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Preparation and Characterization of Mo/W Bimetallic Carbides by Using Different Synthesis Methods

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Abstract Molybdenum and tungsten bimetallic oxides were synthetized according to the following methods: Pechini, coprecipitation and solid state reaction (SSR). After the characterization, those solids were carbureted at programmed temperature. The carburation process was monitored by checking the consumption of carburant hydrocarbon and CO produced. The monitoring process permits to avoid or to diminish the formation of pirolytic carbon.

Keywords Molybdenum · Tungsten · Bimetallic · Oxide · Carbide

1 Introduction

In 1971, Sinfelt and Yates [1] demonstrated that the molybdenum carburation provided a big increase in the specific activity of this metal with the ethane hydrogenolisis. Several subsequent studies state that carbides and metallic transition nitrides are active catalysts in several chemical reactions in which noble metals are normally used [2, 3].

A good performance of these new materials in traditional reactions catalyzed by noble metals is attributed to an increasing electronic density of the metal after carburation and/or nitriding. The introduction of carbon or nitrogen at the unit cell of those metals results in an increase of net parameter *a*. Considering the fact that the electronic band is proportional to $1/a^5$, the increase of the metal–metal distance causes a contraction in band *d* and generates electronic densities similar to those found in noble metals [4, 5].

Among the most important reactions in which these materials can be used, there are reactions of hydrotreatment of petroleum fractions, the most important of them are the catalytic hydrogenation with sulphur removal (HDS) and the one with nitrogen remotion (HDN) [6]. From the year 80 onward, the investigations involving carbides and nitrides got a big recognition with the discovery made by Volpe and Boudart who demonstrated that it was possible to obtain tungsten nitrides or molybdenum nitrides with higher specific areas by the nitriding at programmed temperature of the respective oxides with ammonia [7]. Since then, the synthesis method of nitrides and carbides at programmed temperature, were started to be investigated well. Lee et al. [8] syntethized molybdenum carbides with higher specific areas, carburating the metallic oxide with methane. That material was tested in several reactions as in isomerization, hydrogenolisis, HDS and HDN.

Recently, the investigations on this field have increased considerably, resulting in several projects including synthesis, characterization, and evaluation of the catalytic properties of those new materials [9–11].

The development of new materials that presents similar catalytic properties to the noble supported metals is essential because these metals are widely used in industrial

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processes, their natural reserves are concentrated in only few countries, and they are becoming more and more scarce [12].

In the literature, most of the work on carbides synthesis run from commercial metallic oxides [13]. In the case of bimetallic carbides, the reaction in solid state (SSR) has been used to obtain the respective precursor bimetallic oxides [14, 15]. During this process, a physical mixture of monometallic oxides is submitted to treatments at high pressure and temperature, during long periods of time. In general, the initial mixture of oxides presents particles with different sizes between 1 and 10 mm, having passed by several stages of trituration, mix and calcination necessary to raise the degree of homogenity of the bimetallic oxide. The reproducibility of the synthesis process is compromised by diffusional problems deriving from the oxides that present different particle sizes and formation of unwanted intermediates [16].

Alternative methods to the reaction in the solid state for the synthesis of bimetallic oxides use precursors in solution. Examples of these methods are those involving precipitation phenomenons of the metallic precursors as coprecipitation and sol–gel [17–19]. The precipitation or coprecipitation is frequently used in the synthesis of various important catalytical materials, mainly supports. Some examples include aluminas, silicas and zirconias.

Pechini polymeric process [20] is based on the distribution of metallic cations (normally coming from a salt) in the internal structure of a polymer, inhibiting its segregation and precipitation. Initially, a quelant agent such as the citric acid acts on the present cations in the solution. Under appropriate conditions, the ethylene glycol is the second agent to be added, initiating the process of polymerization. Subsequent calcination of this organic material takes to multicomponent oxides.

Less common processes using citrate, PVA (polyvynilic alcohol), special gels and inverse microemulsion are also described in the literature [21–23].

In general, when looking for products with a more homogeneous composition and moderate reational conditions of synthesis, SSR is substituted by alternative methods already described.

This study includes Mo-W bimetallic carbides that were synthetized from oxide precursors through SSR, Pechini and coprecipitation methodologies. Monometallic carbides of molybdenum and tungsten were also synthetized to compare to the bimetallic materials.

Different techniques of characterization were used to define the most practical preparation method of bimetallic oxides that leads to the best values of specific area and superficial site density (measured by chemisorption of CO), after carburation.

2 Experimental

The experimental work was divided basically in three stages:

- preparation of Mo-W bimetallic oxides according to three different methods;
- preparation of mono and bimetallics carbides;
- characterization of all oxides and carbides previously prepared.

2.1 Preparation of Bimetallic Oxides According to Pechini Process (PEC)

To obtain bimetallic oxides according to Pechini (PEC), the procedure involved 4 stages. Firstly, a solution 3 M of citric acid (Merck) in ethylene glycol (Synth) was prepared, at 60 °C. Secondly, 11.1 g of ammonium molybdate (Mallinckrodt) were dissolved under constant agitation at 80 °C in 400 mL of the citric acid solution. Then, 16 g of ammonium tungstate (Fluka), were added to the resulting solution under the same conditions of temperature and agitation in order to obtain a proportion of Mo:W of 1:1. Third, the solution containing the precursors of Mo and W was kept under controlled temperature (140 °C) during 1 h, resulting in a dark and viscous liquid. The fourth stage consisted of the following sequence of thermal treatments:

- polymerization in oven at 150 °C during 24 h under static air;
- calcination in oven at 400 °C during 4 h under static air and,
- calcination in oven at 700 °C during 5 h under air flow (120 mL min^{-1}).

2.2 Preparation of Bimetallic Oxides by Coprecipitation (COP)

Using the same salt precursors of Mo and W, individual aqueous solutions were prepared on the following conditions: 11.1 g of ammonium molybdate were dissolved in 200 mL of water at room temperature and 16 g of ammonium tungstate were dissolved in 500 mL of water at 60 °C. These solutions were mixed in order to obtain an atomic relation 1:1 between the Mo and W elements, under agitation and temperature at 12 °C. Then, 40 mL of aqueous solution 2,4 N of chlorydric acid (Merck) were added producing a decrease of pH from 5.5 to 1.5 and forming a turbid and white suspension that was kept in agitation during 10 min.

The suspension went through a maturation process for 24 h at room temperature and then, it was submitted to vacuum filtration. The resulting solid was dried at room temperature to get a constant weight and then, calcinated at 700 °C during 5 h under air flow (120 mL min^{-1}).

2.3 Preparation of Bimetallic Oxides by the Solid State Reaction Process (SSR)

Molybdenum Oxide (MoO_3) was prepared by direct calcination of ammonium molybdate (Mallinckrodt) at 450 °C, during 5 h, under air flow (120 mL min^{-1}). This oxide was mixed mechanically during 2 h with commercial WO_3 (Vetec), in order to obtain a Mo/W = 1 atomic theoretical reason. Ethanol was used to help during the mixture homogenization. Then, 7 g of the mixture were pressed at 54.5 MPa for 3 min. The resulting pills were submitted to differentiated thermal treatments in ovens, under static air and temperature of 600 °C during 24 h and at 700, 760 and 785 °C for 6 h, aiming to maximize the metal diffusion in the crystalline net and then, to obtain an homogeneous bimetallic material. It is important to emphasize that the treatment at 785 °C for 6 h was the one used by Oyama et al. [14].

2.4 Carbides Synthesis

The method used to obtain bimetallic oxycarbides was the carburation reaction at programmed temperature (PTC). This reaction was performed in a dynamic quartz reactor, using a flow of carburant mixture constituted by 20% of CH_4 in H_2 (V/V) or 10% of C_2H_6 in H_2 (V/V). The total output was 80 mL min^{-1} (at atmospheric pressure), established by a MKS massic controller model 247. With a tubular oven coupled to a temperature controller Presys, model DCY 2050, the reactor was heated to maximum temperatures of 700 or 750 °C. The average heating rate was 10 °C min^{-1} from room temperature to 330 °C; 5 °C min^{-1} from 330 °C to 480 °C and 1 °C min^{-1} from 480 °C to final temperature of synthesis. The reaction was monitored through the consumption of CH_4 or C_2H_6 and the formation of CO and H_2O, by the passage of effluent gas through a gas cromatographer Varian, model GC 3800, equipped with a detector of thermal conductivity and a Chromossorb 102 column.

2.5 Specific Mass Measures

The specific mass of bimetallic oxides was determined with an Micromeritics helium pycnometer, model 1305.

2.6 Mo/W Atomic Ratio Measures

The atomic ratio (Mo/W) of bimetallic oxides was obtained by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.7 X-rays Diffractometry

The precursors oxides were characterized by X-rays diffractometry by using a Phillips diffractometer, model MPD 1880. The identification of the crystalline phases was obtained by comparing diffractograms with the data bank from ICDD (International Centre for Diffraction Data).

2.8 Specific Area Measures

The carbides had their specific areas evaluated by nitrogen volumetry using a Quantachrome equipment, model Nova 1000, operating in static regime.

2.9 Scanning Electron Microscopy

This technique (SEM) was used to compare the morphology of the three bimetallic oxides. The equipment consisted of a JEOL microscope, model JSM-5310.

2.10 Thermogravimetry Analysis

Thermogravimetry analysis were performed with the physical mixture coming from the SSR process aiming to evaluate losses of mass arising from the sublimation of molybdenum during the calcination. The calcination temperature under synthetic air was continuously raised up to 800 °C, at a rate of 10 °C min^{-1}. The equipment consisted of a Setaram thermobalance, model TG DTA 92.

2.11 CO Chemisorption

The CO chemisorption was a technique used to evaluate the density of prepared carbides sites. For this purpose, a Quantachrome CHEMBET 3000 equipment was used operating in dynamic regime and receiving pulses of 2 mL of CO at regular intervals.

3 Results and Discussion

Oyama et al. [14] sintethized bimetallic oxides of various transition metals by reaction in solid state, where molybdenum and tungsten is included. As previously explained, the technique used by the mentioned authors was reproduced in this project using not only the calcination treatment of the physical mixture at 785 °C/6 h but also treatments at 600 °C/24 h, 700 °C/6 h and 760 °C/6 h.

The X-rays diffractograms of the initial physical mixture and resulting oxides after calcination under different conditions are shown in Fig. 1. It is evident that the initial physical mixture presents peaks corresponding to the superposition of two monometallic oxides. The calcination at 600 °C for 24 h is not enough to promote the diffusion of the metals to transform the physical mixture of individual oxides in a bimetallic oxide. This fact has its beginning between 600 °C and 700 °C, when significant differences can be perceived in relation to the physical mixture and the appearance of new phases.

Chemical analysis for ICP-OES performed with those materials show that with the exception of the initial physical mixture and the calcinated material at 600 °C for 24 h, the Mo/W atomic ratios are inferior to 1, that was the theoretical reason calculated initially, indicating that molybdenum is eliminated by sublimation during the process of bimetallic oxide formation. This information appears on Table 1.

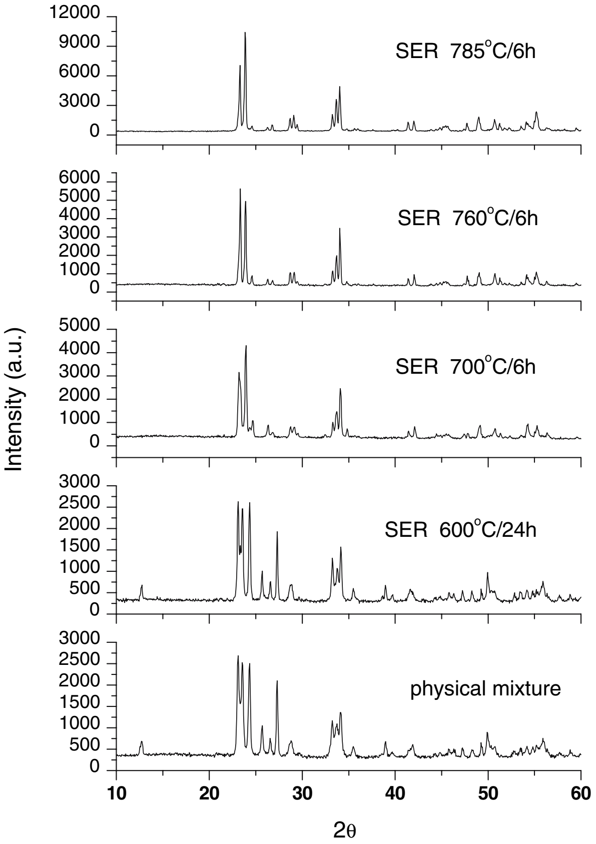

Fig. 1 Diffractograms of Mo–W bimetallic materials obtained by SSR process according to calcination temperatures

It can be seen on Table 1 that the loss of molybdenum by sublimation is bigger at the highest temperature of calcination used. Due to the sublimation of the molybdenum during the calcination from temperatures up to 600 °C, it was possible to identify picks corresponding to the WO_3 phase in small proportion.

A thermogravimetric analysis at programmed temperature performed with a physical mixture confirmed this hypothesis, indicating a continuous mass loss from the 600 °C, according to Fig. 2. It is observed that the loss of mass accentuates at 700 °C and it's maximum around 791 °C. The literature reports that, in spite of MoO_3 melting at 795 °C, a sublimation process starts from the 700 °C [24].

The alternative processes adopted in this study (Pechini and coprecipitation) that involve calcinating stages at 700 °C, also took to bimetallic oxides with Mo/W ratios lower than 1 (0.84 for Pechini process and 0.88 for co-precipitation process), like to occur with one obtained by SSR process at 700 °C.

Figure 3 compares X-rays diffractograms of bimetallic oxides with the use of the three methodologies, noticing a big similarity among them. In order to identify the existent

Table 1 Mo/W ratios obtained by ICP for bimetallic oxides prepared by SSR at different temperatures of calcination

Synthesis conditions	Mo/W ratio
SER-785 °C	0.63
SER–760 °C	0.75
SER-700 °C	0.83
SER-600 °C	1.0
Physical mixture	1.0

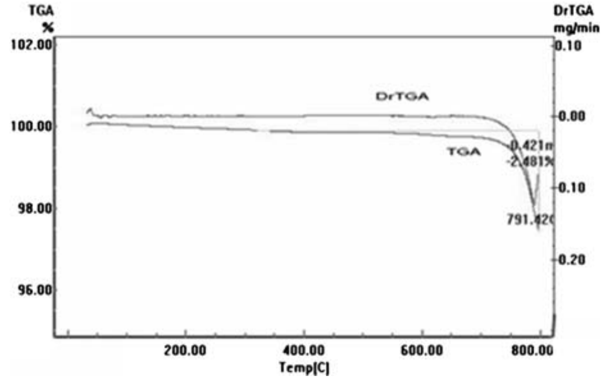

Fig. 2 Thermogravimetric analysis (TGA and DrTGA) shows a continuous loss of physical mixture mass (MoO_3–WO_3) due to the sublimation of molybdenum during SSR process

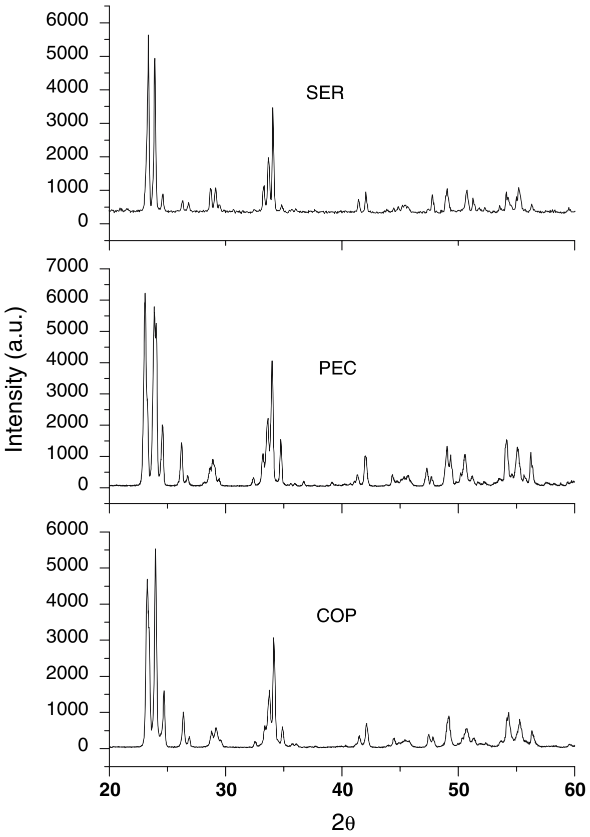

Fig. 3 Diffractograms of bimetallic oxides obtained by the solid state reaction process (SSR at 760 °C/6 h), Pechini (PEC at 700 °C/5 h) and coprecipitation (COP at 700 °C/5 h)

phases, the diffractograms were compared to the data bank of ICDD (International Centre for Diffraction Data). Most probably the products obtained are a combination of $W_{0.53}Mo_{0.47}O_3$ and $W_{0.4}Mo_{0.6}O_3$ phases, the first one being very predominant; this hypothesis was corroborated by the chemical analysis. It is also important to mention that the pioneer work performed by Oyama group [14], already cited, does not inform the chemical composition and the phases of the product obtained.

The specific mass values obtained by helium picnometry are intermediate among the ones obtained in the literature for the monometallic oxides of molybdenum (4.7 g cm^{-3}) and tungsten (7.2 g cm^{-3}): 6.4 g cm^{-3} for solid state reaction, 6.1 g cm^{-3} for Pechini and 5.8 g cm^{-3} for coprecipitation.

Table 2 presents experimental conditions used in the syntheses of bimetallic carbides which consists of: maximum temperature of synthesis, holding at maximum temperature, carburating mixture (gases and composition) and method used in the synthesis of oxide precursor. The results of specific areas are also presented. The carbides are identified on Table 2 as follows: the first two letters are related to the process of synthesis of oxide precursor (CC for coprecipitation, CP for Pechini and CS for reaction in the solid state) followed by the final temperature of synthesis and the last letter corresponding to hydrocarbon present in the carburating mixture (M for methane and E for ethane).

Table 2 shows that the oxides arising from the process for coprecipitation result in the carbides with specific areas superior to those obtained by SSR and Pechini processes. The result of specific area for the carbide CS 750M2 is very close to that of the bimetallic carbide prepared by the same process by Oyama et al. [13] in similar conditions (48 m^2 g^{-1}). However, the carbide CS 750M1 presented a significantly higher specific area (63 m^2 g^{-1}), wich can be explained by the use of calcination temperature at 760 °C, further from the fusion temperature of the molybdenum oxide (795 °C).

Aiming to find an explanation to the fact that the carbides prepared by coprecipitation presented specific areas highly superior than the two other methods, samples of three oxides were submitted to analyses by MEV. The micrographies (Fig. 4) revealed the existence of an inverse relation between the specific areas obtained with the size of the particles. This observation was well consistent because the carbide prepared by coprecipitation was the only one to present small particles. Another evident factor is the best aspect reason for the oxides with bigger medium size particles.

The results of the micrographies can be related to the conditions of the synthesis by different methods. Superior values of temperature and time of calcination used in the SSR process, favor to a bigger growth of particles.

Table 2 Syntheses parameters of the carbides and values of their specific areas

Carbide	Oxide precursor	Final temperature (°C)	Isothermal duration (h)	Carburant mixture (%V/V)	Surface area (m^2 g^{-1})
CS 750M1	SER (760 °C)	750	0.5	20%CH_4/H_2	63
CS 750M2	SER (785 °C)	750	0.5	20%CH_4/H_2	45
CC 700M	COP	700	1	20%CH_4/H_2	100
CC 750M	COP	750	0.5	20%CH_4/H_2	95
CC 750E	COP	750	0.5	10%C_2H_6/H_2	115
CP 750M	PEC	750	0.5	20%CH_4/H_2	68

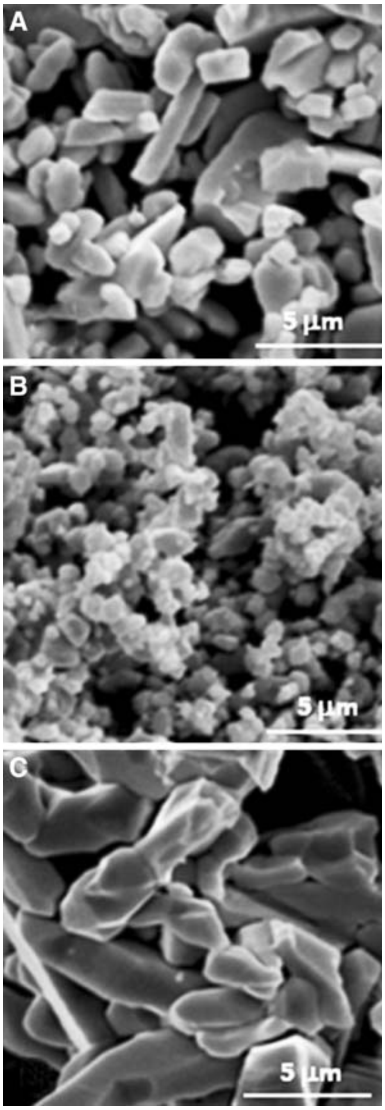

Fig. 4 Micrographies with an increasing degree of 7500× obtained for the bimetallic oxides prepared by Pechini (**A**), Coprecipitation (**B**) and RES (**C**) processes

According to Pechini process, the use of two calcinations for the preparation of bimetallic oxide, at 400 °C and 700 °C, favored the growth of the particles. This does not happen in the process of coprecipitation where the calcinations were performed in a shorter time.

For comparison effects, monometallic carbides were also prepared, that of Mo according to the procedure presented by Lee et al. [25] and the one of W, using the procedure adopted by Ramanathan and Oyama [26]. The specific areas obtained were 35 $m^2\ g^{-1}$ for the tungsten carbide and 50 $m^2\ g^{-1}$ for the molybdenum carbide. The values of this parameter were significantly lower when compared to the materials prepared in this work by coprecipitation, which indicate that the formation of a bimetallic carbide, with the change of the phases occurred during the synthesis, conducted to higher values of the specific area when compared to the correspondent monometallic carbides.

Table 3 Surface areas of various carbides described in the literature

Carbide (ref.)	Surface area ($m^2\ g^{-1}$)	Carburant mixture
W_2C (13)	21	20%CH_4/H_2
WC (25)	42	20%CH_4/H_2
Mo_2C (26)	39	20%CH_4/H_2
Mo–W–O–C (14)	48	20%CH_4/H_2
$W_{0.4}Mo_{0.6}C_x$ (15)	72	10%C_2H_6/H_2
Mo_2C (4)	40 a 91	10–20%CH_4/H_2
Mo_2C (27)	18.6 a 36.2	10%C_2H_2/H_2

When analyzing the results of a specific area, the bimetallic carbides sinthetized by the coprecipitation process have been guaranteed. Table 3 shows several specific area values of carbides found in the literature, all of them obtained by carburation at programmed temperature of the respective oxides, highlighting the excellent results corresponding to the bimetallic carbides synthesized by the coprecipitation process.

The synthesis of carbides followed the traditional route of carburation at programmed temperature (CTP), proposed by Boudart group. The methodology is based on the reaction of metallic oxides in the presence of a carburant mixture, normally constituted of an hydrocarbon and H_2. The mixture CH_4/H_2 is generally used as carburant mixture, although some authors report the achievement of carbides with higher specific areas using other hydrocarbons. Decker et al. [27] sinthetized WC using C_2H_6/H_2, varying the percentage of hydrocarbon and obtaining areas around 25 $m^2\ g^{-1}$, while with the mixture CH_4/H_2 the value obtained was only 10 $m^2\ g^{-1}$. Xiao et al. [15, 28, 29], in a series of three articles about preparation of molybdenum carbides, used carburant mixtures as 10%C_2H_2/H_2, 10%C_2H_6/H_2 and 5%C_4H_{10}/H_2. The specific areas of carbides obtained by those authors were superior to the one obtained with 20%CH_4/H_2. In this article, comparing the specific areas of carbides CC 750 Me CC 750 E, it is observed that the carburant mixture 10%C_2H_6/H_2 provided an increase of 20% of the specific area. These results are in accord with the results presented by Xiao et al. [28].

Carbide CC 700 M was synthetized at 700 °C, maintaining this maximum temperature 60 min during the carburation process. The area obtained (100 $m^2\ g^{-1}$) was slightly superior to the material CC 750 M, synthetized at 750 °C and remaining at this temperature during 30 min. It is necessary to control the process to define the remaining time of the materials on the baseline of the carburation reaction.

Carburation process control was possible by monitoring the consumption of methane and the formation of CO and

H_2O during the reaction, when using the carburant mixture 20%CH_4/H_2. In general, a partial reduction of oxide initially occurs by H_2 forming water and, in higher temperatures, it is given the consumption of CH_4 with consequent formation of CO. At the maximum consumption of CH_4 the maximum formation of CO occurs, that diminishing while the reaction follows. However, the carburation reaction only reaches the end when the baselines of consumption of CH_4 and the formation of CO reach to zero. Figure 5 illustrates the process monitored for the material CC 750 M.

The definition of the remaining time at the final temperature depends on the consumption of CH_4 and the formation of CO observations. Without them, the use of an excessive time can lead to the formation of free carbon (or pirolytic carbon), coming from the hydrocarbon decomposition, compromising the catalytic function by the covering of the active sites.

It was observed that the curves of consumption of methane for the carbides prepared on this work are very similar among them and also to those obtained by Decker et al. [27]. The maximum consumption of hydrocarbon occurs between 705 °C and 715 °C.

When the carburating mixture is formed by 10%C_2H_6/H_2, the reactional mechanism is different. The partial reduction of the oxide occurs initially producing the formation of water, however, with the increase of temperature, an increasing peak of CH_4 results simultaneously to the disappearance of the sign of C_2H_6. Figure 6 illustrates the monitoring of material CC 750E.

The carburation process starts at lower temperatures when using C_2H_6, in comparison with the one using CH_4. This fact may be attributed to the formation of free radicals coming from the decomposition of C_2H_6, which are more active than the molecule of CH_4. Effectively, according to Lange's Handbook of Chemistry [30] the necessary energy to break the bond of C–C is lower (368 kJ mol^{-1}) than the one demanded to break the bond C-H (431 kJ mol^{-1}). Such difference of energies indicate that the molecule of C_2H_6 is initially split into two radicals CH_3, which participate in the carburation process, and the peak of CH_4 that is monitored is due to the hydrogenation of these radicals. In this case, the final control of the reaction is an exclusive function of the sign CO, since is not possible to observe an end for the consumption of CH_4.

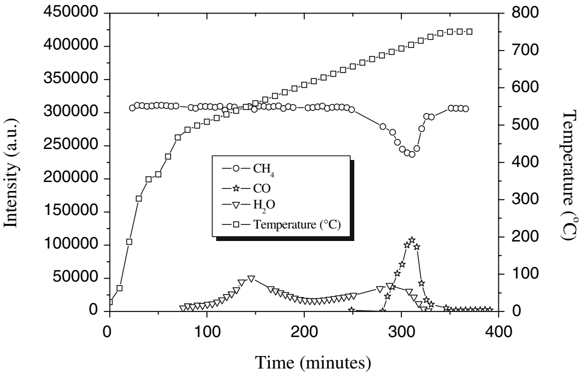

Fig. 5 Evolution of reactional components during the carburation of the material CC 750M with the carburating mixture 20%CH_4/H_2

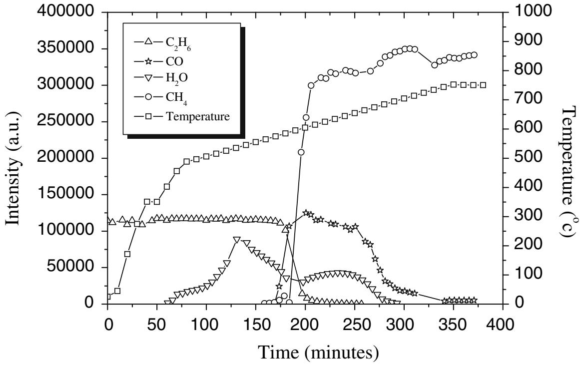

Fig. 6 Evolution of reactional components in gas phase during the carburation of the material CC 750E with the carburating mixture 10%C_2H_6/H_2

Another variable studied in this work was the density of sites, evaluated by chemisorption of CO.

St Clair et al. [31] and Choi et al. [4] determined the density of the sites of molybdenum carbides by chemisorption of O_2 and CO, admitting adsorption stoichiometries of $O_2/Mo_s = 1$ and $CO/Mo_s = 1$. The values found by Choi et al. [4] (0.80×10^{15} molecules of O_2 cm^{-2} and 0.48×10^{15} molecules of CO cm^{-2}) permitted to conclude that CO did not chemisorb on all the atoms of superficial molybdenum. The authors, based on basic theories of catalysis by metals and taking into account the values obtained, observed that the chemisorption of CO is a selective process; thus, CO is only adsorbed chemically on atoms of molybdenum that presents a similar behavior to the noble metals.

The chemisorption results of CO for the carbides prepared in this work and also for the Mo and W monometallic carbides are presented on Table 4.

Table 4 Sites densities obtained by CO chemisorption

Carbide	CO uptake (μmol g^{-1})	Surface area (m^2 g^{-1})	*n*CO ($\times 10^{15}$ cm^{-2})
CC 750M	414	95	0.26
CC 700M	405	100	0.24
CC 750E	531	115	0.28
CP 750M	320	68	0.28
CS 750M1	252	63	0.24
Mo_2C	150	50	0.18
WC	100	35	0.17

The analysis of Table 4 permits to observe that the values of chemisorption for the bimetallic carbides presented an average value 48% superior to those for the monometallic carbides. Among the bimetallic, the average value of n_{CO} was 0.26 ($\times 10^{15}$ molecules cm^{-2}) with a maximum deviation of 12.5%, considering that the bigger values were presented by catalysts prepared by alternative methods (Pechini and coprecipitation).

The similarity of the sites density values obtained for the bimetallic carbides, whatever was the method of synthesis used, permits to assume that the process of monitoring avoids or diminishes the formation of pirolytic carbon.

4 Conclusion

Among the preparation methods of W and Mo bimetallic oxides used in this work, it was evidenced that the coprecipitation was more efficient than the solid state reaction and Pechini's method, because it involves more moderated synthesis conditions which conduct to materials with significantly bigger specific areas. The process by coprecipitation produced bimetallic oxides constituted of particles with smaller dimensions. This justifies the increase of specific area described. The carburation mechanisms with the use of CH_4 or C_2H_6 are different. In the first case, the carburant agent is the CH_4 while in the second, the carburant agent is the CH_3 radical, coming from the dissociation of C_2H_6 molecule. The presence of CH_3radical, more reactive species than the CH_4 molecule, can explain why the carburation can be performed at lower temperatures when using C_2H_6. The monitoring process of the carburation reaction, surveying the consumption of the carburant agent and the formation of CO was essential for the definition of the time parameter in the final temperature of synthesis, because it permits to avoid or diminish the formation of pirolytic carbon as it is indicated by the similar values of density sites presented by all the bimetallic carbides prepared in this work.

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