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## Molybdenum and tungsten carbides can shine too†

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In this perspective, we argue that carbides of transition metals such as molybdenum and tungsten hold great potential for the catalytic conversions of future feedstocks due to their ability to remain active in the presence of impurities in the feedstock. The presence of N and S impurities, found in increasing amounts in fossil-based feedstocks and also in new renewable feedstocks (such as biomass) may cause the carbides to convert to their respective nitrides or sulphides. These phases are catalytically active for similar reactions to the carbides and so these impurities would not lead to complete catalyst deactivation as they do for noble metal catalysts. Establishing the full potential of transition metal carbides as catalysts requires studies that use real feedstocks to look into the role of heteroatoms during the processing of fossil and novel feedstocks.

## 1. Introduction

Catalyzing chemical conversions to produce chemicals and fuels is becoming more demanding since the used feedstocks are changing. Fossil-based feedstocks are becoming heavier and now contain more impurities with N, S and P compounds<sup>1,2</sup> and new renewable feedstocks such as biomass are emerging. An important class of catalysts used to convert the current feedstocks is based on metals (e.g. Pt, Ni, Co, Fe). Particularly noble metal catalysts are highly active and have been widely studied, but their limited availability is leading to an increasing demand for alternative catalysts and it also makes them expensive. In addition, noble metal catalysts have difficulty dealing with the impurities present in the newer feedstocks; these impurities interact strongly with the metal and cause catalyst deactivation.

Transition metal carbides, such as those of molybdenum and tungsten, are considered viable alternatives to noble metal catalysts.<sup>3,4</sup> This is based on the groundbreaking work by Levy and Boudart in 1973 who showed that W carbide and Pt have similarities in electronic structure and catalytic behaviour in the formation of water from H<sub>2</sub> and O<sub>2</sub> at room temperature.<sup>5</sup> Subsequently, these carbides have been shown applicable for a wide variety of catalytic reactions, such as hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodesulphurisation (HDS), hydrodenitrogenation (HDN) and isomerisation.<sup>1,6,7</sup>

In this perspective, we discuss the potential of tungsten and molybdenum carbides as an alternative for noble metal

catalysts for use in the conversion of traditional fossil feedstocks, heavier fossil feedstocks and renewable biomass feedstocks. We point out the tolerance of transition metal carbides with respect to N and S impurities and the ability to (partially) convert the carbides to their respective nitrides or sulphides. The availability and catalytic activity of these carbide catalysts have both been mentioned before, but their relative stability in the presence of such impurities barely has. Although carbides can (partially) convert to nitrides and sulphides under the relevant reaction conditions, that does not necessarily lead to a complete loss of catalyst performance, as is the case for noble metals.<sup>4</sup> Thus, taking the compositions of some fossil as well as most new feedstocks into account, Mo and W carbides may become the preferred choice over noble metals.

### 1.1 Need for non-noble metal catalysts

Noble metals (group 8 in the periodic table) are often used as catalytically active metals because of their good performance (activity/selectivity) and excellent stability.<sup>8</sup> These metals are less prone to oxidation and therefore also less prone to leaching (dissolution) than non-noble metals, which is especially relevant for liquid-phase reactions. However, a major drawback of noble metals is their limited availability. Even though spent catalysts can and should be recycled, the expected growth of applications such as in electrolyzers and fuel cells will require a vast amount of catalyst material and thus of noble metals.<sup>9-11</sup>

Fig. 1 shows the abundance in the earth's crust of some relevant metals used in catalysis.<sup>12,13</sup> As expected, each metal's abundance is inversely proportional to its price and its CO<sub>2</sub> footprint, which makes non-noble metals an obvious choice as replacements for noble metals.<sup>14,15</sup> Well known is the use of

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nickel for reactions for which Pt used to be the preferred catalyst.<sup>16–18</sup> For example, Ni-based catalysts have been applied in the production of renewable hydrogen *via* aqueous-phase reforming.<sup>18–20</sup> However, the stability of Ni for its use in the aqueous phase is still an issue.<sup>18</sup> Cobalt and copper have also been considered as a replacement for noble metal catalysts. For example, cobalt and copper are highly active in the (steam) reforming of methane, methanol and ethanol.<sup>21</sup>

Based on the abundance of the non-noble metals, iron (not shown in Fig. 1) is always the preferred choice as it is the most abundant of all metals (5% by weight). However, not all catalytic conversions can be performed with that single element. Therefore, a plethora of catalysts based on different metals is both needed and currently available. Next to an element's abundance on earth, the efforts associated with recovery, processing as well as accessibility are points of attention. For example, the European Union has published a list of critical raw materials.<sup>22</sup> Their supply is not necessarily limited in terms of (future) abundance, but can also be restricted by their (currently) limited accessibility due to, for example, geopolitical circumstances. Therefore, adopting a general strategy of diversification, *i.e.* having alternatives for a given metal, is highly recommended. We argue that Mo and W, each having an elemental abundance that lies between that of the non-noble and the noble metals and a price comparable to that of non-noble metals, should be further explored as alternatives for noble metals.

## 2. State of the art of tungsten and molybdenum carbides

### 2.1 Mo and W carbides *versus* noble metal catalysts

Since the 1970s, tungsten and molybdenum carbides have emerged as alternatives for noble metal catalysts.<sup>23,24</sup> From a characterisation point of view<sup>25–27</sup> and from a performance<sup>5,28</sup> point of view, these carbides resemble noble metals (especially Pt). For instance, in 1992, Oyama made a comparison between transition metal carbides and nitrides and noble metals.<sup>3</sup> The crystallographic structure of these nitrides and carbides is determined by geometric and electronic factors. The geometric factor as identified by Hägg<sup>29</sup> determines that simple

structures (*i.e.* fcc, hcp and hex) are formed if the ratio between the atomic radii of the non-metal and the metal is less than 0.59; this is the case for carbides and nitrides of transition metals. The electronic factor finds its basis in the Engel–Brewer theory,<sup>30</sup> which states that nitrogen and carbon atoms combine their valence s–p electrons with those of the interstitial sites of the host metal (s–d–p bands of Mo and W). This explains why the catalytic activity of carbides and nitrides resembles that of noble metals.<sup>3,4,31</sup> Mo and W nitrides and carbides have excellent catalytic activities in reactions such as HYN, HDO, isomerisation and methanation. Particularly in HDO reactions, transition metal carbides reach yields close to those of noble metal catalysts. However, the selectivity of these newer catalysts differs from those of the noble metal catalysts.<sup>3</sup> Some carbide catalysts enable unique reaction pathways that result in valuable products (*e.g.* enhanced HDO and isomerisation selectivity); this leads to the suggestion that carbides and nitrides catalysts can even be more desirable than noble metals.<sup>4</sup> For instance, for the *n*-hexane reaction (614–630 K, excess H<sub>2</sub>), WC was twice as active as W<sub>2</sub>C and 0.5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> and showed enhanced selectivity for isomerisation products.<sup>3</sup> Further, Stellwagen and Bitter<sup>32</sup> studied the activity and selectivity of W and Mo carbide supported on carbon nanofibers in stearic acid HYD (batch reactor, 350 °C, 30 bar of H<sub>2</sub> pressure). Interestingly, supported W carbides catalysts were selective (>50%) towards highly valued alkenes at the intermediate conversion level, while supported Mo carbides were selective for oxygenates (octadecanol and octadecanal). Both intermediate products (the alkenes and the oxygenates) are platform chemicals for synthesising a wide range of value-added products<sup>32</sup> and are not normally observed with noble metal catalysts. For example, the conversion of stearic acid over Pd and Pt catalysts yields primarily heptadecane *via* the decarboxylation pathway.<sup>33</sup>

### 2.2 Challenges and opportunities for Mo and W carbides

Mo and W carbides are versatile and diverse catalysts, yet even after fifty years of research, captured in many reviews on the use of metal carbides in catalysis,<sup>4,6,7,34–42</sup> it is still often unclear what the exact nature of the active site in these catalysts is. For example, Sullivan *et al.*<sup>7</sup> reviewed the role of different synthesis techniques (temperature-programmed reduction and ultra-high vacuum) in the performance and characteristics of metal carbide catalysts, especially supported and unsupported W and Mo carbides. They emphasised that metal carbides undergo changes in their morphology and surface composition during synthesis and/or when used for a reaction under oxidative conditions. The authors stressed the need for *in situ* studies<sup>7</sup> to enable preventing the influence of O<sub>2</sub> on the material.

Recently, a number of review papers have described the use of metal carbide-based catalysts to upgrade biobased feedstocks.<sup>6,7,41–43</sup> For example, Chan-Thaw and Villa<sup>6</sup> reviewed both the influence of the synthesis techniques (temperature-programmes reduction, ball milling and

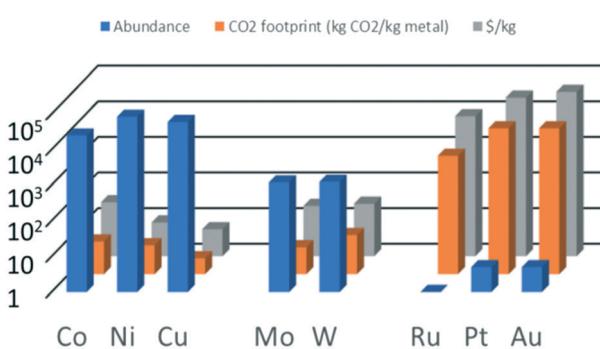


Fig. 1 Abundance, CO<sub>2</sub> footprint and price of some metals relevant for catalysis.



carbothermal hydrogen reduction) for unsupported and supported metal carbides and their use in the transformation of biomass to biofuels and fine chemicals. Examples of HYD and HDO of first-generation (vegetable oils) and second-generation (cellulose, hemicellulose and lignin) biomass with molybdenum and tungsten carbide catalysts were given. The carbides exhibit similar catalytic performances as Pt-group metals for HDO, HYD and isomerisation of biomass feedstocks. Although carbides are more resistant towards sulphur and nitride poisoning (see section 3), the carbide catalysts become deactivated due to coke deposition, leaching and over-reduction. The use of a support, *e.g.* a porous support (carbon nanotubes or mesoporous carbon), increases the stability of the carbides and leads to better control of the particle size.<sup>6,36</sup>

Pang *et al.*<sup>40</sup> also reviewed the use of metal carbides (supported and unsupported W & Mo) for biomass conversion and indicated their great potential in HDO of cellulose, lignin and other platform chemical conversions. They emphasised that the use of carbides in biomass conversions needs to be explored more thoroughly and suggested to explore traditional carbides (Re, Ti, V or Zr carbides) further to gain a fundamental understanding regarding structure–performance relationships of Mo and W carbides for biomass conversions.<sup>40</sup> In addition, Pang *et al.* looked at issues encountered during carbide synthesis.<sup>40</sup> Obtaining highly dispersed and phase-pure (WC vs. W<sub>2</sub>C) metal carbides is still challenging. Carbon decomposition during the reaction and the existence of mixed carbide phases (WC or W<sub>2</sub>C) hamper the comprehension of the structure–performance correlation of these materials, which again stresses the need for *in situ* investigations.<sup>40,44</sup>

To gain more insight into the property–performance relationships of carbides, also quantum mechanical calculations have been applied. For example, Alaba *et al.*<sup>38</sup> reviewed different density functional theory (DFT) studies on Mo carbide nanoparticles (as a catalyst for hydrogenation and hydrogen production) to identify and categorise the different existing Mo carbide phases. Depending on the preparation method and the carburisation agent, five different crystal structures were characterised:  $\alpha$ -MoC<sub>1-x</sub>,  $\alpha$ -Mo<sub>2</sub>C,  $\beta$ -Mo<sub>2</sub>C,  $\gamma$ -MoC and  $\eta$ -MoC. These structure differences do not only affect the stability of the catalyst but also influence the electrochemical activity. Among the different Mo carbide phases,  $\alpha$ -MoC<sub>1-x</sub> and  $\beta$ -Mo<sub>2</sub>C are the most stable and they display remarkable catalytic behaviours in electrochemical catalysis due to their large ionic contribution.<sup>38</sup>

The aforementioned studies and reviews have demonstrated the applicability of transition metal carbides in a wide range of reactions and their potential as a replacement for noble metal catalysts for fossil and biomass feedstocks. However, almost all of these studies also highlighted the need for further (*in situ*) investigations to obtain information on structure–performance relationships.

### 2.3 Carbides, nitrides and sulphides in reactions involving H<sub>2</sub> activation/transfer

Carbides are efficient catalysts for reactions involving H<sub>2</sub> activation/transfer, *i.e.*, carbides are able to split hydrogen and transfer the hydrogen atoms to different reactant molecules in a reversible manner. That makes them suitable catalysts for reactions that involve hydrogen activation, such as ammonia synthesis and decomposition, hydrogenation, hydrogenolysis, hydro-isomerisation, methanation and hydroprocessing.<sup>45</sup> The ESI† contains a summary of those thermocatalytic reactions.

It is noteworthy that aside from the transition metal carbides, also nitrides and sulphides have emerged as catalysts with activity for H<sub>2</sub> activation and transfer reactions.<sup>31,46</sup> For example, Monnier *et al.* tested  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported molybdenum, tungsten and vanadium nitrides for the HDO of oleic acid and canola oil.<sup>47</sup> The molybdenum nitride showed a superior oleic acid HDO performance in comparison with the other nitrides; after 20 h of steady state conditions, the Mo nitride yielded a three times higher selectivity for *n*-alkane than was obtained by V and W nitride. Furthermore, the Mo nitride was operated for 450 h in the continuous operation of canola oil hydrotreatment with only minimal deactivation. Grile *et al.*<sup>48</sup> studied the hydrodeoxygenation of liquefied lignocellulosic biomass over unsupported MoS<sub>2</sub>, MoO<sub>2</sub>, Mo<sub>2</sub>C and WS<sub>2</sub>. MoS<sub>2</sub> showed the highest hydrogenolysis selectivity as nearly 85% hydroxyl group conversion was reached within 30 min at 300 °C (~30% for MoO<sub>2</sub>, ~40% for Mo<sub>2</sub>C, ~60% for WS).<sup>48</sup> This shows that Mo and W nitrides and sulphides can be active for the same type of reactions as their respective carbides.

## 3. Potential of Mo and W carbide catalysts for use with S- and N-containing feedstock

Clearly, Mo and W carbides (as well as nitrides and sulphides) are versatile catalysts and potential replacements for noble metal catalysts even though the exact working mechanism and the nature of the active site of the carbide catalyst are not always known. However, with respect to stability, more research efforts are required.

Often, four pathways are defined for catalyst deactivation *i.e.*, 1) blocking of the active site (*e.g.* coke deposition), 2) crystallite growth, 3) leaching and 4) oxidation. These pathways have also been reviewed for metal carbides in liquid phase reactions by our group.<sup>36</sup> For Mo and W carbides, minor changes in the atmosphere of the catalyst can already result in different catalytic behaviours. A prime example is the exposure to air which can change the surface of the carbide through the formation of oxy-carbides and oxides.<sup>39,49,50</sup>

### 3.1 S and N impurities in novel feedstocks

Sulphur and nitrogen compounds are present in fossil feedstocks such as crude oil and coal. The exact amounts of



sulphur and nitrogen in crude oil and coal depend on origin and type. For example, Furimsky *et al.*<sup>51</sup> stated that conventional crude oil contains 1.8 wt% sulphur and 0.1 wt% nitrogen, whereas the sulphur content of coal samples lies between 0.1 and 10 wt% depending on the source of the coal, while the nitrogen content ranging from 0.5 to 1.5 wt% (see ESI†).<sup>52–54</sup> Traditional catalysts based on noble metals cannot cope well with these heteroatoms. Catalysts based on metals like Fe, Pt, Ru, Ni and Co as used in (de)hydrogenation, (steam) reforming and ammonia and Fischer–Tropsch (FT) synthesis are poisoned by H<sub>2</sub>S and NH<sub>3</sub>.<sup>55</sup> The removal of such harmful impurities from the feedstock is therefore essential to maintain catalyst activity and selectivity. In current refineries, (reduced) metal catalysts are protected by upstream hydrotreating steps, *i.e.* hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN).<sup>56–58</sup>

Significant amounts of sulphur/sulphide (S) and ammonia (N) can also be present in biomass-derived feedstocks before and after processing (gasification, pyrolysis, digestion). According to Robinson *et al.*, the sulphur content ranges from ~14 to 2200 ppm depending on the biomass source and the season.<sup>59,60</sup> Even pure vegetable oils still contain ~10 ppmw of sulphur.<sup>61</sup>

Converting biomass or a fossil resource to syngas (H<sub>2</sub>/CO) followed by conversion of the syngas to the desired products (alcohols, alkenes, alkanes) *via* FT synthesis is gaining interest. When using syngas obtained from biomass, additional gas cleaning steps should be implemented to protect the FT catalyst (based on Fe or Co) against poisoning with S. This issue is exemplified by the increased interest in the fermentation of syngas<sup>62</sup> as an alternative to metal-based conversions.

Mo and W carbide catalysts could be employed as alternatives for reduced metal catalysts in the upgrading of many of the biomass-derived sources (either syngas or other more complex molecules). The use of Mo<sub>2</sub>C in gas-to-liquid (GTL) processes has already been established for the synthesis of MeOH,<sup>63</sup> higher alcohols<sup>64</sup> and FT of fuel/diesel/hydrocarbons<sup>65,66</sup> from pure syngas sources. The use of Mo and W carbides in the decarboxylation and hydrodeoxygenation of vegetable oils is another example.<sup>67</sup> Both the hydrogenation of pyrolysis oil<sup>68</sup> and reforming of methane<sup>69–73</sup> with Mo<sub>2</sub>C and W<sub>2</sub>C have been demonstrated. To evaluate the true potential of Mo and W carbides, the effect of the S and N content in these feed sources needs to be taken into account.

### 3.2 Stability and activity of carbides, nitrides and sulphides

For reduced metal catalysts, the formation of a strong metal–S bond inevitably results in surface sulphidation and consequently in deactivation.<sup>74</sup> Especially noble metals, such as platinum and palladium, suffer from deactivation in the presence of sulphur compounds.<sup>75</sup> During simultaneous HDS, HDO and HYD (450 °C, 200 ppm O<sub>2</sub>, 5 wt% cumene, 95% tetradecane), a Pt catalyst supported on alumina deactivated immediately upon addition of sulphur.<sup>56</sup>

Also the effect of nitrogen compounds on noble metal catalysts has been studied. Augusto *et al.* showed that Pt or Pd supported on zeolite Y catalysts used for tetralin HYD was deactivated by quinoline (499 ppm) as well as by dibenzothiophene (100 ppm).<sup>76</sup> Similarly, the catalytic activity of Rh-based catalysts is strongly inhibited by sulphur compounds during methane oxidation or steam reforming.<sup>77</sup> Already after addition of 1 ppmv of SO<sub>2</sub> or H<sub>2</sub>S, the catalytic activity of Rh/γ-Al<sub>2</sub>O<sub>3</sub> during the methane/steam reforming can become significantly decreased; after adding 10 ppmv, the catalytic activity decreases to zero.<sup>77</sup> Transition metals such as Co and Ni are also prone to deactivation by sulphur poisoning. As an example, a drop in methanation activity of more than 3 orders of magnitude can occur for Co, Ni and Ru in the presence of only 15 ppb of H<sub>2</sub>S.<sup>78</sup>

For Mo and W carbides, their response to S and N impurities also needs to be considered. The presence of S or N in the feedstock can result in the transformation of carbide to a nitride and sulphide under relevant reaction conditions. Fig. 2 shows that the transition of Mo<sub>2</sub>S to Mo<sub>2</sub>C occurs in a temperature range of 400 to 700 °C in the presence of 0.01 to 10 ppm H<sub>2</sub>S, while the stability of WS<sub>2</sub> already is affected at 600 °C at only 0.01 ppm. In general, equilibrium calculations using the HSC Chemistry package show that, thermodynamically, W<sub>2</sub>C is unstable in the presence of both S (as H<sub>2</sub>S) as well as N (as NH<sub>3</sub>) and strongly favours the formation of W sulphides and nitrides. Mo<sub>2</sub>C is only resistant to sulphur at very high temperatures and low sulphur concentrations (*e.g.* above 650 °C at 1 ppm H<sub>2</sub>S). Thus, the conversion of carbides to sulphides or nitrides is thermodynamically possible at conditions relevant for crude oil processing and biomass upgrading (with the exception of high-temperature steam reforming). It should be noted that the thermodynamic calculations are valid for the bulk phase and that the results will be different for more reactive (supported) nanoparticles. The rate at which a favourable transformation occurs also depends on other factors besides bulk *versus* supported catalyst, *e.g.*, support type and particle size. Furthermore, partial transformations might occur, *e.g.*, surface sulphidation might result in a passivation layer, serving as a diffusion barrier that prevents or slows down the sulphidation of the whole particle.<sup>79</sup>

Transformation from carbide to sulphide or nitride might, therefore, occur during processing of heavy oil-based feedstocks (which contain more sulphur)<sup>80–82</sup> or biomass (which contains N and S in the feed). Interestingly, the (partial) conversion of Mo or W carbides to sulphides or nitrides should not necessarily result in deactivation because also the nitrides and sulphides are active for reactions involving hydrogen transfer (hydrogenation/dehydrogenation), as we already mentioned.<sup>56,83–86</sup>

This is further illustrated by the fact that prime examples of Mo catalysts are hydrotreating catalysts (CoMo- and NiMo-based), which are active in the sulphide state. That the relevant reactions are hydrogenation reactions shows that Mo sulphides could also play a role in the catalysis of



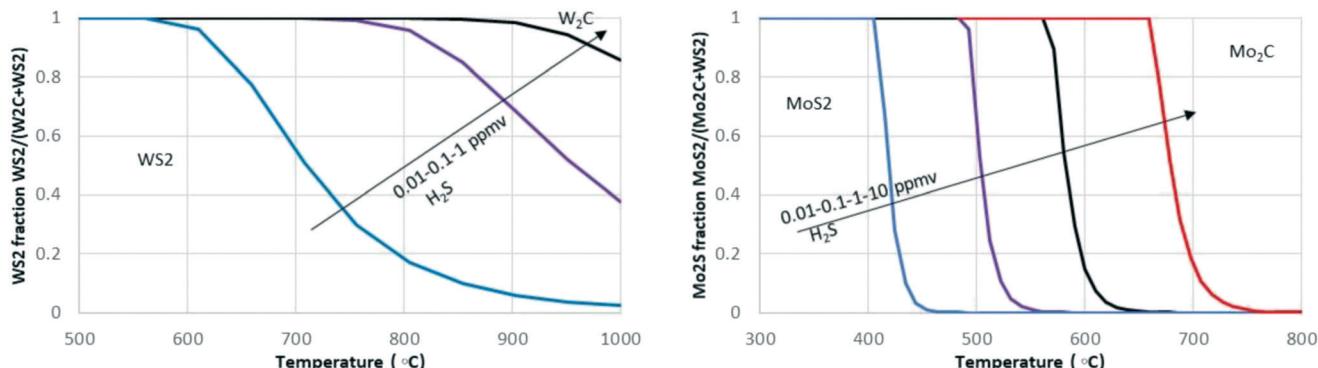


Fig. 2 The stability regions for Mo and W sulphides and carbides as the fraction of sulphide *versus* temperature for  $WS_2$ – $W_2C$  (left) and  $MoS_2$ – $Mo_2C$  (right) in the presence of 0.01–10 ppm of  $H_2S$  in  $H_2$  calculated with the HSC Chemistry software (metallic species omitted).

other (de)hydrogenation reactions. For instance, the Mo sulphides traditionally used for hydrotreating reactions ( $NiMoS_2$ ,  $CoMoS_2$ ) are also active for HDO reactions of fatty acids and bio oils.<sup>87</sup> In addition, there are examples of the use of  $W_2C$  (ref. 58) and especially  $Mo_2C$  (ref. 88–92) in HDS (see Table S1 in the ESI†). In addition, Mo and W nitrides are active for HDO, HDN and HDS reactions and in some cases ( $CoMo$  and  $NiMo$ ) are even superior to the sulphide catalysts.<sup>93</sup> Although  $Mo_2C$  carbides display greater activity in HDS reactions than  $MoS_x$ , the difference in activity can either be explained by the change in the number of active sites on the catalyst surface or is due to the difference in intrinsic chemical activity.<sup>79</sup> However, this clearly shows that for Mo- and W-based catalysts, sulphur is not a poison, although it is for noble metal catalysts. For both the Mo carbide and the Mo nitride catalysts, their

activity is retained when the surface becomes sulphated during HDS of thiophene at 400 °C.<sup>94</sup>

Considering the above, one might expect that Mo and W carbide and/or sulphide catalysts are a good choice for other hydrogen transfer reactions in which S or N impurities are expected. However, this potential advantage appears to have been overlooked so far since not many studies have focused on the effect of impurities. Therefore, for reactions other than HDS, only limited experimental information is available on the actual performance of Mo and W carbides in the presence of real feedstocks containing S and N. Already in 2002, Furimsky *et al.* mentioned that experimental information on hydrogen adsorption in the presence of  $H_2S$  or by partially sulphided carbides and nitrides was lacking.<sup>1</sup>

A few studies have been conducted with bulk  $Mo_2C$  and the addition of S compounds to the feed; Table 1 summarises

Table 1 Overview of use of  $Mo_2C$  and  $WC$  in the presence of S

Reaction	T/p	S-Source	Performance/remarks	Ref.
Steam reforming, oxidative-stream reforming of tri-methyl pentane	1000 °C 1 bar	≤1000 ppm thiophene	- Activity remains up to 100 ppm - Higher concentrations of S result in surface oxidation and coke formation	95
$CO_2/CH_4$ reforming	1050 °C 1 bar	250–500 ppm dimethyl sulphide	- $Mo_2C$ deactivates at 800 °C due to reversible $CS_2$ chemisorption - Rh is S-tolerant under these conditions	73
Steam reforming of methanol	185–240 °C 1 bar	5 ppm $H_2S$	- S decreases the activity but the catalyst does not become fully deactivate - Deactivation is reversible	63
Hydrogenation of cumene	250 °C 51 bar	30–100 ppm S (thiophene, (di-)benzo-thiophene)	- With 30–60 ppm S, $Mo_2C$ is superior to noble metals - At 100 ppm, $Mo_2C$ deactivates	56
Aqueous phase hydrogenation of furfural	120–150 °C 120 bar	380 ppm thiophene	- S present as surface sulphide - Similar activity in presence and absence of S	80
Steam reforming of hexadecane	965 °C 1 bar	125–500 ppm benzo-thiophene	- Deactivation dependent on sulphur concentration	101
Water gas shift reaction	200–240 °C 1 bar	Without and with 5 ppm $H_2S$	- Deactivation minimal at S concentration below 100 ppm - $MoS_2$ sites active in the presence of sulphur - $Mo_2C$ catalyst quickly poisoned by sulphur, but partly regenerated	60
Partial oxidation of methane to syngas	750 °C 8 bar	0.1% of $H_2S$	- High S concentration leads to carbon deposition and sulphidation of the catalyst (catalyst deactivation) - At lower S concentration (<0.1%), no change in catalyst phase, but carbon acceleration on the reactor wall	102
Tetralin hydrogenation	300 °C 40 bar	200 ppm $H_2S$ (dimethyl-sulphide)	- Decrease in tetralin conversion upon adding $H_2S$ - Minimal deactivation of supported $Mo_2C$ and $WC$ - Near-complete deactivation of $Pt/Al_2O_3$	96

them. Two of these studies (steam reforming at 1000 °C (ref. 71) and dry methane reforming at 1050 °C (ref. 73 and 95)) used conditions in which, according to Fig. 2, sulphide formation is not expected. Indeed, the authors reported no  $\text{MoS}_2$  formation for increased temperatures and the activity of the catalyst remained intact at high sulphur concentrations. On the other hand, the introduction of sulphur during steam reforming of  $\text{MeOH}$  resulted in an immediate but limited decrease in activity (of about 30%) and the formation of surface sulphur was detected with XPS.<sup>63</sup> Also in the liquid phase HYD of furfural, trace amounts of S were found with XPS while the catalytic activity remained. In the hydrogenation of cumene, the formation of a surface carbosulphide phase was identified with XPS, while XRD showed that the bulk  $\text{Mo}_2\text{C}$  was unaffected,<sup>56</sup> revealing that only surface modification had occurred.

Thompson *et al.* investigated the effect of sulphur on  $\text{Mo}_2\text{C}$  and  $\text{Pt}/\text{Mo}_2\text{C}$  during the water–gas-shift reaction.<sup>60</sup> Both catalysts became deactivated by exposing them to  $\text{H}_2\text{S}$  but the  $\text{Mo}_2\text{C}$  became only partially deactivated due to the formation of a still active  $\text{MoS}_2$  phase, while the  $\text{Pt}/\text{Mo}_2\text{C}$  catalyst showed irreversible deactivation of the platinum. We found only one study that included Mo and W carbides as supported catalysts.<sup>96</sup> In this work, da Costa *et al.* compared the effect of  $\text{H}_2\text{S}$  on  $\text{Mo}_2\text{C}$  and WC supported on  $\text{Al}_2\text{O}_3$ . The carbide activity was tested and compared in the presence and absence of 200 ppm  $\text{H}_2\text{S}$  during tetralin HYD (300 °C, 4 MPa). In the absence of sulphur, the supported  $\text{Mo}_2\text{C}$  and WC reached a yield of 6.5 mol% and 8 mol%, respectively. In the presence of sulphur, the conversion was slightly lower (4.5 mol% for  $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ ; 6 mol% for  $\text{WC}/\text{Al}_2\text{O}_3$ ), but there was no complete deactivation of the carbide catalysts.<sup>96</sup>

While these studies concern very different reactions and conditions, they show that the carbides are able to tolerate sulphur in the feedstock. For the further development of stable carbide-based catalysts, it is essential to explore the mode of interaction of the N/S compound with the catalyst first. The partial transformation of a carbide to a sulphide or nitride might have a limited influence on catalytic performance as argued before; however, blocking of the active sites by a nitrogen/sulphur compound may still lead to deactivation. Therefore, a fundamental understanding of the interaction between the carbides surfaces and the sulphur/nitrogen-containing molecules is needed to understand the catalytic performance of these materials.<sup>4,97</sup>

A few articles have been published regarding the behaviour of Mo carbide towards sulphide adsorption/desorption.<sup>79</sup> For instance, Rodriguez *et al.* used photoemission and XANES to establish the chemistry of  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{CH}_3\text{SH}$  on Mo carbide (and metallic Mo). The adsorption of  $\text{SO}_2$  on  $\text{Mo}_2\text{C}$  at around -123 to 26 °C first led to the formation of  $\text{SO}_3$  and  $\text{SO}_4$  and, with increasing temperatures, to the formation of sulphided and oxidised carbides. The interaction between  $\text{H}_2\text{S}$  and the Mo carbides was strong and led to substantial sulphidation, even at low temperatures. For the  $\text{CH}_3\text{S}$ , the methyl group dissociated

with increasing temperature while  $\text{CH}_2\text{S}$  species coexisted on the carbide surface. However, the carbide was not modified by the sulphide. This shows that molybdenum carbides are either tolerant towards sulphur-containing molecules or form a still active  $\text{MoS}_x$  phase, depending on the molecule in question and the temperature. Thus, the adsorption/desorption behaviour of carbide material depends on the sulphur compound and conditions (e.g. temperature).

Limited research has been conducted towards the effect of sulphur on bulk tungsten carbide.<sup>98–100</sup> In 1981, Ko *et al.* published a study on the effect of oxygen and surface on the bonding and reactivity of carbon monoxide, hydrogen, formaldehyde, and methanol on tungsten and tungsten carbide surfaces. They found that the  $\text{W}(100)-(5 \times 1)\text{C}$  surface rapidly adsorbed  $\text{H}_2\text{S}$  which led to site competition with CO. The surface reactivity for formaldehyde and methanol decreased significantly after the sulphur treatment; however, it was still more active than metallic tungsten.<sup>98</sup> Schulz-Ekloff and co-workers (1975) showed that in the presence of 25  $\mu\text{g m}^{-2}$   $\text{H}_2\text{S}$ , the ammonia yield was reduced by 50%. After adding 50  $\mu\text{g m}^{-2}$   $\text{H}_2\text{S}$ , the complete inhibition of the tungsten carbide occurred.<sup>99</sup>

In summary, based on thermodynamic arguments carbide catalysts might change the nature of their active site when used in the presence of S and N impurities during the processing of crude oil or renewable feedstock. However, they can remain catalytically active since the sulfide and nitride phases also possess activity for the same type of reactions. This distinguishes them from noble metal catalysts which quickly deactivate in the presence of sulfur or nitrogen containing compounds. The limited direct evidence available from experiments appears to support this view. Under which conditions the different types of carbides remain (partially) active and how the impurities interact with the carbides needs further investigation to define an operational window of the carbides.

## 4. Outlook

Future feedstock for chemicals and fuels, whether fossil or renewable in nature, will put new demands on the robustness of catalysts used in their processing. Tungsten and molybdenum carbides hold great potential for catalytic applications as replacements for noble metals. Both W and Mo have higher abundance and as a result lower cost compared to their noble metal counterparts. However, it has previously been stressed in a number of reviews that more detailed investigations into the nature of the active sites of these materials is still required.<sup>7,40,43</sup>

It is our view that W and Mo carbides possess advantages beyond their availability and lower cost which should be the focus of further research to advance the field of W and Mo carbide catalysis and move towards industrial applications. We, therefore, stress that there is the need to study and gain more insight into the role of heteroatoms in the performance of carbide catalysts. We have argued that Mo and W carbide



and/or sulphide catalysts can become the preferred choice for a wide range of hydrogen transfer reactions relevant to the upgrading of both novel crude oil and renewable feedstock in which S or N impurities are present. This is because Mo and W carbides are either less susceptible to poisoning by these S-containing compound compared to noble metals or can be converted into their still active sulfide/nitride phases. Although not many studies have focused on the effect of impurities, the limited experimental evidence available for mainly bulk molybdenum carbide in the presence of thiols/thioesters supports this view.

Therefore, we propose that more studies are needed that focus on realistic feedstocks to show the true potential of these catalysts under real conditions, especially considering the effect that impurities like N and S in real feedstocks may have on the nature of the active site and the stability of these catalysts.

Secondly, more fundamental studies are still needed to understand the interaction of different S and N compounds, *e.g.* sulphide *versus* sulphate species, with the various types of Mo and W carbide catalysts. For this also the use of *in situ* surface-sensitive spectroscopic techniques would be required, understandably involving controlled conditions and the use of model compounds and feedstocks. In addition, theoretical calculations can provide us with a broader insight into adsorption of sulphur and sulfidation of Mo and W carbide catalysts in relation to their structural and electronic properties.

We propose these as the next avenues to explore. In any case, the potential for Mo and W carbides as supported catalysts is evident. It is not only noble metals that shine.

## Conflicts of interest

There are no conflicts of interest to declare.

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