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Abstract Unsupported Mo carbide and Mo nitride catalysts have been synthesized by temperature programmed synthesis, and characterized by X-ray diffraction, X-ray photoelectron spectroscopy, H₂-temperature programmed reduction and desorption and N₂ physisorption. These solid compounds have been tested for the hydrodechlorination (HDCI) of polychlorinated biphenyls (PCBs) at 1 bar in a fixed bed reactor. The Mo carbides and the corresponding Mo nitride phases showed a catalytic activity higher than a conventional HDS catalyst consisting of alumina-supported NiMo sulfides (~35 %). Aroclor 1260 HDCI conversion results were related to spilt-over hydrogen species that were proposed to favor the hydrogenolysis of C–Cl bond on refractory phases. The original PCBs broad distribution changed almost completely to non-chlorinated biphenyl on the carbide and nitride catalysts.

Keywords Mo carbide · Mo nitride · Hydrodechlorination · PCB · NiMo catalyst

1 Introduction

There is growing demand in the public opinion (as reflected from governmental and nongovernmental organizations

and from the scientific community efforts) that stocks, stores and environmental reservoirs of obsolete chemicals and persistent organic pollutants (POPs)-contaminated wastes must be rapidly identified, properly collected and correctly destroyed in order to arrest their continued migration into the environment. Such POPs are highly stable organic compounds used either as pesticides, in industry or unintentionally produced as the by-products of industrial processes (mainly incineration) and/or other human activity.

Chlorinated organic substances have been used in industry and some of them in abundance. A considerable quantity of chlorinated organic substances was accumulated in previous years as transformers and condenser oil; for instance, polychlorinated biphenyl (PCBs) stocks in Venezuela are estimated at just over 8,700 t [1]. Thus the threat of PCBs for the environment and health of population on a global scale is so serious that it requires urgent and effective measures. The technologies used for destroying stockpiles of POPs must meet the following fundamental performance criteria: (i) destruction efficiencies of effectively almost 100 % and (ii) containment of all residues and outflowing streams.

Liquid and gas phase catalytic hydrodechlorination (HDCI) of chlorinated and a polychlorinated aromatic compounds is a better process for the treatment of organic wastes as compared with the conventional incineration and other destructive methods. Advantages of HDCI include operations at relatively low temperature and pressure, high conversion, negligible harmful side products (e.g., dioxins), less sensitivity to pollutants concentrations and possibility of selective Cl removal. Furthermore, catalytic HDCI is now considered an alternative economically viable process for more efficient ecological treatments of chlorinated organic wastes [2–10]. Catalytic hydrodehalogenation of organic

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halides produce the corresponding hydrocarbons and hydrogen chloride. The produced HCl can be readily separated while the hydrocarbons can be recycled to minimize the waste. The potential destruction of chlorinated wastes by hydrogen over noble metal catalysts has been recognized for many years [11]; however, noble metal catalysts are particularly susceptible to poisoning by a range of compounds found in real world situations (e.g., H₂S, HCl), thus limiting the applicability of this technology. Therefore it is necessary to use catalytic systems more robust and tolerant to most catalyst poisons.

Carbides and nitrides of transition metals have been employed as catalysts in several catalytic applications [12–21]. These materials have a high mechanical strength and are resistant to corrosion, exhibiting appreciable chemical durability and thermal shock resistance. Due to the relative size of the non-metal versus metal atoms, groups 4, 5 and 6 elements tend to form the so-called interstitial carbides and nitrides. One consequence of interstitial carbide/nitride formation is a contraction of the d-band and modification of electron density that alters the adsorptive, electronic, magnetic and catalytic properties of the parent metal [16, 22–24]. Such interstitial compounds exhibit catalytic properties similar to those of the platinum-group metals [15, 16, 18]. In the last two decades the application of transition metal carbides and nitrides for hydrotreating reactions has been studied in great detail [19, 25–28]. Unfortunately, many of the studies of these reactions have been isolated examinations of a few types of compounds and widely varying catalysts have been employed. Information available on reactions of HDCl on transition metal carbide catalysts is very limited [29, 30]. The investigation of molybdenum carbide/nitride for treating PCBs gas streams could lead to the development of new HDCl catalyst materials.

The aim of this work was to contribute to the understanding of the surface mechanism involved in polychlorinated biphenyl HDCl over molybdenum carbide (or nitride) catalysts. HDCl conversion results were compared with a hydrotreating commercial catalyst (alumina-supported NiMoS).

2 Experimental

2.1 Synthesis

The synthesis of molybdenum carbide involved three stages. The first step consisted of the preparation of molybdenum oxide (MoO₃), obtained from ammonium heptamolybdate tetrahydrate (Merck). The salt was dried previously to calcination at 500 °C for 5 h. Afterwards, it was cooled to room temperature, and then ground to 35

mesh size. The second step involved the formation of molybdenum nitride by the temperature programmed synthesis method (TPS) from the oxide using a flow of ammonia. The MoO₃ powder was transferred to a quartz reactor, which was placed inside a tubular resistance furnace (Themolyne, 2100 model, vertically aligned), controlled by a temperature-programmer device. Gaseous NH₃ was passed through the oxide precursor at a flow of 66 μmol s⁻¹ for a 4.0 g batch of MoO₃. Then the temperature was increased at a linear rate (3 °C min⁻¹) from room temperature to 700 °C, and held at this temperature for 2 h. In third step, the flow was switched to a mixture of 20 vol% CH₄ in H₂ at a flow rate of 100 mL min⁻¹, and the nitrated samples were carburized isothermally for 2 h at 750 °C. To produce molybdenum nitride a stream of NH₃ was passed through the reaction cell, as described above using only steps 1 and 2. After either synthesis, samples were cooled down to room temperature and passivated with flowing O₂/Ar (<1 vol% O₂) for 30 min to avoid the mass oxidation of the solids.

Crystalline MoS₂ was synthesized by sulfidation of MoO₃ precursor passing a stream of H₂S/H₂ (10 vol% H₂S) through the powder at 800 °C for 4 h.

2.2 Characterization

Elemental analyses were performed on an inductively coupled plasma-optical emission spectroscopy (ICP-OES). Some standardized dissolution procedures were necessary to dissolve the sample. The CHN content of samples was determined by combustion using an Exeter Analytical CE440 Elemental analyzer.

The N₂ adsorption and desorption isotherms were measured on a Micromeritics ASAP 2010C instrument. Prior to the physisorption, fresh catalyst samples were vacuum-dried at 120 °C in N₂ flow for 30 min.

X-ray diffraction (XRD) patterns of the passivated samples were obtained using a Bruker D-8 Advance apparatus (Cu Kα radiation, λ = 0.154178 nm, nickel filter, 30 mA, 35 kV) with a scanning speed of 2° min⁻¹. Interpretation of XRD data was made by comparing experimental patterns with those reported in the standard JCPDF files.

The X-ray photoelectron spectra were recorded with a VG 220i-XL, spectrometer equipped with a Mg source (Mg Kα = 1253.6 eV). The analyzer was operated in a constant pass energy mode (E = 30 eV) using the electromagnetic mode for the lens. Binding energy correction was performed by using the O 1s peak of molybdenum (VI) oxide at 531 eV as a reference. The C 1s signal could be decomposed into graphitic-like carbon at 285 eV, C–O bond at 287 eV, and carbidic C–Mo at 282 eV. Experimental envelopes were decomposed into component peaks

using mixed Gaussian–Lorentzian functions and a nonlinear least-squares fitting algorithm; Shirley background subtraction was applied [31], and quantification was performed using the sensitivity factors reported by Wagner et al. [32]. Binding energies (BE) were reproducible to within ± 0.2 eV.

The temperature-programmed decomposition of the nitrides was performed on a flow system equipped with a mass spectrometer. The sample of 0.05 g was first pretreated under a N_2 stream at 600 °C for 30 min, and then cooled to room temperature. A 5 vol% H_2/N_2 stream (20 mL min^{-1}) was passed over the sample while it was being heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1} . The effluent gases were monitored continuously as a function of temperature. Temperature programmed desorption of H_2 (H_2 -TPD) was performed on Mo_2N and Mo_2C catalysts by a TPD/R/O apparatus (ThermoQuest TPD/R/O 1100 analyzer).

2.3 Catalytic Test

The catalytic tests were performed in a fixed-bed microreactor with a co-current downward flow of the PCBs feed in H_2 at 350 °C and atmospheric pressure for up to 2 h time-on-stream. The reactor temperature was monitored by a thermocouple inserted in a thermowell within the catalyst bed; reactor temperature was constant to within ± 1 °C. The H_2 (AGA gases) was passed through a Pd/C O_2 -trap before entering the reactor. The delivery of reaction gases were controlled by mass flow controllers (Porter Instrument Co.). A standard PCBs mixture of known chlorine content (Aroclor 1260) was used as feed. Aroclor 1260 is liquid at room temperature and was added to the reaction mixture by passing hydrogen through the PCBs/heptanes mixture in a saturator maintained at constant temperature (25 °C) using a thermostatic bath. The H_2 /PCBs molar ratio was kept constant at 750. To estimate the vapor pressure of commercial Aroclor 1260 it was used the Knudsen effusion method ($p_{\text{vap}} \sim 0.135 \text{ Pa}$). Before a new sample of catalyst was used, it was first sulfided with a flow of 60 mL min^{-1} H_2S/H_2 at 350 °C for 2 h. In order to avoid condensation, all lines of the experimental unit were heated. For quantification and identification of the PCBs congeners, the products were collected and analyzed off-line by GC–MS analyses using a HP 6890 series gas chromatograph with an HT8-PCB column (60 m, 0.25 mm i.d., 0.33 μm film thickness, SGE) and an AutoSpec Ultima mass spectrometer (Micromass). Following the end of the catalytic test, the used catalyst was cooled to room temperature and removed from the reactor for further analysis. GC-ECD analyses were performed in a separated Hewlett Packard 5890 gas chromatograph equipped with a HP-1 capillary column (25 m; 0.200 mm; 0.11 mm film

thickness). Single PCBs congeners (99 % purity, Accu-Standard) used to prepare calibration standards were obtained dissolved in iso-octane at concentrations of 35 or 100 mg mL^{-1} .

After exiting the system, the gases flowed through a caustic wash trap (KOH) to neutralize the HCl in the stream before being vented. Chlorine concentration was determined by measurement of the ionic conductivity (Amber Science, model 3082). A chlorine balance between the reaction feed and effluent showed closures of >95 % for all of the catalyst activity data reported herein.

All catalytic tests were repeated three times to assure reproducibility. Preliminary experiments indicated that no diffusional limitations were present within the range of operating conditions. In a blank test, passage of the PCBs in a H_2 stream through the empty reactor, did result in a very slight conversion. The commercial catalyst NiMo/ Al_2O_3 (Aero HDS 3A, specific surface area $\sim 200 \text{ m}^2 \text{ g}^{-1}$) was used to compare its activity with the synthesized unsupported Mo carbide/nitride catalysts for the HDCl of PCBs. The catalyst was crushed to a particle size of 35 mesh and presulfided at 350 °C for 2 h in a flow of 15 vol% H_2S/H_2 at flow rate of 100 mL min^{-1} . The sulfided catalyst was subsequently stored in decane to minimize oxidation.

3 Results and Discussion

The ammonolysis of molybdenum trioxide resulted in a black powder. The product composition was determined to be $Mo_2N_{1.07}$, by elemental analysis (N: 6.87 wt%), while the carburization of the molybdenum nitride also yielded a black powder of composition $Mo_2C_{1.01}$ (C: 5.97 wt%).

The BET specific surface area (SSA), total pore volume (TPV) and average pore diameter (APD) of different solid samples are shown in Table 1. The SSA of the MoO_3 precursor, obtained by N_2 physisorption at -197 °C, was found to be $4 \text{ m}^2 \text{ g}^{-1}$. After sulfidation at 800 °C, the surface area was $5 \text{ m}^2 \text{ g}^{-1}$. The SSA of the synthesized molybdenum nitride and carbide were 12 and $13 \text{ m}^2 \text{ g}^{-1}$, respectively. These surface areas are low compared to those reported in the literature [17, 18], probably due to the high heating rates employed in this study.

In order to determine the phase composition and crystal structure of the synthesized powders, XRD measurements were carried out on the samples. The XRD patterns of the molybdenum trioxide precursor and passivated carbided/nitrided solids are shown in Fig. 1. The oxide precursor pattern shows lines corresponding to MoO_3 according JPCPDF file No 76-1003 (Fig. 1a).

The XRD patterns of molybdenum nitride and carbide are shown in Fig. 1b, c. A single phase, γ - Mo_2N , was

Table 1 BET specific surface area, average pore diameter, and total pore volume

Sample	SSA _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	APD ^a (Å)
MoO ₃	4	0.00658	77
Mo ₂ C	13	0.00513	41
Mo ₂ N	12	0.03096	175
MoS ₂	5	–	–

^a Pore diameter determined from the adsorption isotherms by the BJH method

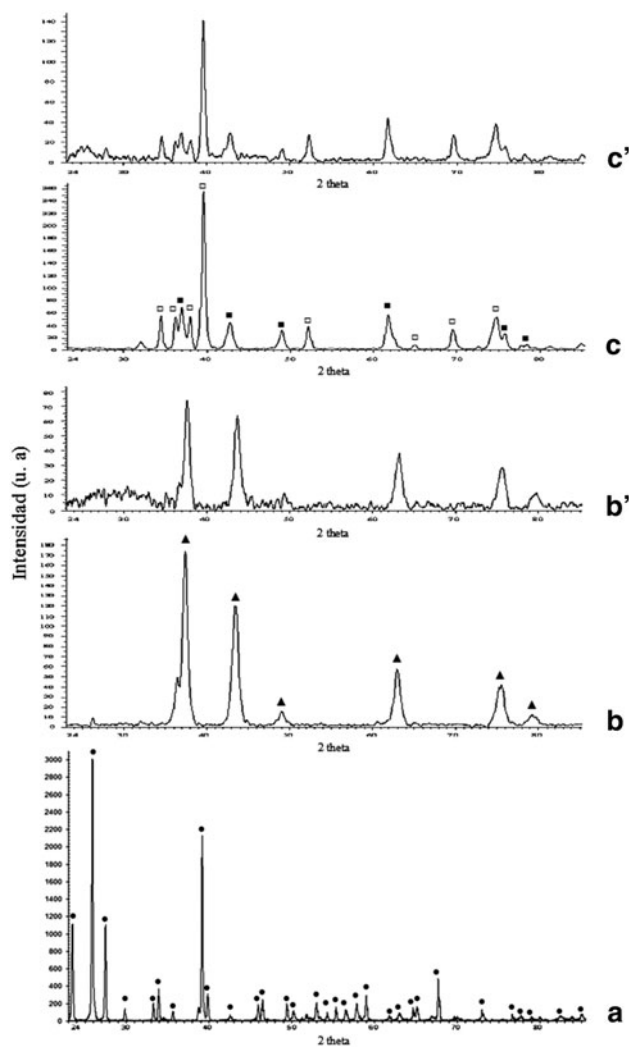


Fig. 1 XRD patterns of synthesized solids. **a** Precursor, **b** fresh Mo-nitride, **b'** spent Mo-nitride, **c** fresh Mo-carbide, and **c'** spent Mo-carbide. Crystallographic phases: MoO₃ (circle); γ -Mo₂N (triangle); α -Mo₂C (filled square), and β -Mo₂C (open square)

observed in the case of the nitride, while a mixture of two phases was obtained for the carbide; both the stable hcp β -Mo₂C as well as fcc α -MoC_{1-x} were produced under the conditions used. Given the results of the elemental analysis, and following Keane et al. [29], the metastable fcc

phase will be designated from this point onwards as α -Mo₂C. It can be seen that there are no diffraction peaks attributed to Mo oxides or other Mo compounds besides those of α -Mo₂C, β -Mo₂C and γ -Mo₂N. These results are in agreement with the elemental analysis of the unsupported samples which showed the approximate compositions of C and N for the stoichiometric compounds. The findings with the samples have show that the oxide-to-nitride and nitride-to-carbide transformations are topotactic (retention of external particle size and shape). Thus, it was found that the original [010] planes of MoO₃ were parallel to the [001] planes of γ -Mo₂N, and similarly those planes were parallel to the [001] planes of α -Mo₂C [33]. This explains the presence of the less stable α -Mo₂C phase in our synthesized molybdenum carbide. There was no evidence of crystalline MoO₃ in the bulk of catalysts passivated at room temperature. No crystalline oxycarbides or oxynitrides were observed in the XRD patterns.

The XRD data provides details of the crystallographic structure of materials; however it provides little information about the surface structure of materials which is hugely important in catalysis. Thus, XPS analysis was performed over molybdenum nitride and carbide.

The XPS results for prepared solids are summarized in Tables 2 and 3. For Mo₂C, a characteristic species with a Mo 3d_{5/2} binding energy lower than 229.0 eV was identified. According to the literature, the binding energy (BE) found around 228.0 eV can be attributed to a carbide phase [34] close to molybdenum in a zero-valent state, which is generally found at 227.9 eV in bulk molybdenum carbides [35]. It has been denoted as Mo^{δ+} and is assumed to be involved in a Mo–C bond. A Mo^{δ+} species is also present in Mo₂N, as revealed by a signal at similar BE. For molybdenum carbide, the carbon C 1s signal was also deconvoluted. Three components were found, the lowest binding energy one being attributed to carbon from the carbide phase, this component appearing at 283.3 eV. A second component around 284.6 eV was attributed to adventitious, graphite-like carbon and a third component, at higher binding energy, was attributed to oxidized carbon entities (C–O) [36], probably remaining from the passivating treatment. On the other hand, molybdenum nitride shows an N 1s signal at 396.9 eV. This signal had been previously reported [37] for nitrides.

There is a large proportion of oxygen at the surface, the O/Mo atomic ratio being much higher than the C/Mo or N/Mo ones (Table 3). Thus, although XRD does not reveal the presence of oxidic phases, the passivation treatment does oxidize efficiently the outer surface species of both catalysts.

Hydrogen TPD of the catalysts is a useful method that can help in understanding the heterogeneity of catalyst surface and the nature of interaction between hydrogen and catalytic surface species. The H₂-TPD profiles of Mo₂C and Mo₂N

Table 2 XPS binding energies data of precursor and catalysts

	Mo 3d _{5/2}			O 1s			S 2p _{3/2}			C 1s			N 1s
	Mo ^{δ+}	Mo ⁴⁺	Mo ⁶⁺	Mo ⁴⁺	Mo ⁶⁺	ads	S ²⁻	S ₂ ²⁻	S ⁰	Graphite	C _{carbide}	C–O	N _{nitride}
MoO ₃													
f	–	–	232.4	–	–	–	–	–	–	–	–	–	–
Mo ₂ N													
f	228.0	230.0	232.0	530.1	530.9	532.9	–	–	–	–	–	287.3	396.9
s	228.0	230.0	232.0	529.9	530.9	532.2	161.5	163.0	164.0	–	–	287.3	396.9
Mo ₂ C													
f	228.4	229.6	232.2	530.2	530.9	533.0	–	–	–	284.7	283.3	286.1	–
s	228.0	230.0	232.0	529.9	530.9	533.0	161.5	163.1	164.1	284.6	283.3	286.1	–

δ+: 0 < δ < 2

f fresh; s spent

Table 3 XPS analysis of fresh and spent catalysts (at.%)

Sample	C	N	O	S	Mo	S/Mo	C/Mo	N/Mo	O/Mo
Fresh									
Mo ₂ C	3.84	–	47.31	–	28.59	–	0.89	–	4.16
Mo ₂ N	–	10.55	28.30	–	30.15	–	–	1.38	2.36
Spent									
Mo ₂ C	2.80	–	44.57	2.34	20.75	0.35	0.90	–	5.40
Mo ₂ N	–	9.64	38.77	2.57	29.20	0.27	–	1.30	4.08

catalysts are shown in Fig. 2. For both catalysts, there were two main desorption peaks, centered at about 143–405 °C for the Mo₂C catalyst and at about 100–502 °C for the Mo₂N catalyst. The low temperature peak is related to chemisorbed hydrogen on metal surfaces [38], while the one at higher temperature peak has been assigned to spilt-over hydrogen [39]. Compared with the Mo₂C catalyst, the Mo₂N catalyst possessed more spilt-over hydrogen species as illustrated in the H₂-TPD results. It must be remembered that group 6 carbides and nitrides have been reported to show noble metal-like catalytic behavior [15, 16, 18]. Associated with the catalytic performance, it was suggested that the spilt-over hydrogen species played an important role in the HDCl. Shin et al. [49] reported that conversions depend not only on the surface metal area but also on the amount of spilt-over hydrogen, which being hydrogenolytic in nature is responsible for promoting HDCl activity. Molybdenum carbides and nitrides are capable of adsorbing, activating and transferring active surface hydrogen to reactant molecules. Thus, they fulfill the essential requirement to be active hydro-treating catalysts. Even though a more accurate discussion of this point is complicated due to lack of knowledge about the surface composition of Mo-(carbide/nitride) catalyst, it is worth stressing that the presence of mixed Mo₂C(or Mo₂N)–MoS₂ seems to be useful for chlorine removal. Although a complete analysis of the state on the catalyst surface is not

easy because of a great variety of species (chlorine/chloride, coke, including chloro-containing compounds) attached more or less strongly on the metal surface, the C–Cl bond dissociation appears to be a rate-determining step in HDCl.

The decomposition profile of the as-prepared Mo₂N sample is presented in Fig. 3. Over the sample, no notable presence of N₂ signal at low temperatures, while about 600 °C there was an increase in the amount. There are also desorption peaks of NH₃ and H₂O in the low temperature range from 50 to 400 °C. Since the freshly nitride sample was synthesized in a flow of NH₃, it is reasonable to presume that there are NH_x species on the sample surface. The NH₃ peak could therefore be considered as the result of desorption of weakly adsorbed NH₃. The N₂ peak at higher temperatures (>600 °C) can be considered as a result of nitride decomposition; it can be seen that part of the Mo₂N started to decompose at 600 °C with the release of nitrogen.

Because hydrogen desorption does not result from molybdenum oxidation by adsorbed protons and desorbed water (Fig. 3), such hydrogen must be present in the spill-over form. Notoriously, the hydrogen adsorption by molybdenum nitride is more extensive than that on Mo₂C. In this sense, Colling and Thompson [43] have suggested that the hydrogen adsorbed on the Mo-nitride surface migrated into the crystallites interior which served as the hydrogen “reservoir”. The amount of hydrogen retained

increased with the decreasing SSA and/or the increasing size of the crystallites [44]. The later observation is consistent with the studies of Choi et al. [45, 46] who observed increased activity during the hydrodenitrogenation of pyridine with the decreasing surface area of Mo₂N. We must keep in mind that Nagai et al. [47, 48] have suggested that the major desorption peak was observed at ~550 °C, which is coincident with the decomposition of NH_x

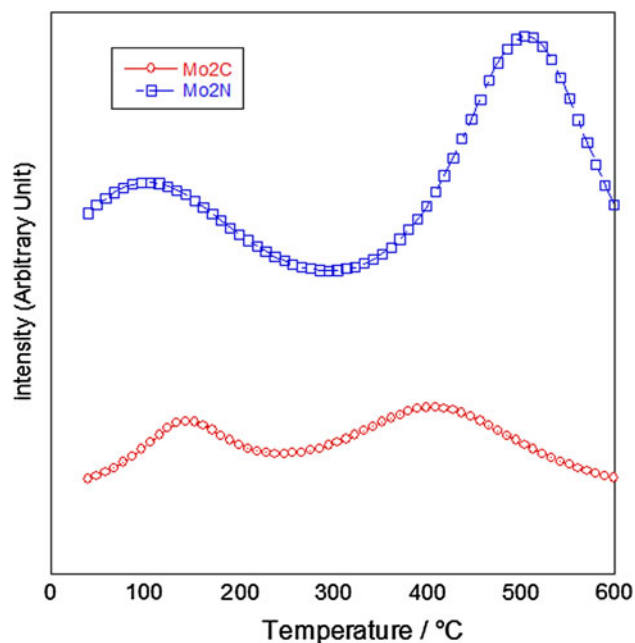


Fig. 2 H₂-TPD profiles of Mo₂N and Mo₂C after hydrogen adsorption

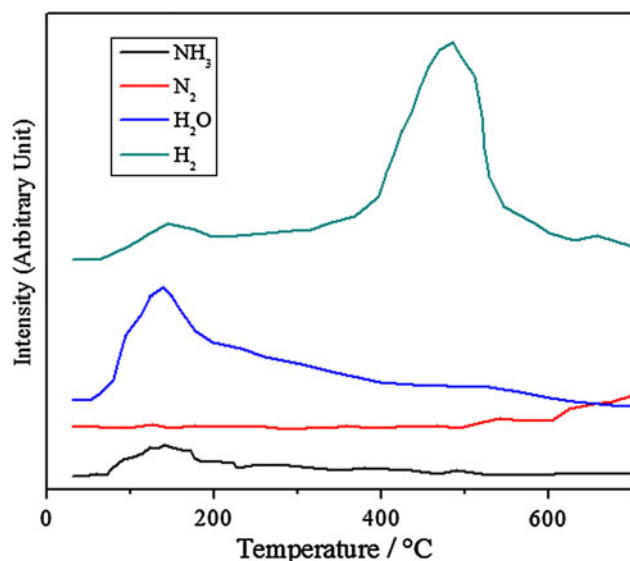


Fig. 3 Hydrogen TPR profiles of Mo₂N passivated

species. However, our TPR results showed in Fig. 3 indicate no evolution of either NH₃ or N₂ near this temperature. So our results show unequivocally a kind of subsurface hydrogen. We assign the high temperature H₂ desorption (irreversible) to spillover hydrogen stabilized by species present on the surface of molybdenum nitride (or molybdenum carbide).

By the above discussion, the TPD results suggest that hydrogen is strongly held, apparently on the nitrogen (or carbon) deficient patches of Mo atoms on the surface or either it entered into the lattice of Mo₂N (Mo₂C) [19]. However, few attempts have been made in the literature to propose a convenient mechanism of the hydrogen adsorption/activation by Mo-carbides and nitrides. Therefore, the limited information only allows a tentative discussion. In

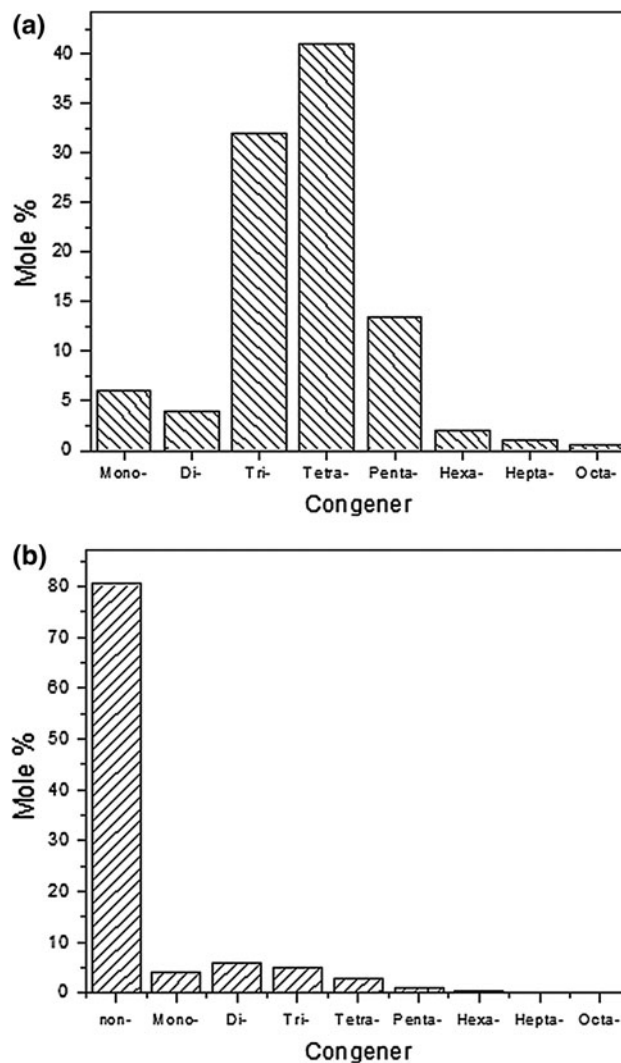


Fig. 4 Products distribution after PCBs hydrodechlorination reaction using Mo-carbide catalyst. **a** Original Aroclor 1260 and **b** Hydrotreated Aroclor 1260

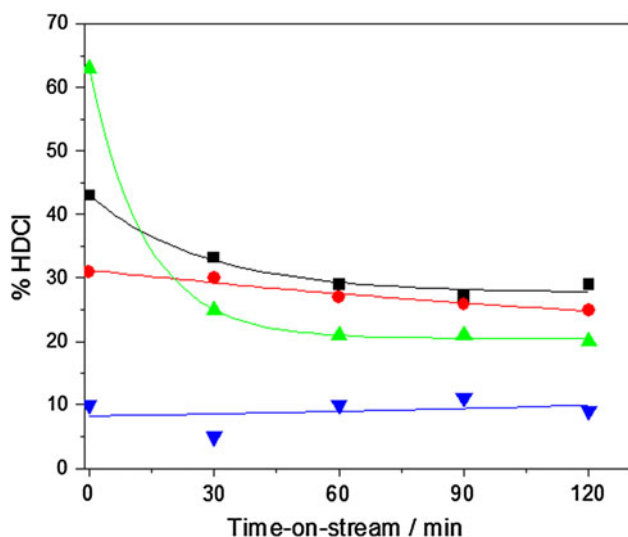


Fig. 5 PCB HDCI conversion: MoS₂ (blue inverted triangle), Mo-carbide (red circle), Mo-nitride (black square) and reference NiMoS alumina catalyst (green triangle)

our understanding, the migration of hydridic species from the surface to the sub-surface layer and/or interstices may occur, and this sub-surface hydrogen can be efficiently transferred to reactant molecules during surface reaction. Moreover, we should consider that under typical hydro-processing conditions, when sulfur is present in the feed, the surface of metal carbides/nitrides could be modified. The surface of Mo carbide (nitride) may include the pairs of Mo-S and Mo-carbide (or Mo-nitride) as active sites for hydrogen activation. This involves the formation of additional sites to those which are previously present.

Such modification will occur principally on the outermost surface of Mo-carbide (or Mo-nitride) crystals. Mo₂C and Mo₂N catalysts were characterized after HDCI runs. Elemental analysis shows widespread retention of sulfur with time-on-stream. The carbon content of the post reaction Mo₂C sample is in relatively good agreement with the calculated carbon contents for these materials. In the case of γ -Mo₂N the slightly lower nitrogen content could be explained by the incorporation of sulfur into the structure. XRD of the spent catalysts shows that they retain their bulk carbide and nitride phases (Fig. 1b', c'). There was not crystallographic evidence of MoS₂ in the XRD patterns, leading to conclude that there is not a substantial modification of the materials during the HDCI reactions. Thus, XRD indicates the tolerance to MoS₂ formation; however, sulfur could be remaining onto the material.

Figure 4 shows the difference in PCBs distribution between the original (Fig. 4a), and the hydrotreated Aroclor 1260. Note that in the carbide hydrotreated samples (Fig. 4b), the PCBs distribution changed essentially to non-chlorinated biphenyl. The same result was obtained for the nitride (not shown). The obtained results

indicate that the Mo-carbide and Mo-nitride catalyst had better HDCI activity than the NiMoS/alumina catalyst. Furthermore, these catalysts also yielded products with lower chlorine contents. There is a possibility that binary phases could be formed between the metal sulfides and carbides/nitrides, which would further contribute to the enhanced activity. In general, these results suggest that the nitride catalyst was slightly more active toward chlorine removal.

The catalytic behavior of Mo₂N and Mo₂C prepared by TPS was examined for HDCI of PCBs. Figure 5 shows conversions of PCBs (Aroclor 1260) as a function of reaction time-on-stream for Mo₂N, Mo₂C, MoS₂ and a commercial NiMoS catalyst. The HDCI conversion of the molybdenum carbide and nitride catalysts was substantially higher than that of the blank reactor (<1 % conversion), and it is noticeable that they were active. The catalysts showed no signs of deactivation for the duration of the run of 2 h. The blank reactor product characteristics are close to those of the feed.

It can be noticed that the catalysts show XPS O 1s signal after HDCI reaction, which could be due to residual oxygen arising from the passivation. The XPS data for the molybdenum carbide/nitride catalyst withdrawn from the reactor are reported in Tables 2 and 3. Sulfur-to-molybdenum ratio for carbide and nitride were 0.35 and 0.27, respectively. Both values are well below the expected ratio of 2 should MoS₂ have been formed within the sampling depth for XPS. Consequently, it does not appear that extensive sulfiding of the molybdenum nitride or carbide occurred during their use. A concern with using molybdenum carbide and nitride for hydrotreating applications is that the formation of molybdenum sulfide is thermodynamically favored in the presence of sulfur [40]. Thus, it is possible that some MoS₂ were formed at the topmost atomic layers of the carbide (nitride) surface. The decomposition of the S 2p peak of catalyst indicates the presence of three sulfur species with S 2p_{3/2} BE at 161.5, 163.0 and 164.1, assigned to S²⁻ and S₂²⁻ species, and elemental sulfur, respectively [41, 42]. An analysis of the oxidation states of molybdenum in the used molybdenum carbide and nitride catalysts indicates that not all the molybdenum was reduced to the Mo⁴⁺ state during the pre-treatment and reaction. These spectroscopic results confirm that the final materials present some oxygen and sulfur phases (oxide and MoS₂-like) rather than pure Mo₂C/Mo₂N. Thereafter, chlorine was not observed on the catalyst samples surfaces after HDCI.

One final remark about PCBs HDCI, none dioxins were formed in the reducing environment and the recovery of valuable chemical feedstock is facilitated. Moreover, the HDCI temperature employed in this study (350 °C) is significantly lower than that associated with catalytic

combustion. This hydroprocessing strategy promotes an efficient use of resources, greatly reducing both direct and indirect waste/emissions costs and fosters sustainable development.

4 Conclusion

The synthesis of unsupported Mo carbides was carried out by the ammonolysis and subsequent carburization of the metal phases from methane decomposition onto dispersed metal oxide. The Mo nitride was prepared by direct ammonolysis. The XRD characterization of the Mo carbide and nitride showed the presence of several phases, i.e., β -Mo₂C, α -Mo₂C and γ -Mo₂N. In the HDCI of polychlorinated biphenyls (Arochlor 1260), the catalytic properties of the refractory phases were generally outstanding with respect to the reference catalysts based on NiMoS/Alumina, which was closely related to its more spilt-over hydrogen species that was proposed to favor the hydrogenolysis of C–Cl bond. The unsupported Mo carbide or nitride will be promising catalysts for HDCI process.

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