Novel phosphorus-doped alumina-supported molybdenum and tungsten carbides: synthesis, characterization and hydrogenation properties

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The effect of atomically dispersed phosphorus on Mo_2C- and WC-supported γ-Al_2O_3 has been studied. Phosphorus was introduced via molybdenum or tungsten heteropolyanions. Mo- and W-based heteropolyanions were used to synthesize supported materials. Propene and tetralin hydrogenation were used as molecular probe reactions to test the activity and selectivity of the alumina-supported molybdenum or tungsten carbides. The effect of phosphorus on the hydrogenation activity of materials was also considered. Catalysts were characterized by X-ray diffraction, transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS) and CO chemisorption. Phosphorus was found to increase significantly the activity of molybdenum and tungsten carbides. Supported molybdenum carbides are highly dispersed. Tungsten carbide particles are well dispersed with sizes ranging from 2 to 4 nm. To check the stability of carbides they were characterized after catalytic runs.

KEY WORDS: hydrogenation; molybdenum carbide; tungsten carbide; heteropolyanion precursor; phosphorus

1. Introduction

Deep hydrodesulfurization (HDS) of gasoils will remain a target for the scientific community due to the regulation of sulfur and polyaromatics in diesel fuels. Furthermore, it is not easy to hydrogenate these feedstocks due to the presence of sulfur-containing compounds. There are two ways to achieve hydrogenation. The first one, using current commercial sulfided catalysts, NiMoS or CoMoS [1] supported on alumina, in a one-step process, can be used at high pressure and temperature to get a high level of desulfurization or hydrogenation. The second way is by means of a two-stage process, using two reactors. In the first stage, a conventional catalyst is used to obtain a first level of conversion of aromatics and hydrodesulfurization. In the second stage (hydrogenation), noble metal catalysts exhibiting sulfur tolerance are used [2]. The use of transition metal carbides or nitrides instead of noble metals can be envisaged for this second stage. They have been shown to have activity close to or surpassing those of the group VIII noble metals [3] for such diverse reactions as reforming (isomerization and cracking of alkanes) [4]; CO hydrogenation and alkane hydrogenolysis [5], hydrogenation of benzene [6]. Moreover, they exhibit high thermal stability and mechanical strength. Some authors have developed this kind of material with high specific surface areas [7,8] for catalytic applications. Recent research has been devoted to supported transition metal carbides and nitrides [9–11]. It has been recognized that molybdenum carbides and nitrides present high activity in hydrodenitrogenation (HDN) or HDS reactions, and high resistance to poisoning [12–17]. Carbides or nitrides modified by additives such as phosphorus have been reported. Phosphorus promotion increases metal dispersion [18], modifies the distribution, number and strength of acid sites [19,20], and leads to good hydrogenation [21,22] and hydrotreating [23,24] properties. The effect of promotion was studied on bulk materials [25–27]. Phosphorus was introduced as heteropolyanions which has the advantage of associating all elements in the same unit; the hydrogenation properties were found to be enhanced [26,27]. Recently, alumina-supported carbides were studied [28], and phosphorus was introduced by using P-containing salts. Phosphorus was also found to increase HDN and HDS activities [28] as well as the isomerization activities [26] of transition metal carbides. The aim of the present work was to design a supported hydrogenation catalyst: molybdenum- and tungsten-based catalysts were synthesized by temperature-programmed reaction, then characterized and tested in two probe reactions: propene hydrogenation, at atmospheric pressure, and tetralin hydrogenation, at a total pressure of 4 MPa. CO chemisorption measurements, XRD, TEM and EDS were used to characterize the materials.

2. Experimental

2.1. Materials

The support consisted of γ-alumina extrudates provided by Procatalyse (specific surface area, $S_g = 205\ m^2\ g^{-1}$, total

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pore volume $V_p = 0.7$ cm^3 g^{-1}). Different heteropolyanions with various P/Mo atomic ratios ranging from 0 to 0.4 were purchased ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with P/Mo = 0 and $H_3PMo_{12}O_{40}\cdot xH_2O$ with P/Mo = 0.08, Acros) or synthesized ($(NH_4)_6P_2Mo_{18}O_{62}\cdot xH_2O$ with P/Mo = 0.11 and $(NH_4)_6P_2Mo_5O_{23}\cdot xH_2O$) with P/Mo = 0.4) and used as precursors. Two ammonium heteropolyanions with different P/W atomic ratios were purchased ($(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ with P/W = 0, Acros) or synthesized ($(NH_4)_6P_2W_{18}O_{62}\cdot xH_2O$, with P/W = 0.11) and used as tungsten precursors. For sake of comparison, alumina (specific surface area 240 m^2 g^{-1}) supported molybdenum oxide (the loading was found to be 10.2 wt% Mo) was also investigated. This material was sulfided *in situ* at 632 K for 15 h before runs.

The gases employed were methane, Ar, O_2 and H_2 (all supplied by Air Liquide, 99.995%).

2.2. Catalyst preparation

2.2.1. Molybdenum/phosphorus-based catalysts

Supported molybdenum materials were prepared using the incipient wetness method with aqueous solutions containing the appropriate amounts of molybdenum precursors in order to obtain 10% w/w metal loading. The extrudates once impregnated were dried at 393 K for 12 h. Carbides were prepared by temperature-programmed reaction (TPR) using a modification of the procedure described elsewhere [7]. Carbide synthesis was divided into two steps. First the impregnated extrudates were heated in flowing argon (flow rate 60 cm^3 min^{-1}) and held at 673 K for 8 h. The material was then carburized by TPR in flowing CH_4/H_2 (20% v/v mixture, total flow rate 60 cm^3 min^{-1}), the temperature being raised linearly from 673 to 950 K. At this final temperature the CH_4/H_2 flow was switched to hydrogen and the material was cooled to room temperature (RT) after 1 h. At RT, hydrogen was switched to an O_2/Ar mixture (1% v/v), for a passivation step (170 cm^3 min^{-1} for 1 h) before characterization or catalysis experiments.

2.2.2. Tungsten/phosphorus-based catalysts

Supported tungsten materials were prepared using the incipient wetness method with aqueous solutions containing the appropriate amounts of tungsten precursors in order to obtain 18% w/w metal loading. The impregnated extrudates were dried at 393 K for 15 h. As described for molybdenum samples, a similar TPR procedure was applied for tungsten carbide synthesis. The dried impregnated extrudates were quickly heated in flowing argon (60 cm^3 min^{-1}) and held at 823 K for 5 h with the same flow rate. Carburization was then performed (temperature raised linearly from 823 to 1123 K) in flowing CH_4/H_2 (20% v/v, total flow rate 83.3 cm^3 min^{-1}). The samples were held at 1123 K for 3 h and treated as described for molybdenum materials. The final temperature (1123 K) for carburization of supported tungsten carbides was selected, because there are two carbides, W_2C and WC [29], the alumina-supported WC requiring the higher temperature.

Extrudates of supported carbides were ground and sieved between 0.25 and 0.4 mm. These powders were used for characterization and catalytic tests. Catalysts were designated as PxMoC and PxWC, x being the P/Mo or P/W ratio.

2.3. Characterization

Powder X-ray diffraction (XRD) was carried out on a Siemens model D-500 diffractometer with Cu Kα radiation. Measurements were performed for 2θ ranging from 10° up to 110°.

The selective chemisorption of CO was used to count noble-metal-like surface molybdenum sites [30,31] before runs and was performed by a pulse technique at 293 K. A known volume of CO controlled by an automatic valve was passed through a quartz reactor containing the material (0.3 g), He being used as carrier gas. A catharometric cell detected the remaining non-adsorbed CO at the outlet of the reactor. Hence, the consumption of CO could be determined and the amount of CO chemisorbed by the sample deduced. Prior to chemisorption, the passivated supported molybdenum carbides were reduced in flowing H_2 (12 cm^3 min^{-1}) at 773 K for 4 h. The passivated supported tungsten carbides were pretreated similarly at 873 K for 2 h.

High-resolution transmission electron microscopy (HRTEM) was performed to determine the particle size of molybdenum and tungsten carbides supported on alumina and to check their dispersion. HRTEM studies were run on a Jeol-JEM 100 CXII apparatus associated with a top-entry device and operating at 100 kV (with microscope resolution: 0.194 nm for point image and 0.14 nm for lattice image).

EDS analysis (STEM mode) was performed with the same apparatus using a LINK AN 10000 system, connected to a silicon–lithium diode detector, and multichannel analyser. EDS analyses were obtained on large domains of samples (150 × 200 nm^2 to 400 × 533 nm^2). The Mo, W and C contents of both the fresh and spent catalysts were determined by chemical analysis at the "Service Central d'Analyses du CNRS".

2.4. Propene hydrogenation

Propene hydrogenation was chosen as a model reaction to determine the hydrogenation properties of the materials at atmospheric pressure. The reaction was carried out at 250 or 353 K. The gas mixture (the H_2/C_3H_6 molar ratio was fixed at 6.7 and the total flow rate at 117 cm^3 min^{-1}) was fed into a Pyrex reactor loaded with 0.1 g of catalyst on a sintered glass disc (1 cm in diameter). The effluent composition was analysed with a HP 5890 series II gas chromatograph equipped with a KCl-modified Al_2O_3 capillary column and a flame ionization detector. The only product observed was propane. Prior to each run, passivated molybdenum-based catalysts were pretreated *in situ* at 773 K in flowing H_2 (12 cm^3 min^{-1}) for 4 h, and tungsten-based catalysts were pretreated under the same conditions at 873 K for 2 h.

2.5. Tetralin hydrogenation

Tetralin hydrogenation was chosen as a model for the hydrogenation of aromatics in diesel fuels. The reaction was carried out at 573 K, and a total pressure of 4 MPa. Tetralin was diluted in *n*-heptane, the mixture being injected by a high-pressure pump (Gilson Pump, model 307). Partial pressures of tetralin, *n*-heptane and hydrogen were 0.01, 0.93 and 3.06 MPa, respectively. A contact time (t_c) of 0.4 s was chosen. The contact time is defined as the catalyst volume (cm^3) divided by the total feed flow rate ($cm^3\,s^{-1}$). The products of the reaction were collected periodically (every hour) and analysed on a 50 m long capillary column (HP PONA).

Before reaction, 0.2 g of supported carbides were pretreated *in situ*, at 423 K and 4 MPa in flowing hydrogen ($17\ cm^3\,min^{-1}$) to remove the passivation layer. Under our experimental conditions, the only products of transformation were decalins (*trans*- and *cis*-decalin, hydrogenation products) and a small amount of naphthalene (dehydrogenation product), as already reported for alumina-supported catalysts [32].

3. Results and discussion

3.1. Molybdenum-based catalysts: influence of phosphorus

As reported in table 1, the C/Mo ratios of supported carbides are lower than the theoretical values. These unexpectedly low values suggest a strong interaction between the support and the molybdate [33]. In the literature, the theoretical ratio is never observed and supported carbides are never stoichiometric [29].

Table 1
Chemical and EDS analysis of alumina-supported molybdenum or tungsten carbides.

Catalyst	EDS analysis[a]			Chemical analysis[a]
	P/M theoretical	P/M measured	M/Al measured	C/M measured
Mo_2C	0	0	0.07	0.35
P0.08MoC	0.08	–	0.07	0.3
P0.11MoC	0.11	0.12	0.07	0.3
P0.4MoC	0.4	0.41	0.07	0.3
WC	0	0	0.065	–
P0.11WC	0.11	0.08	0.065	–

[a] M – molybdenum or tungsten.

EDS measurements (table 1) show that Mo/Al ratios are constant throughout the sample (0.07) indicating a homogeneous distribution of the carbides on the alumina surface.

Phosphorus was introduced with molybdenum during the impregnation using heteropolyanions and, after drying and carburization, P/Mo ratios were investigated in order to check that the distribution of both elements was homogeneous after each stage of the synthesis. As P/Mo ratios are quite constant, it appears that phosphorus and molybdenum are always “intimately mixed” after carburization. The only detectable peaks in the X-ray diffraction patterns for the alumina-loaded materials are due to γ-Al_2O_3; since Mo_2C and Al_2O_3 phases present some overlapping diffraction lines, Mo_2C identification was very difficult. No molybdenum carbide particles were detected by HRTEM; these observations allow us to conclude that the carbide domains are very small and highly dispersed.

Table 2 presents CO chemisorption data. No correlation can be observed between P contents and CO uptakes. The supported molybdenum carbide, synthesized from the P/Mo = 0.4 precursor, has the lowest CO uptake ($25\ \mu mol\,g^{-1}$). The CO chemisorption uptakes are nearly identical for the other molybdenum supported carbides, ranging from 40 to 45 $\mu mol\,g^{-1}$. The percentage of surface Mo atoms exposed was calculated from these values and found to range from 3.9 to 4.3%, except for P0.4MoC which gives a value of 2.5%.

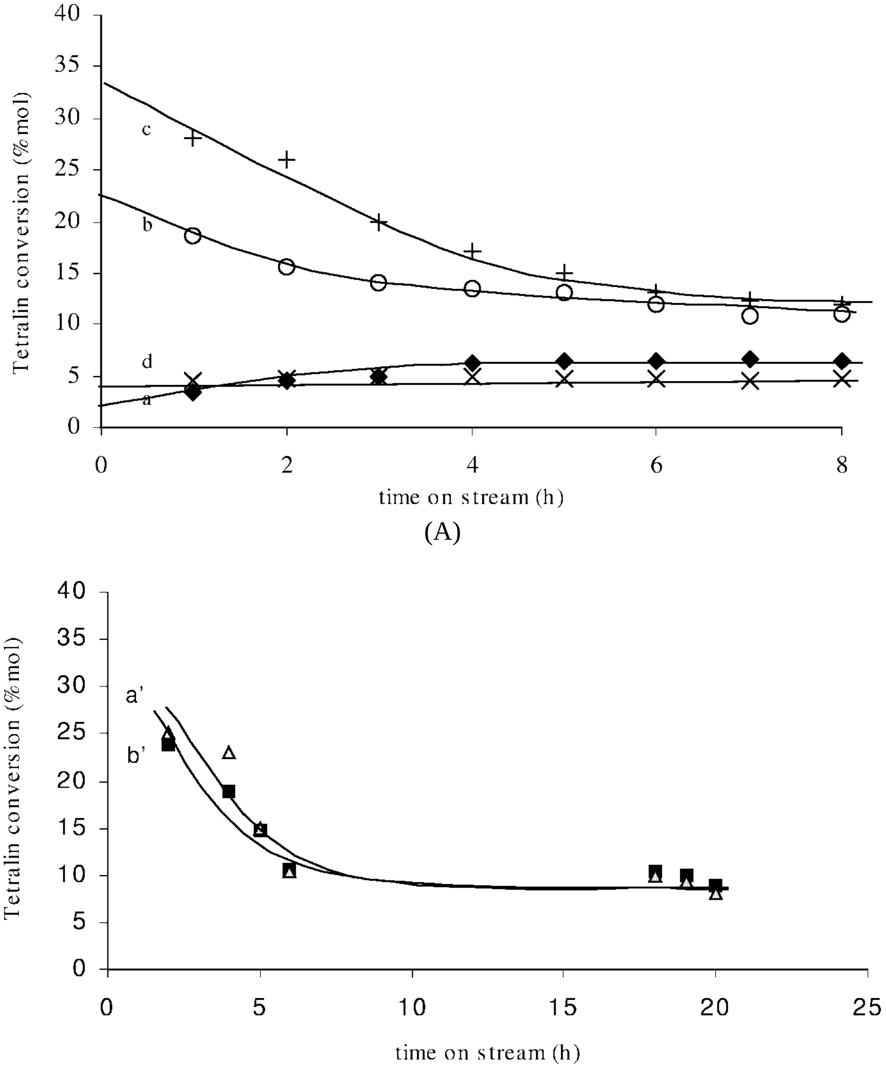
Reactivity in propene hydrogenation was then tested to check the metallic properties of the materials. Table 2 reports the results on propene hydrogenation at 250 K and atmospheric pressure. Since the catalysts are deactivated during the reaction, the initial conversion was determined according to a second-order deactivation law: the reciprocal value of the conversion τ versus time on run (t) was used to determine the initial conversion τ_0 by extrapolation to zero time $1/\tau = 1/\tau_0 + \kappa t$, where κ is an empirical deactivation constant [34]. The number of accessible Mo atoms being known from CO chemisorption, it was thus possible to calculate the initial propane formation as a site time yield (STY, i.e., the number of molecules of propane at the reactor exit produced per surface active site in the reactor per second).

Table 2
Supported molybdenum and tungsten carbides: CO chemisorption, conversion and STY for propene hydrogenation at initial time.

Catalyst	P/Mo	CO uptake ($\mu mol\,g^{-1}$)	Percentage of active sites (%)	Conversion at initial time (mol%)		STY at initial time (s^{-1})	
				250 K	353 K	250 K	353 K
Mo_2C	0	40	3.9	3.3	–	0.04	–
P0.08MoC	0.08	45	4.3	6.1	–	0.07	–
P0.11MoC	0.11	41	4.0	15.1	–	0.19	–
P0.4MoC	0.4	25	2.5	18.5	–	0.37	–
WC	0	41	4.2	–	3.1	–	0.03
P0.11WC	0.11	30	3.1	–	33.3	–	0.50

Phosphorus-containing materials give the highest initial conversion, which increases with the percentage of phosphorus. The ranking of catalyst activity for propene hydrogenation is as follows: Mo_2C < P0.08MoC < P0.11MoC < P0.4MoC (the activities of Mo_2C and P0.4MoC differing, by one order of magnitude). This last material, P0.4MoC, has the highest activity (STY $= 0.37\ s^{-1}$), but the lowest carbide dispersion (2.5% of accessible surface Mo atoms determined by CO chemisorption): it has fewer exposed sites than the other molybdenum-based catalysts, but these sites are more active. As shown, the addition of phosphorus enhances the hydrogenation properties of molybdenum carbides.

Figure 1(A) shows tetralin hydrogenation conversions vs. time on stream for the supported catalysts. The deactivation of tetralin hydrogenation can be explained by the presence of coke on the surface, inhibiting the active sites. Tetralin hydrogenation reveals differences in the activity of the various materials. Under our experimental conditions P0.11MoC presents the highest tetralin conversion at the steady state. The phosphorus-containing molybdenum carbides deactivate with time on stream and reach a steady state after 8 h, whereas over supported Mo_2C conversion goes from 3% after 1 h to 6.5% at the steady state. This behaviour is probably due to a carburization of supported molybdenum carbide with time. There is no evolution of tetralin conversion after 8 h on stream (figure 1(A)). For the sake of comparison, supported MoS_2 was also studied (figure 1(A)) without any added H_2S. At the steady state at 573 K supported MoS_2 presents a tetralin conversion of 5% compared to 6.5% for the least active supported carbide, the non-phosphorus-containing carbide. Table 3 reports the conversion (mol%) of tetralin at the steady state, for supported molybdenum carbides and sulfide, together with the *trans*-decalin selectivity. The same trend is observed for propene hydrogenation, P-containing catalysts being more active than Mo_2C/Al_2O_3. After 1 h on stream, P0.11MoC is more active than P0.4MoC, 28 against 18%, but at the steady state nearly the same conversion is obtained (12% for



(A)

(B)

Figure 1. Tetralin hydrogenation at 4 MPa and 573 K, $t_c = 0.4$ s: (A) over molybdenum-based catalysts: (a) Mo_2C, (b) P0.4MoC, (c) P0.11MoC and (d) MoS_2; (B) over tungsten-based catalysts (a′) WC and (b′) P0.11WC.

P0.11MoC and 11% for P0.4MoC). The better hydrogenation capacity of P0.4MoC can be explained by higher activities of the active sites.

In conclusion, phosphorus addition clearly enhances the activity of supported molybdenum carbides and, furthermore, these new materials are better than supported molybdenum sulfide.

The supported carbides were characterized after the runs. XRD patterns and EDS reveal that the composition of the materials does not change. These data suggest that molybdenum-based catalysts are stable during hydrogenation runs.

Table 3
Supported molybdenum-based and tungsten-based carbides: tetralin hydrogenation at 573 K, total pressure 4 MPa, conversion at steady state ($t_c = 0.4$ s, 0.2 g of catalyst).

Catalyst	Conversion at steady state (mol%)	*Trans*-decalin selectivity (mol%)
Mo_2C	6.5	55.0
P0.11MoC	12.0	54.9
P0.4MoC	11.0	54.8
WC	8.0	53.2
P0.11WC	9.0	53.2
MoS_2	5.0	74.9

3.2. Tungsten-based catalysts: influence of phosphorus

Characterization of tungsten/phosphorus-based catalysts shows that supported tungsten carbides are different from supported molybdenum carbides. Tungsten carbide particles were detected by HRTEM with sizes ranging from 2 to 4 nm (figure 2). A diffraction peak could be identified at $2\theta = 75°$ (figure 3). This XRD line is not well defined and cannot be clearly attributed to either WC (JCPDS 25-1047) or WC_{1-x} (JCPDS 20-1316). Depending on the carburization temperature (1123 K), it may be due to a carbide phase intermediate between WC and WC_{1-x}. EDS measurements are reported in table 1: they show that W/Al ratios are practically constant throughout the sample (0.065) indicating an homogeneous distribution of the tungsten carbides on the alumina surface. Furthermore, when phosphorus is introduced as a heteropolyanion during alumina impregnation, the P/W ratios are constant during all steps of the synthesis (drying and carburization). Nevertheless, the EDS P/W ratios of 0.08 after drying and after carburization are always lower than the theoretical value (0.11).

As already described for supported molybdenum carbides, supported tungsten carbides were submitted after synthesis to CO chemisorption measurements at room temperature in order to determine the accessible W atom sites. Results are reported in table 2. The CO chemisorption uptakes over tungsten-based carbides are nearly identical to those

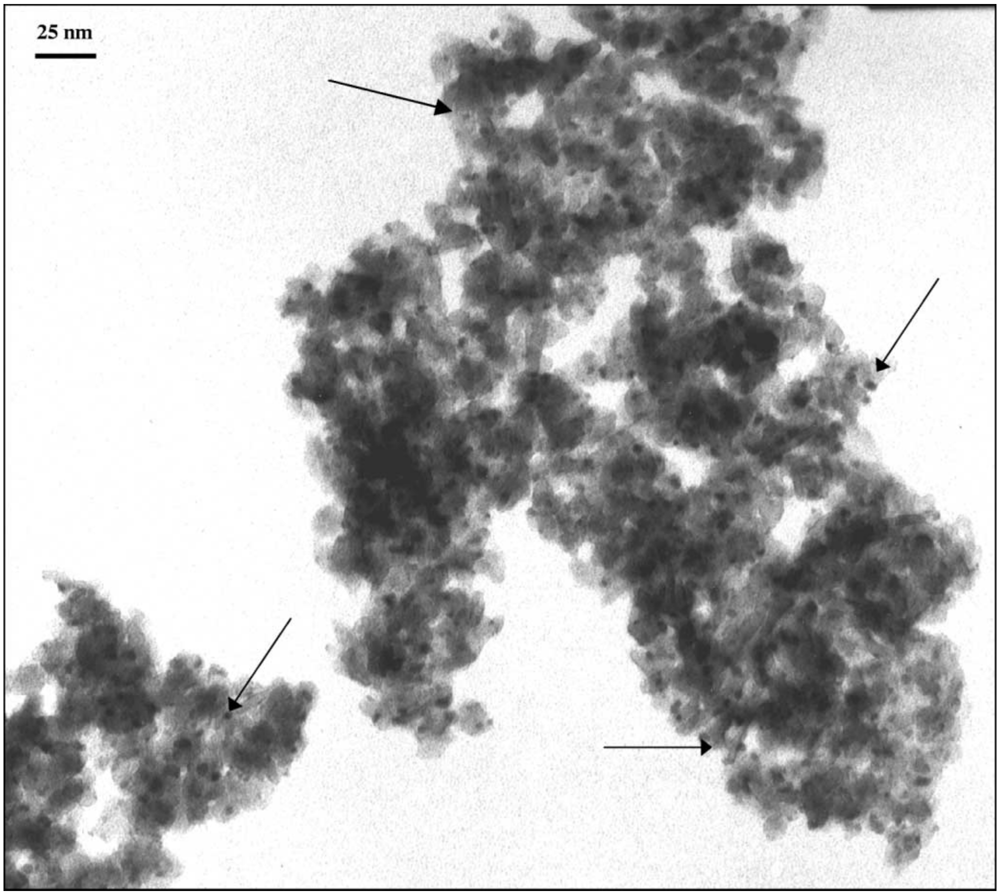


Figure 2. TEM micrograph of supported tungsten carbide, WC/Al_2O_3. Arrows indicate carbide particles.

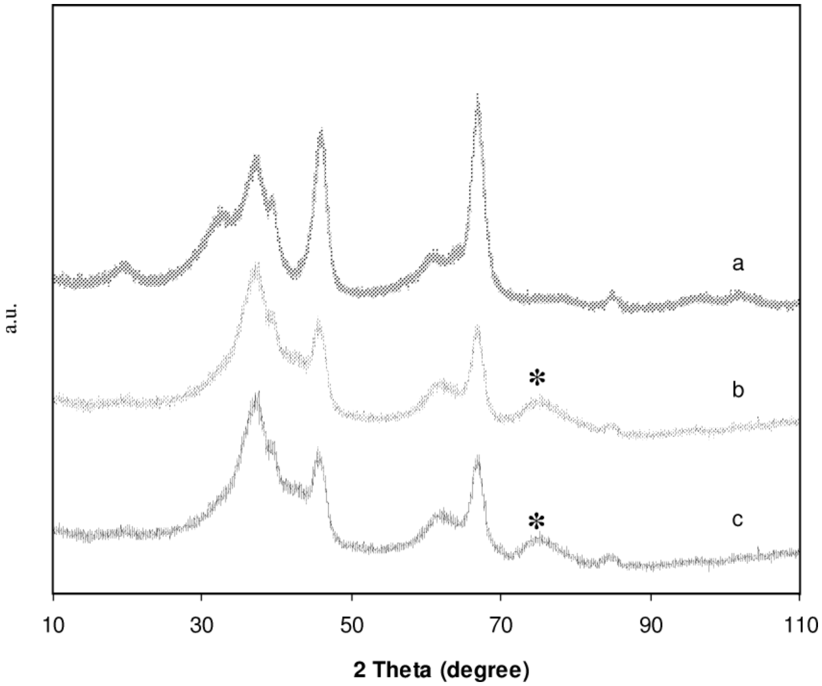


Figure 3. XRD patterns of alumina-supported tungsten-based carbides: (a) alumina, (b) WC and (c) P0.11WC; $*$ WC or WC_{1-x} phase.

of molybdenum carbides, with values ranging from 30 to 41 μmol g^{-1}. These values show that tungsten and molybdenum carbides have nearly identical numbers of accessible W or Mo atom sites.

Hydrogenation of propene and tetralin was carried out to check the hydrogenation activities of supported tungsten-based carbides. A difference in propene hydrogenation was observed for molybdenum and tungsten carbide materials, a higher temperature (353 as against 250 K for molybdenum catalysts) being needed for the latter to give a measurable propene conversion. As for molybdenum compounds, the initial conversion was determined according to a second-order deactivation law, and an initial STY was calculated using the accessible surface W atoms determined by CO chemisorption. Results are presented in table 2, phosphorus-containing materials exhibiting again a higher hydrogenation activity.

Tetralin hydrogenation was also conducted over these tungsten carbides. As already reported for molybdenum carbides, the only products were *cis*- and *trans*-decalin and a small amount of naphthalene. In contrast to molybdenum carbides, tungsten carbides with or without P exhibit similar pseudo-initial conversion (about 25% tetralin conversion after 2 h) and the two materials suffer equivalent rapid deactivation with time on stream (figure 1(B)). At the steady state, obtained after 6 h, tungsten-based carbides give conversion values of the same order of magnitude as supported molybdenum carbides.

The trend observed for the supported carbide catalysts is in marked contrast with the ranking for propene hydrogenation at atmospheric pressure. We assume that the high-pressure activation prior to tetralin hydrogenation leads to active surface sites free of coke and hence produces a cleaner surface, which reveals the intrinsic properties of the tungsten-supported carbides. In contrast, carbon deposition from methane decomposition during synthesis is significant enough to decrease the site density at atmospheric pressure whatever the activation temperature.

The XRD patterns and EDS analysis show that the materials are the same before and after a tetralin hydrogenation run, except that the particle size increases, ranging from 3 to 5 nm. The deactivation of materials could be a consequence of the sintering of the tungsten carbide particles.

4. Conclusions

Novel alumina-supported molybdenum and tungsten carbides with phosphorus dispersed at molecular level were synthesized by temperature-programmed reactions. EDS characterization shows that for all steps of the synthesis they are well dispersed (constant metal/Al ratios) and intimately mixed (P/metal ratios nearly constant after carburization).

XRD data and TEM micrographs reveal differences between molybdenum-based and tungsten-based materials. No carbide particles were detected for the former whereas particles with sizes ranging from 2 to 4 nm were observed for the latter.

The catalysts were tested in propene hydrogenation at atmospheric pressure and in tetralin hydrogenation at high pressure (4 MPa). The catalytic properties of molybdenum-based materials, for propene hydrogenation at 250 K and at atmospheric pressure, were enhanced by phosphorus addition, and an initial STY deduced from CO uptake led to the following ranking: P0.4MoC $>$ P0.11MoC $>$ P0.08MoC $\approx$ Mo_2C. The STY values for tungsten-based materials were very low at the same temperature. Nevertheless, at higher temperature (353 K) phosphorus addition clearly increases propene conversion.

Conversion values for the hydrogenation of tetralin (high pressure, 4 MPa) at the steady state show a different trend. For supported molybdenum carbides, the addition of phosphorus doubles the conversion whatever the phosphorus content, whereas for supported tungsten materials the effect of phosphorus addition is not clear. This activity variation for the two hydrogenation probe reactions at different pressures is interpreted in terms of different activation of the materials.

In conclusion, the addition of any amount of phosphorus only enhances the activity of supported molybdenum carbides, in the high-pressure hydrogenation of aromatics. Further work will be presented on catalyst optimization for industrial applications to cleaner fuel production.

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