

The X-ray photoelectron spectra (XPS) were recorded with a VG ESCALAB 220XL spectrometer equipped with a monochromatized Al source (Al K$_\alpha$ = 1486.6 eV). The calibration of the samples in binding energy was based on three photopeaks: Cu 2p$_{3/2}$ (928.7 eV), Ag 3d$_{5/2}$ (368.3 eV) and Au 4f (84 eV). Spectra of all solids were recorded before and after reduction in flowing hydrogen.

The reduction of the catalysts was carried out in a flow of pure hydrogen (2 l.h^{-1}) in the preparation chamber close to the analysis chamber for 5 h at 673 K for Ru and 673 or 773 K for Co based catalysts (β = 3 K.min^{-1}).

The catalytic tests were performed in a stainless steel fixed-bed flow reactor operating at 473 K and total pressure of 20 bar with VSV equal to 6000 h^{-1}. The H_2/CO ratio was 2 in all experiments. N_2 (0.3 l.h^{-1}) was used as internal standard. The catalysts loadings were of about 2.5-2.7 g. Prior to the catalytic test, all the samples were activated in a flow of pure hydrogen (3.6 l.h^{-1}, 12h) at atmospheric pressure from room temperature either to 673K for WC(A), WC(B) and Ru based catalysts, and 773K for Co based catalysts. The temperature of reduction was chosen in order to get Co or Ru at the metallic state. Analysis of the gaseous products were carried out on line with a gas chromatograph (Varian 3400) equipped with TCD and FID detectors with CTR-1 for C1 products and a Tenax column for hydrocarbons (C_1-C_{10}) and alcohols up to C_3, respectively. High-molecular-weight products (C_{10}^+ hydrocarbons) were collected from a hot condenser heated at 393K. The wax analysis was performed on a WCOT ULTI-METAL column (coating HT SIMDIST CB). Catalytic rates and selectivities were measured at the stationary regime after circa 24 h time-on-stream. The conversion X, expressed in percentage, is the ratio of the number of moles of CO converted to the initial number of moles of CO. Product selectivity (S) was reported as the percentage of CO converted into a given product expressed in C atoms, excluding CO_2. $S(C_n)$ and $S(C_{5+})$ were referred respectively to the selectivity in hydrocarbons with n carbon atoms and to the selectivities of all hydrocarbons in the gas phase with a carbon atom number higher than or equal to 5. By the same way, S(COH) is the global selectivity in alcohols. Carbon mass balances were respected within the margin of error of around 20% for all catalysts.

Results and discussion

a) Tungsten carbide

The X-ray diffraction pattern of WC(A) is characteristic of a simple hexagonal structure of WC (Fig.1d). For WC(B) lines of metal W at 2Θ = 40.2° and 58.5° are observed.
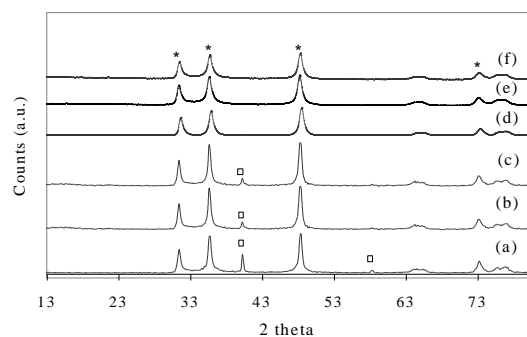
Figure 1. XRD pattern of : (a) WC(B), (b) Co/WC(B), (c) Ru/WC(B), (d) WC(A), (e) Co/WC(A), (f) Ru/WC(A)
∗ : lines of WC, □ : lines of W metal

Chemical analysis results give an atomic C/W ratio of 1.4 in agreement with an excess of carbon deposited on WC(A) (Table 1). The C/W ratio of 0.7 obtained for WC(B) shows that free carbon as also a little fraction of carbidic carbon have been removed from the surface. The surface area of the catalysts was low but not optimized.

Table 1. Characterization of the catalysts

Catalyst	Me (wt%)	C (wt%)	W (wt%)	Atomic ratio C/W	S_{BET} ($m^2.g^{-1}$)
WC(A)	-	8.36	91.63	1.4	6
Ru/WC(A)	1.06	7.90	90.82	1.3	6
Co/WC(A)	0.82	7.68	88.89	1.3	6
WC(B)	-	3.89	88.56	0.7	5
Ru/WC(B)	1.04	3.29	87.87	0.6	4
Co/WC(B)	0.77	3.1	86.98	0.6	4

Surface characterization has been performed by XPS. The W 4f signal shows a doublet at binding energy of 31.7 eV (W $4f_{7/2}$) and 33.7 eV (W $4f_{5/2}$) characteristic of tungsten carbide (Fig. 2) [7-8]. The components at around 35 and 37 eV indicate the presence of W^{6+} surface oxide species.
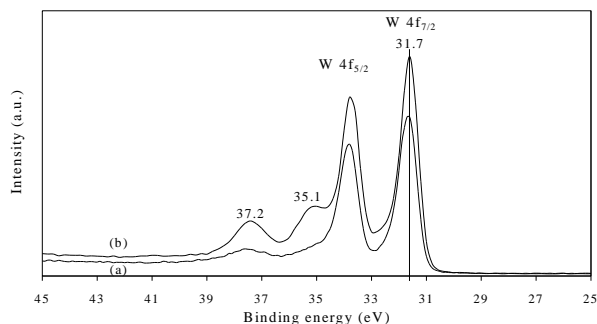
Figure 2. W 4f XPS spectra of (a) WC(A), (b) WC(B)

The atomic ratio W_{ox}/W_T is higher for WC(B) (0.26) compared with WC(A) (0.1) (Table 2). Indeed after air exposure, WC(A) surface is protected by excess of carbon, whereas a W^{6+} phase appears during the passivation step for WC(B). The metal tungsten phase can not be evidenced because of the small binding energy difference between tungsten carbide and tungsten metal (~ 0.5 eV).

For the two samples, the C1s spectra (not represented here) show two peaks at 282.8 eV and 284.5 eV respectively attributed at carbidic carbon and free carbon. A component at about 288 eV is relative to oxidized carbon. The ratio C/W determined by XPS is higher than the one determined by chemical analysis showing that most of carbon is located at the surface of the carbide.

Table 2. Surface composition of catalysts before and after reduction in H_2 from XPS experiments.

Catalyst	$M_xWC_yO_z$	Atomic ratios		
		W_{ox}/W_T	C_f/C_T	C_{ox}/C_T
WC(A)	$WC_{4.6}O_{0.9}$	0.10	0.64	0.14
WC(B)	$WC_{1.6}O_{0.8}$	0.26	0.44	0.05
Ru/WC(A)	$Ru_{0.13}WC_{4.8}O_{1.0}$	0.13	0.60	0.13
Ru/WC(A) (1)	$Ru_{0.12}WC_{3.6}O_{0.4}$	0.23	0.74	~ 0
Ru/WC(B)	$Ru_{0.49}WC_{5.7}O_{3.1}$	0.54	0.40	0.29
Ru/WC(B) (1)	$Ru_{0.27}WC_{0.6}O_{0.7}$	0.14	0	~ 0
Co/WC(A)	$Co_{0.15}WC_{4.1}O_{0.8}$	0.10	0.67	0.13
Co/WC(A) (1)	$Co_{0.10}WC_{4.2}O_{0.5}$	0.09	0.76	~ 0
Co/WC(A) (2)	$Co_{0.05}WC_{3.4}O_{0.3}$	0.15	0.77	~ 0
Co/WC(B)	$Co_{0.61}WC_{3.4}O_{3..2}$	0.54	0.62	0.23
Co/WC(B) (1)	$Co_{0.32}WC_{0.6}O_{0.9}$	0.23	0.28	~ 0

M = Co or Ru, W_T = total tungsten content, W_{ox} = tungsten oxide, C_T = total carbon content, C_f = free carbon, C_{ox} = carbon oxide, (1) : reduced at 673 K, (2) reduced at 773 K

To resume, after synthesis, the two tungsten carbides differ from their surface state. Then the samples surface are respectively composed of polymeric carbons layers for WC(A) and of oxygen species and W metal with tungsten carbide for WC(B).

After reduction in hydrogen 12h at 673 K, whereas WC(A) surface remains covered with free carbon layers, the surface of WC(B) is cleaned from carbonaceous impurities and oxygen of passivation. The two samples are active for FT reaction at 20 bar and 473 K but conversion remains relatively low (Table 3). The activity of WC(A) could be explained by diffusion of CO and H_2 inside carbons layers through cracks. Catalysts give mainly light alkanes. For WC(A), formation of alcohol is observed by opposition with WC(B). In WC(B) the presence of W metal can be responsible of alcohols

hydrogenolyse as it is well-known that W metal dissociates CO.

**Table 3.** Catalytic behavior of parent tungsten carbide (T = 473 K, P = 20 bar, VSV = 6000 h^{-1})

Catalyst	X (%)	Rate (10^{-3} mol.h^{-1}.g^{-1})	Selectivity (%)			
			C_1	C_2-C_4	C_{5+}	COH
WC(A)	~ 1	~ 0.3	26.2	36.8	15.3	21.7
WC(B)	~ 1	~ 0.3	40.1	37.9	22.0	0

b) Supported catalysts

The X-ray diffraction pattern of Co and Ru supported catalysts are rather similar with that of parent tungsten carbide (Fig. 1). The proportion of metallic tungsten previously observed for WC(B) decreases due to its reoxydation during aqueous impregnation. Co and Ru weight percents were closed to 1wt% as expected and the specific surface area are in accordance with the parent samples ones (Table 1).

Impregnation of WC(A) with Co or Ru solutions do not modify the surface of the carbide parent (Table 2). The carbide surface is protected by carbon layers. By opposition, impregnation of WC(B) with aqueous solutions of Co or Ru leads to an increase of the oxide W^{6+} phase, as shown by the raise of W_{ox}/W_T XPS atomic ratio (Table 2). This result shows that tungsten carbide starts to corrode by aqueous impregnation.

The reduction temperature before catalytic test has been chosen at 673 K for Ru and 773 K for Co supported catalysts to ensure obtaining a totale reduction of metal species. XPS experiments confirm these results. Indeed on the Co2p XPS spectra of the two samples (Fig. 3) a well doublet Co $2p_{1/2}$-Co $2p_{3/2}$ is observed at binding energy of 793.2-778.4 eV, which is characteristic of Co^0 [9].
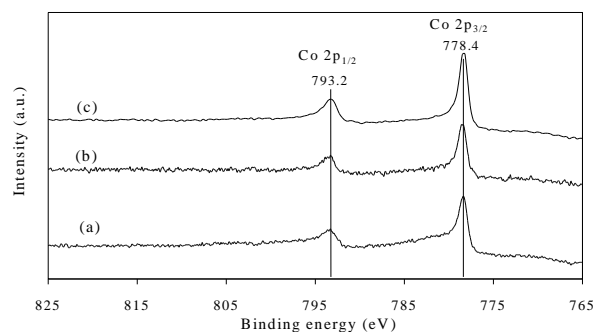
Figure 3. Co 2p XPS spectra of : Co/WC(A) after reduction in H_2 (a) at 673 K, (b) at 773 K and (c) Co/WC(B) after reduction in H_2 at 673 K.

A small oxide component is present at 780.9 eV for a reduction at 673 K. This component disappears at 773 K. The Ru $3d_{5/2}$ peak, initially observed at 281.9 eV characteristic of Ru^{3+} for ruthenium supported catalysts, shifts at lower binding energy of 280.2 eV characteristic with Ru^0 [10]. So at temperatures chosen for H_2 pretreatment before catalytic test, Ru and Co are totally reduced in Ru^0 and Co^0.

For WC(A) supported catalysts, H_2 reduction does not change the surface of the tungsten carbide as shown by XPS analysis (Table 2), but just allows metal reduction. On the contrary, for Co and Ru supported WC(B), modification of the carbide surface takes place. Indeed, XPS results (Table 2) are in agreement with a removal of oxygen of passivation layer from the carbide surface.
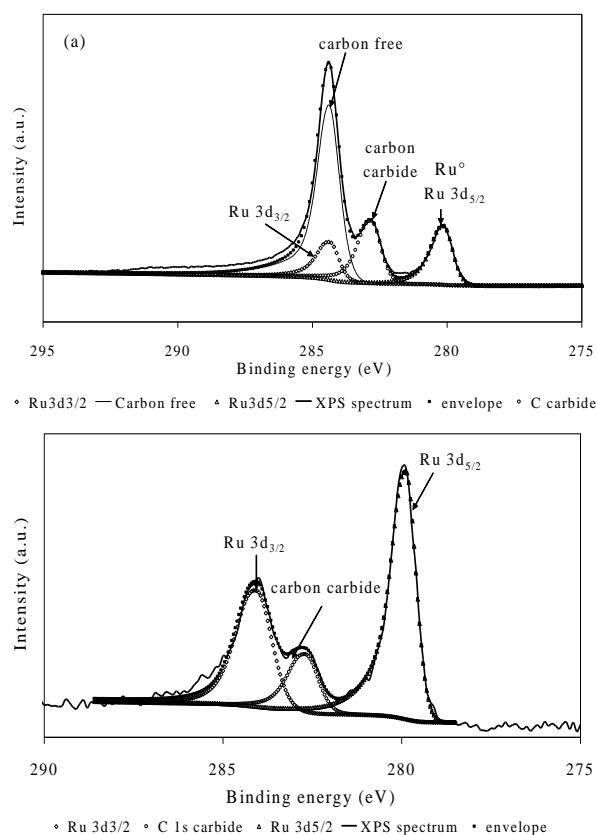
Figure 4. Decomposition of C 1s and Ru 3d XPS spectra of catalysts after reduction in H_2 at 673 K : (a) Ru/WC(A), (b) Ru/WC(B).

To conclude characterizations show that after H_2 pretreatment Co and Ru are totally reduced respectively on a surface of tungsten carbide protected by carbon layers (M/WC(A)) and on clean tungsten carbide (M/WC(B)).

Moreover, a different repartition of the actives species at the surface of the catalysts has been evidenced by XPS analysis. The XPS Ru/W_T and Co/W_T atomic ratios, which reflect the dispersion of the metal, have been

calculated before and after reduction in hydrogen and reported in Table 5. A similar ratio Ru/W_T and Co/W_T for WC(A) based catalysts indicates a better dispersion of ruthenium on carbon layers compared with cobalt, as the atomic weight of Ru is about two times higher than the Co one. However the decrease of Co/W_T ratio observed after treatment at 673 K and 773 K seems to indicate a coalescence of cobalt particles. This behavior is not observed with Ru/WC(A). A similar dispersion is expected for Co and Ru supported on WC(B), as the ratio Co/W_T is about two times higher than Ru/W_T. After reduction, a decrease of these ratios is observed, in accordance with an increase of particle size. The dispersion of Co and Ru is always higher over WC(B) than WC(A).

Table 5. M/W_T atomic ratio before and after reduction in H_2 from XPS experiments.

Catalyst	Atomic ratios
Ru/WC(A)	0.13
Ru/WC(A) (1)	0.12
Co/WC(A)	0.15
Co/WC(A) (1)	0.10
Co/WC(A) (2)	0.08
Ru/WC(B)	0.49
Ru/WC(B) (1)	0.26
Co/WC(B)	0.96
Co/WC(B) (1)	0.36

M = Co or Ru, W_T = total tungsten content,
(1) : reduced at 673 K, (2) reduced at 773 K

The Co and Ru supported catalysts have been tested at 473 K and 20 bar to be compare with the parent tungsten carbides (Table 4).

Table 4. Catalytic behavior of Co and Ru supported catalysts (T = 473 K, P = 20 bar, VSV = 6000 h^{-1})

Catalyst	X (%)	Rate (10^{-3} mol.h^{-1}.g^{-1})	Selectivity (%)			
			C_1	C_2-C_4	C_{5+}	COH
Ru/WC(A)	15	4.4	8.4	4.6	87	0
Co/WC(A)	~ 1	~ 0.3	21.2	27	46	5.8
Ru/WC(B)	~ 1	~ 0.3	34.2	37.4	28.4	0
Co/WC(B)	7	2.3	28.0	31.4	40.6	0

As expected due to a better dispersion of Co on WC(B), Co/WC(B) is more active than WC(B) and Co/WC(A). This behavior is not observed with ruthenium supported catalysts. Indeed, as Ru/WC(B) is poorly active a formation of a Ru-W alloy could be considered. The FT conversion obtained with Ru/WC(A) catalysts is higher compared with WC(A) and Co/WC(A). This is related to the better dispersion of Ru on WC(A) compared with Co and to the absence of coalescence of Ru particle after reduction. In the gas phase, selectivity in C_{5+} is very high, in agreement with the presence of Ru which is well-known to favor the chain length of the hydrocarbons. However, for this catalyst, liquids are trapped in the hot condenser (0.67 g for 24 h) and analyzed by chromatography. The distribution of hydrocarbons in the liquid phase is represented on figure 5 and shows a repartition of alkanes from 10 to 50 carbon atoms number, centered at about 21 carbon atoms.
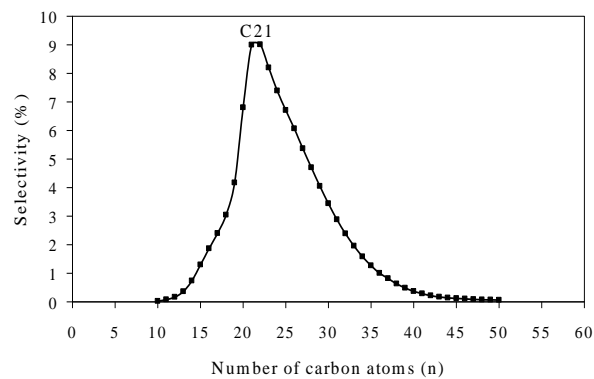
Figure 5. Repartition of hydrocarbons products obtained in the hot condenser for Ru/WC(A) at 473K

For supported catalysts on WC(B) no alcohol formation is observed as for parent tungsten carbide, the selectivities being only towards hydrocarbons. Addition of Co on WC(A) raises the heavy hydrocarbons selectivity (C_{5+}: 46%) at the expense of alcohol formation (COH ~ 6%). For all catalysts, Co and Ru allow to increase the C_{5+} selectivity as they are well-known to favor the chain length of the hydrocarbons.

Conclusion

A study of 1 wt% Ru and Co dispersed on tungsten carbide has been realized. Two types of WC were synthezised : tungsten carbide protected by free carbon on the surface (WC(A)) and clean tungsten carbide (WC(B)). The H_2 pre-treatment before catalytic test allows to obtain Ru and Co totally reduced on respectively carbon layers on tungsten carbide (as M/WC(A) surface does not change after reduction) and on clean tungsten carbide (as on M/WC(B) oxygen of the passivation is removed). Catalysts have been compared in Fischer-Tropsch

reaction in a fixed bed reactor at 473 K and 20 bar. Co and Ru dispersions are better on WC(B) compared to WC(A). Then Co/WC(B) is more active than Co/WC(A). This behavior was not observed with ruthenium as Ru/WC(B) is poorly active. The formation of a Ru-W alloy could be consider. By opposition, addition of Ru on WC(A) allows to obtain an high activity and C_{5+} production, which could be attributed to a better dispersion of Ru on carbon layers compared to cobalt.

Acknowledgements

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