ON THE SYNTHESIS OF MOLYBDENUM CARBIDE WITH COBALT ADDITION VIA GAS-SOLID REACTIONS IN A CH₄/H₂ ATMOSPHERE

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Abstract - Due to ever more severe environmental regulations regarding SOₓ, NOₓ and other pollutants’ emissions, there has been an interest in developing new and improved catalysts for hydroprocessing reactions. Mo₂C has been reported to display good selectivity and activity for those reactions, especially for HDS. Addition of another metal to the carbide structure may improve catalytic properties. Mo₂C with low cobalt addition (2.5 and 5%) was obtained via gas-solid reaction in a fixed bed reactor with CH₄ (5%)/H₂ atmosphere. XRD and TG/DTA analysis of the precursors were carried out in order to understand its mass loss profile, doping metal presence and phase distributions. CoMoO₄ as well as MoO₃ were identified after calcining doped precursors at 600 °C/180min. SEM, XRD, XRF, BET and laser granulometric analysis of the reaction products were also performed. Compositions verified by XRF and theoretical values were compatible. At 700 °C both carbide (Mo₂C) and oxide (MoO₃) phases are present, as identified in XRD analysis and observed by SEM. At 750 °C only single phase Mo₂C was verified by XRD, indicating Co dispersion on the carbide matrix. Morphology at this temperature is compatible with pure Mo₂C, though XRF indicates Co presence on the material.

Keywords: Molybdenum carbide; Cobalt; Fixed bed reactor; Solid state doping.

INTRODUCTION

Environmental regulations related to the emission of sulfur compounds constantly decrease the maximum allowed content of this element in transportation fuels (ANP, 2013). This, associated with the increase of contaminant content in crude oil worldwide, has introduced severe changes in processing of petroleum feeds, requiring more hydrogen, catalysts and heat input, which increase operational costs (Grange and Vanhaeren, 1997; Furimsky, 1998). This scenario points towards the need of developing new and improved catalysts that could substitute the traditional Ni(Co)-Mo(W)/Al₂O₃ materials currently in use. Transition metals carbides and nitrides, especially...
Mo, W, and Nb, find interesting applications in heterogeneous catalysis for important industrial reactions, especially for hydroprocessing, such as hydrogenation of heavy fractions and HDS (Furinsky, 2003), as well as for catalytic oxidation (Gomes, 2006), FT reaction (Griboval-Constant et al., 2004), methane reforming (Cheng and Huang, 2004), HDN (Al-Megren, 2005; Al-Megren, 2007) and others (Nagai and Matsuda, 2006; Vieira, 2010; Oyama, 1992a; Oyama, 1992b; Volpe and Boudart, 1985; Matar et al., 1988; Serge, 2003). These materials, besides having catalytic behavior similar to noble metals, also present resistance to poisoning by sulfur compounds which is an important feature of catalysts for HDT reactions (Oyama, 1992a,b).

For its use in catalysis, carbide materials are required to display a high density of active sites, small particle size and a surface area free of pollutants such as carbon or others that could impair the reaction process (Oyama, 1992a; Volpe and Boudart, 1985). These features can improve the contact between catalysts and reactants, and enhance the catalytic process (Matar et al., 1988; Serge, 2003).

Traditionally, carbide production derives from metallurgical processes where liquid metal is reacted with a carbon source, usually carbon black, at high temperature (1500 – 2300 °C) (Pierson, 1996; Atkins and Jones, 2006). This process, besides high temperature and energy, also demands for long residence time in order to overcome solid-state diffusion limitations (Borovinskaya et al., 2012).

Another route for producing monometallic carbides was developed in the 1980’s at lower temperature ranges, typically by a TPR (Temperature Programmed Reaction) method using gaseous carbonaceous materials as carbon source (Oyama, 1992a; Volpe and Boudart, 1985; Lee et al., 1987).

An increase of the density of active sites and, therefore, of the catalytic activity, could be attained by adding other metals to the carbide structure ideally forming systems which were similar in composition to catalysts currently in use for HDT, i.e., low Co/Mo ratio.

Bimetallic synthesis of carbide materials has been studied by several authors (Xiao et al., 2001; Cheng and Huang, 2004; Al-Megren, 2005; Nagai and Matsuda, 2006; Nagai et al., 2007; Wang et al., 2008), usually with compositional range above 10%Co/Mo. Most of these precursors are also prepared with high carbon source content in the gas mixture: ≥20% for CH₄ (Cheng and Huang, 2004; Nagai et al., 2007; Izhar and Nagai, 2008; Izhar et al., 2009; Ma et al., 2014) or ≥10% for C₂H₆ (Al-Megren, 2005; Al-Megren, 2007). This can produce a higher free carbon percentage in the final product and ultimately impair the catalytic process.

This paper aims to evaluate the synthesis and characterization of molybdenum carbide with low Co addition (Co/Mo=2.5 and 5 mol%) at two temperature levels (700 and 750 °C) by using a carburizing/reducing atmosphere with low CH₄ content (5%) in order to avoid free carbon formation.

Reaction products were characterized by XRF, XRD, SEM, BET, TOC and granulometric analysis. Crystal sizes were calculated by the HWL (Halder-Wagner-Langford) equation with the integral method.

MATERIALS AND METHODS

Precursor Synthesis

Ammonium heptamolybdate (AHM) [(NH₄)₆Mo₇O₂₄.4H₂O] (VETEC, Brazil, 99%) and cobalt nitrate [Co(NO₃)₂.6H₂O] (CROMATO, Brazil, 98%) were manually mixed at the 2.5 and 5% molar ratios (Co/Mo) with mortar and pestle. These materials, hereafter called precursors, were subject to carbo-reduction reaction in order to synthesize the carbide materials.

TG/DTG (NETZSCH TG 209F3- Al₂O₃ crucible) analysis was carried out on precursors with 5% Co, on pure AHM, and on cobalt nitrate. All analysis’ were performed in a stagnant nitrogen atmosphere with 5 °C.min⁻¹ heating rate from room temperature (25 °C) to 700 °C in order to evaluate the mass loss behavior.

Precursors with 2.5 and 5% Co were calcined in a muffle furnace (EDG Inox Line 3000, Brazil) at 600 °C for 180 min for phase composition evaluation by XRD (SHIMADZU XRD- 6000, Cu Ka, operated at 30 kV and 30 mA, 2°.min⁻¹) as in the reactant atmosphere it is expected that the materials obtained via calcination are present, to some extent, as intermediates.

Carbide Synthesis

For the carbide synthesis, approximately 2 g of the precursors produced from the physical mixture of reactants, were loaded into an alumina crucible and subjected to the carbo-reduction reaction in an alumina fixed bed reactor (d_{in}=35 mm, ℓ = 80 cm), coupled with a resistance furnace (EDG Tünel FTHI-40, Brazil). This system is presented on Figure 1, where the flow control system is also indicated.

An argon (Linde, Brazil, >99%) atmosphere was
used to purge the reactor for ~20 min before the reaction. Then the CH₄ (Linde, Brazil, >99%) and H₂ (Linde, Brazil, >99%) flow was started at a total flow rate of 15 L h⁻¹ with 5% of CH₄. Heating rates of 5 °C min⁻¹ and a soaking time of 180 min were used for the materials synthesized at 700 and 750 °C. Samples were tagged according to the cobalt/molybdenum ratio followed by reaction temperature (x % - T °C).

In Figure 2 four weight loss steps can be identified, accounting for a total loss of 18.97%. This result is compatible with the production of MoO₃ if (NH₄)₀₋₆Mo₇O₂₄·₄H₂O is considered to be the starting material. This is also in good agreement with the data published by Weinold et al. (2003) for AHM. All steps are accompanied by endothermic DTG signs which are relative to water and ammonia evolution of the material throughout the temperature range (RT~450 °C).

Figure 1: Fixed bed reactor coupled with resistance furnace. 1) CH₄ mass flow controller; 2) H₂ flow meter; 3) Argon flow meter; 4) Alumina crucible; 5) Resistance furnace; 6) Alumina reactor; 7) Sealing system; 8) Bubble system.

Reaction products were packed in suitable containers (closed plastic sample holders) once room temperature (25 °C) was reached. Afterwards samples were characterized by XRF (SHIMADZU EDX-720, air atmosphere), XRD, BET (Micrometrics, ASAP 2020), TOC (SHIMADZU Total Carbon Analyzer with 400ml/min O₂ flow at 900 °C) and SEM (SHIMADZU MEV SSX550 with amplifications in the range of 3, 5 and 8.10³X).

Crystallite size was estimated by the HWL (Halder-Wagner-Langford) method with integral calculations from the mathematical profile obtained from XRD data. Laser granulometric analysis (CILAS 920 from 0.30 – 400 μm, using water as medium with no dispersing agent) were also performed.

RESULTS AND DISCUSSION

Precursors Analysis

Thermal Analysis

TG/DTA analysis was carried out on pure AHM (Figure 2), on cobalt nitrate (Figure 3), and on the precursor with 5% Co (Figure 4).
Two endothermic events between room temperature and ~180 °C are relative to water volatilization, and can only be distinguished by DTG curve evaluation. In comparison with Figure 2, for the temperature range between ~100-140 °C, only one event is present and is also attributed to water evolution. In Figure 3 the same event is present but in a lower temperature range (from RT to ~70 °C).

The third decomposition step of the 5%Co precursor occurs between 180-230 °C and is attributed to NOx elimination by nitrate groups of Co(NO3)2.6H2O, which is in accordance with the TG data presented here in Figure 2, and accounts for a total of 2.81%. The two last events, from 230-320 °C and from 320-430 °C, are related to ammonia and water evolution and account for a total of 8.07%.

**XRD Analysis**

Figure 5 shows XRD patterns for precursors with 2.5 and 5% Co addition calcined at 600 °C for 180 min. Peaks marked with ■ refer to CoMoO4 (ICSD: 023808) phase, whereas peaks marked with ● display a mixed contribution of both CoMoO4 and MoO3.
MoO$_3$ phases. All other peaks refer to the MoO$_3$ (ICSD: 076651) phase. MoO$_3$ phase shows orthorhombic structure, while the CoMoO$_4$ phase is monoclinic. A MoO$_3$ phase with this structure was identified by other authors for the thermal decomposition of AHM (Weinold et al. 2003), whereas CoMoO$_4$ was found in the synthesis of bimetallic Co-Mo carbides from various starting materials with Co and Mo (Cheng and Huang, 2010).

Upon decreasing the Co content, an intensity decrease in CoMoO$_4$ peaks at 14.5, 23.4, 27.3, 28.2 and 32.6 can be noted. This is more pronounced for the peak at $\theta=32.6^\circ$, which is no longer identified for the lower compositional level. As the Co/Mo atomic ratio increases, the CoMoO$_4$ diffraction peaks become more intense, suggesting that more CoMoO$_4$ is being formed in the bimetallic oxides (Cheng and Huang, 2010).

### Reaction Products Analysis

### X-Ray Fluorescence

Cobalt content in the final product was determined by X-ray Fluorescence. Table 2 shows the data obtained. It can be noted that there is agreement between expected and achieved values, showing that only relatively small loss occurred during the process. To our knowledge only a few papers, (Griboval-Constant et al., 2004; Al-Megren et al., 2005) present quantitative chemical or physical analysis for the elemental composition of the produced materials. The majority of the published articles present their phenomenological analysis based on labeling materials according to intended metal addition, as in the works of Cheng and Huang (2010), Al-Megren et al. (2007), Nagai and Matsuda (2006), Nagai et al. (2007) and Chen et al. (2013).

The data presented by Al-Megren et al. (2005) show greater deviations (~43.4%) from the intended Co/Mo ratio than the verified values presented here. Griboval-Constant et al. (2004), however, managed to obtain ~3% deviations in their Mo$_2$C supported Co catalysts.

### Table 2: Co Content in the Final Product (XRF).

<table>
<thead>
<tr>
<th>Sample</th>
<th>%wt. Co</th>
<th>(%)Co/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5% - 700 °C</td>
<td>1.349</td>
<td>2.23</td>
</tr>
<tr>
<td>2.5% - 750 °C</td>
<td>1.359</td>
<td>2.24</td>
</tr>
<tr>
<td>5% - 700 °C</td>
<td>2.754</td>
<td>4.61</td>
</tr>
<tr>
<td>5% - 750 °C</td>
<td>2.762</td>
<td>4.62</td>
</tr>
</tbody>
</table>

### X-Ray Diffraction

Figure 6 shows XRD patterns for the products of the carburization reactions at 700 and 750 °C with 2.5 and 5% Co addition. Peaks marked with ■ refer to Mo$_2$C (ICSD: 065701) all other peaks refer to MoO$_2$ (ICSD: 062210). MoO$_3$ is not detected in the reaction products’ XRD pattern because it is reduced by H$_2$ forming MoO$_2$ before it is completely converted to carbides (Li et al., 1998). No cobalt-containing phases could be identified. This could be due to the low Co content added or due to the fact that this metal can be considered to be dispersed on the carbide structure. The absence of a cobalt-containing phase in the carburization product was also identified by other authors (Xiao et al., 2001) even when higher Co/Mo ratios were tested. The MoO$_2$ phase displays monoclinic structure, while Mo$_2$C is orthorhombic (Gomes, 2006; Wang et al., 2008; Li et al., 1998, Wang et al., 2006).

Figure 6: XRD patterns for the reaction products at 700 and 750 °C with 2.5 and 5% Co addition. △ refers to peaks of the MoO$_2$ (ICSD: 062210 monoclinic) phase, and ■ refers to Mo$_2$C (ICSD: 065701, orthorhombic) peaks.

Other authors indicate that, because the radius of cobalt atoms is smaller than that of molybdenum atoms, the incorporation of cobalt atoms into Mo$_2$C
will lead to a shift to higher diffraction angle (Cheng and Huang, 2010). This phenomenon was visualized in this paper, but with a much lower intensity than those authors were able to identify since the cobalt addition was also smaller. Table 3 summarizes these angle variations for the materials where only the carbide phase was identified. This is also an indication of the presence of Co atoms in the structure of the carbide as a promoter (Cheng and Huang, 2010).

**Table 3: XRD peak position deviations with increasing Co content for the materials where only the carbide phase was identified.**

<table>
<thead>
<tr>
<th>Peak number/Position (2Theta)</th>
<th>2.5%Co 750 °C</th>
<th>5%Co 750 °C</th>
<th>Δθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.346</td>
<td>34.365</td>
<td>0.019</td>
</tr>
<tr>
<td>2</td>
<td>37.912</td>
<td>37.949</td>
<td>0.037</td>
</tr>
<tr>
<td>3</td>
<td>39.393</td>
<td>39.416</td>
<td>0.023</td>
</tr>
<tr>
<td>4</td>
<td>52.107</td>
<td>52.136</td>
<td>0.029</td>
</tr>
<tr>
<td>5</td>
<td>61.559</td>
<td>61.582</td>
<td>0.023</td>
</tr>
<tr>
<td>6</td>
<td>69.541</td>
<td>69.561</td>
<td>0.020</td>
</tr>
<tr>
<td>7</td>
<td>72.455</td>
<td>72.468</td>
<td>0.013</td>
</tr>
<tr>
<td>8</td>
<td>74.649</td>
<td>74.681</td>
<td>0.030</td>
</tr>
<tr>
<td>9</td>
<td>75.598</td>
<td>75.619</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Crystal Size Estimates

Table 4 presents crystal size calculations for the reaction products. Calculations were carried out by applying the HWL integral method on the mathematical profile of the fitted XRD data. Correlation coefficients, as well as micro-strain estimates are also presented. For the materials produced at 700 °C, crystal sizes were 10.86 and 15.09 nm for samples with 2.5 and 5% of Co addition, respectively. At 750 °C the estimates were 30.55 and 43.25 nm for samples with 2.5 and 5% of Co addition.

Even with increasing reaction temperature the crystal sizes remained nano scale. It can be noted that, with increasing temperatures, crystal size increased (~180%), which is in accordance with Avrami’s theory (Avrami, 1940). The same effect can be verified upon increasing cobalt content, though with less intensity (~40%). This could be due to the fact that the Co radius is close to that of Mo and it could potentially deform the crystal network, as previously stated and verified above by XRD. Souto (2008) also verified this increase in crystal size with increase in dopant content for the synthesis of niobium carbide with copper addition. Xiao et al. (2001) also indicate that an increase in Co content would lead to an increase in particle size of the bimetallic Co-Mo carbide, which is in accordance with the phenomena observed here.

**Table 4: Crystal size calculation results for the reaction products. The HWL integral method was used. Correlation coefficients and micro strain estimates are also presented.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>HWL (nm)</th>
<th>ε</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%Co_700 °C</td>
<td>10.86</td>
<td>0.012</td>
<td>0.94</td>
</tr>
<tr>
<td>5%Co_700 °C</td>
<td>30.55</td>
<td>0.009</td>
<td>0.94</td>
</tr>
<tr>
<td>2.5%Co_750 °C</td>
<td>15.09</td>
<td>0.006</td>
<td>0.91</td>
</tr>
<tr>
<td>5%Co_750 °C</td>
<td>43.25</td>
<td>0.009</td>
<td>0.97</td>
</tr>
</tbody>
</table>

SEM

Scanning Electron Microscopy images are presented in Figure 7 for the reaction at 700 °C, and in Figure 8 for the carbides obtained at 750 °C. On the right side, the images refer to samples with 5%Co addition, and, on the left side, to samples with 2.5%Co addition. Highlighted regions of Figure 7(A) and (B) indicate agglomerating behavior, showing an increased tendency for agglomeration with increased Co content. In (C) and (E) the circled regions show both platelet morphology (MoO₂) and undefined morphology (Mo₂C). In Figure 8 only one type of morphology can be noted, which presents undefined shape and is attributed to the Mo₂C phase.
Figure 7: SEM images for reaction products at 700 °C. On the left side, samples with 2.5% Co, on the right side, samples with 5% Co addition. (A) and (B) with 500x magnification. (C) 1500x amplifications; platelet morphology as well as regions with undefined shape can be seen. (D) 2400x, absence of platelets morphology. (E) and (F) 10000x magnification; regions with platelets and undefined morphology.
Wang et al. (2006) indicate, for one, that MoO$_2$'s orthorhombic structure, which presents itself as fine platelets, can no longer be identified when carburized, as it turns into isotropic particle agglomerates formed by the broken intermediate oxide particles forming the carbide material. Other papers (Gomes, 2006; Vieira, 2010; Li et al., 1998; Medeiros et al., 2001) also identify agglomerates formed by particles of unidentified shape as relative to pure carbide phase. This is in agreement with the attribution applied here.

No indication of cobalt could be found by analyzing the morphological identity of the material.

**Carbon Content**

Carbon content was determined by total combustion of samples at 900 °C with pure O$_2$. Table 5 presents the total carbon content (%wt.), as well as the carbon to metal ratio. It can be noted that only for the sample synthesized at 750 °C with lower cobalt (2.5%) content a ratio above the theoretical 0.5 value was reached. This confirms the complete conversion of oxides to carbide materials, as well as the production of a small amount of free carbon (8.9%). All other samples display ratios below the theoretical value, indicating incomplete reactions; this phenomenon is more pronounced for the 700 °C samples, in accordance with the XRD data presented here. For the material with 5% Co produced at 750 °C, approximately 86% conversion was obtained. This high conversion could explain the difference between this data and the phases identified by XRD, as the majority of the material consists of carbide phase.

Griboval-Constant et al. (2004) produced molybdenum carbide with low ruthenium or cobalt addition, at 700 °C and 10%CH$_4$–H$_2$ with a 6 h soaking time and obtained carbon contents of 4.5 and 5.2% (wt.) for the doped materials. This is over 30% of the maximum carbon content verified here. A possible explanation would be the longer soaking time applied coupled with higher methane content in the reactant mixture.

Al-Megren et al., (2005) also evaluated the carbon content of their carbide materials and attained 6.1% wt. before the HDN reaction. This result is 78% above the highest value achieved in this paper. This higher carbon percentage is probably due to the carbon source used (C$_2$H$_6$) and its amount in the total mixture (10%).

As can be noted, the use of methane as a carbon source and shorter soaking times managed to reduce the free carbon content in the final product in comparison to these authors, though the synthesis of pure carbide materials needed a finer flow/synthesis control.

**Table 5: Carbon content analysis of the reaction products.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total carbon content (%wt.)</th>
<th>C/Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%Co 700 °C</td>
<td>1.84</td>
<td>0.31</td>
</tr>
<tr>
<td>2.5%Co 750 °C</td>
<td>3.45</td>
<td>0.59</td>
</tr>
<tr>
<td>5%Co 700 °C</td>
<td>2.17</td>
<td>0.37</td>
</tr>
<tr>
<td>5%Co 750 °C</td>
<td>2.71</td>
<td>0.46</td>
</tr>
</tbody>
</table>

**BET**

Superficial area was determined by BET analysis of the carburized materials and is presented in Table 6. Low values were obtained, as these materials were not passivized. No tendency regarding the change of parameters could be noted.
These surface areas values are compatible with the work of Griboval-Constant et al. (2004), who also verified (for molybdenum carbide with Ru or Co addition) superficial areas in the range of 3-9 m².g⁻¹, with the highest area being relative to pure Mo₂C (9.2 m².g⁻¹). Al-Megren et al. (2005) also managed to obtain superficial areas close to 20 m².g⁻¹ for bimetallic cobalt molybdenum carbide with a Co/Mo ratio of 0.67 produced by TPR with ethane at 10%

Xiao et al. (2001), however, by using an elaborate series of steps (mixture, dissolution in organic solvent, evaporation, calcination, pelletization and carbo-reduction reaction) were able to achieve higher superficial areas 15.5-39.6 m².g⁻¹. One would still need to provide an evaluation of the cost of these operations vs. superficial area increase, as these values are close to the ones obtained here and required much more processing.

### Table 6: BET evaluation of the reaction products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore size (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%Co 700 °C</td>
<td>16.68</td>
<td>0.040</td>
</tr>
<tr>
<td>2.5%Co 750 °C</td>
<td>24.39</td>
<td>0.040</td>
</tr>
<tr>
<td>5%Co 700 °C</td>
<td>16.76</td>
<td>0.030</td>
</tr>
<tr>
<td>5%Co 750 °C</td>
<td>17.88</td>
<td>0.025</td>
</tr>
</tbody>
</table>

### Laser Granulometric Analysis

Laser granulometric analysis was carried out on the carburized materials to identify if the tendency noted in SEM analysis could be extended to the entire material. Figure 9 shows the distributions obtained. Table 7 provides the data for average agglomerate diameter, and the diameter obtained when the smallest 10, 50 and 90% fractions of the distribution were considered.

![Results for the laser granulometric analysis of the reaction products.](image-url)

**Figure 9:** Results for the laser granulometric analysis of the reaction products. (A) at 700 °C with 2.5%Co and d_{average} = 14.94 μm. (B) at 750 °C with 2.5% Co and d_{average} = 26.34 μm. (C) at 750 °C with 5% Co and d_{average} = 39.85 μm. (D) at 750 °C with 5%Co and d_{average} = 168.45 μm
Table 7: Agglomerates size distribution for the reaction products. The cut sizes for 10, 50 and 90% of the particles are presented, as well as the average for the entire sample.

<table>
<thead>
<tr>
<th>D (μm)</th>
<th>2.5% Co_700 °C</th>
<th>2.5% Co_750 °C</th>
<th>5% Co_700 °C</th>
<th>5% Co_750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>3.98</td>
<td>5.97</td>
<td>6.64</td>
<td>12.65</td>
</tr>
<tr>
<td>50%</td>
<td>14.7</td>
<td>24.55</td>
<td>38.55</td>
<td>134.48</td>
</tr>
<tr>
<td>90%</td>
<td>25.98</td>
<td>48.64</td>
<td>73.4</td>
<td>359.30</td>
</tr>
<tr>
<td>Average</td>
<td>14.94</td>
<td>26.34</td>
<td>39.85</td>
<td>168.45</td>
</tr>
</tbody>
</table>

This analysis was able to quantify the agglomerate size distribution and indicated that an increase in cobalt content led to the formation of larger agglomerates, for the same reaction temperature. If the temperature is increased there was also an increase in the agglomerate sizes. This could be explained on the basis of the carbide formation process, as intermediate oxide particles are broken to form the carbide phase, which then has a smaller particle size and, therefore, is more prone to agglomerate due to electrostatic forces. No other paper, to our knowledge, has presented this kind of analysis of their carbide materials. We find that this is important information for future process scale-up as the agglomerating behavior of the powder has a direct effect on the final use of the materials and can be altered, to some extent, by reactor parameters such as type of reactor, gas flow and precursor loading.

CONCLUSIONS

From the method proposed here it was possible to obtain MoO₃ and CoMoO₄ phases by providing heat treatment to the precursor produced from the physical mixture of cobalt nitrate and AHM. The presence of CoMoO₄ at this stage is an indicative of the intimate contact of Co and Mo atoms in the precursor.

Precursors with 2.5% cobalt addition were able to produce single phase molybdenum carbide at 750 °C with a 180min soaking time with low free carbon content (~8.9%). For the powder produced at this temperature with 5% Co, TOC analysis indicated that an 86% conversion was achieved, which suggests that probably longer soaking times would be needed to form pure Mo₂C with this Co content.

All materials produced at 700 °C were composed of a mixture of molybdenum oxide and carbide, indicating incomplete reactions, which were identified by XRD and confirmed by TOC and SEM images. This could be due to the low methane composition used in the gas mixture.

It was found that cobalt addition produced a shift in diffraction angles of the molybdenum carbide phase, which indicates its presence in the carbide structure, as no cobalt-containing phases were identified by XRD for the reaction products. XRF data also confirmed the Co presence in all materials, which, coupled with the XRD verification, suggests the actual presence of this metal in the structure as a promoter.

Co addition also altered the agglomerating behavior of the carbide materials making them more prone to form larger agglomerates, as electrostatic forces are changed with increasing cobalt content.

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SYMBOLS AND UNITS

AHM Ammonium Heptamolybdate
d Crystal size (nm)
θ Diffraction angle (°)
HDS Hydrodesulphurization
HDT Hydrotreatment
TOC Total organic carbon
XRD X Ray Diffraction
XRF X Ray Fluorescence
HWL Halder-Wagner-Langford

REFERENCES


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