

The role of carburization temperature on the molybdenum carbide surface and their catalytic activity

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Received 8 June 2018; received in revised form 12 February 2019; accepted 3 March 2019

ABSTRACT

The surfaces of molybdenum carbide were varied by changing the carburization temperature between 823 and 1123 K. The surfaces of the catalytic material were investigated using *in-situ* temperature program carburization followed by temperature program reduction and oxidation. *In-situ* temperature program oxidation (TPO) showed the surfaces of the catalysts contain a similar amount of carbonaceous deposit, while temperature program reduction (TPR) showed their ability to consume hydrogen in different amounts. The result shows the surface of the carbide at 823 K contained oxygen, while those carburized at higher temperature (≥ 923 K) were pure carbide. The catalysts tested for hydroisomerization of n-heptane and the catalyst with oxycarbide surface showed higher activity and iso-heptane selectivity. Hence, carburization temperature plays a crucial role in the formation of an active catalyst.

Keywords: Hydroisomerization, Carburization temperature, Activity, Reduction, Oxidation.

1. Introduction

Molybdenum carbide (supported or unsupported) has long been adjudged to have comparable catalytic properties compared to noble metal, because of their unique d-band electronic structures and ability to catalyze conversion of hydrocarbon and other reactions [1–3]. This carbide has resistance to poisoning and thus is stable under reaction conditions [2]. Carbide has been used either in their pure form or modified form with oxygen. The catalytic properties of molybdenum carbides are linked with size, shape, and their crystalline structures [4]. The carbide can be in six phases, but the two common phases are α -MoC_{1-x} and β -Mo₂C. The latter is thermodynamically more stable with the hexagonal close-packed structure (HCP), while α -MoC_{1-x} is the metastable phase and has a face-centred cubic structure [4]. This study is not intended to study the size, shape and crystal phase of molybdenum carbide because this has recently been reported [4], but this study aims to understand the effect of carburization temperature on the molybdenum carbide catalyst, and to understand the role of the surface species.

Carburization with a gas mixture of methane and hydrogen (1: 4 v/v) resulted in the formation of β -Mo₂C [2,5–7], so this mixture was used for this study. This gas mixture [CH₄/H₂] is unreactive and requires high temperature to cause carburization. The advantage of high temperature is the formation of pure carbide and avoiding the coke formation [4]. The higher the carburization temperature, the higher the probability of forming pure carbide [8]. Clean carbide and oxygen modified carbide can both be prepared directly from oxidized molybdenum metal or molybdenum oxide under a mixture of hydrocarbon and hydrogen [9]; what differentiates the final surface species of the carbide is their operating temperature. Leudox and co-workers [10,11] concluded that clean carbide surfaces obtained by the reductive treatment after synthesis yield mostly hydrogenolysis products. However, conversion of an oxygen modified carbide resulted in high selectivity to iso-heptane [10,12]. Galadima *et al.* [5] obtained high selectivity to iso heptane when n-C7 hydro-convert over carbided molybdenum supported sulfated zirconia [5]. This study involved investigation of surface species formed after temperature program carburization (TPC) using temperature program oxidation (TPO) and temperature program reduction (TPR) to understand the nature of their surfaces.

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2. Experimental

The catalyst support (sulfated zirconium hydroxide, MEL Chemicals, UK) was pre-calcined in the air at 823 K for 3 h to obtain sulfated zirconia (SZ). A solution of ammonium heptamolybdate tetrahydrate ($[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, Fisher Scientific, UK), 1.840 g in 100 ml ultra-pure water, 10 Mo wt %) was added to 9 g of SZ and stirred vigorously for 2 h. Excess water was removed by rotary evaporation at 353 K prior to overnight drying at 393 K. The resultant powder was heated in air at 823 K (50 ml min^{-1}) for 3 h and stored as 10 MoO₃/SZ.

Temperature program carburization was achieved *in-situ* by loading *ca.* 0.12 g of the catalyst between two quartz wool plugs into a quartz reactor tube. The sample was then heated (at 10 K/min heating rate) in a flow of 1:4 mixtures of CH₄:H₂ at 10 ml/min to either 823 or 923 K and maintaining this condition for 4 h. The system was at that point flushed with nitrogen while cooling to room temperature (313 K). Nitrogen was later replaced with either hydrogen (for TPR) or oxygen (for TPO), before slowly raising the temperature to 1273 K (at heating rate 10 K/min).

Conversion of heptane was carried out with a quartz reactor (1.0 cm i.d., 29 cm long) at 723 K under atmospheric pressure in the presence of hydrogen (0.68 ml/min). The weight hourly space velocity was 0.035 h⁻¹ and the molar ratio of n-heptane to H₂ was set at 0.012. The effect of carburization temperature was investigated in separate experiments by varying the temperature as follows, 823, 923, 1023 and 1123 K. The eluent stream was sampled automatically using an electrically activated ten-port multi-loop VICI Valco sampling valve and samples were later analyzed using a Perkin-Elmer 8410 GC fitted with a 5.6 m long 15 % squalene on chromosorb WHP column and FID detector. The conversion (*X*), research octane number (*RON*), selectivity (*S*) and rate (*r*) were calculated as follows:

$$\% X = \frac{X_i - X_f}{X_i} 100$$

$$RON = \sum_{f=7}^{i=5} \frac{X_n}{X_i - X_f} RON_n$$

$$\% S = \frac{X_n}{X_i - X_f} 100$$

$$\text{rate [mol [gh]}^{-1}] = \frac{Vd}{Mwt} \ln\left[\frac{1}{1-X}\right]$$

Where, *X_i* is the initial amount [μmol] of heptane before reaction, *X_f* is the amount of heptane remaining after reaction, *X_n* is the amount of the individual product, *RON_n* is the research octane number of the individual product, *V* is the volume of hydrocarbon injected, *d* is hydrocarbon density (g/l), *M* is the n-heptane molecular weight, *ω* is the weight of the catalyst (g) and *t* is the contact time.

3. Results and Discussion

The reactions of heptane over 10 MoO₃/SZ carburized at different temperatures were performed under atmospheric pressure. The conversion, rate of reaction and RON obtained are given in Table 1. The conversion for the catalyst carburized at ≥ 923 K was fairly the same, nevertheless, there was a slight decrease in the conversion between 923 and 1023 K. The rate of n-heptane conversion over the catalyst carburized at 823 K was approximately four times higher compared to those carburized at ≥ 923 K. The RON obtained from the product distribution was greater for the catalyst activated at 823 K compared to those carburized at ≥ 923 K.

Fig. 1 shows the effect of varying carburization temperatures on product selectivity. Carburization at temperatures ≥ 923 K gave high selectivity to C₁ – C₃ [methane to propane] compared to carburization below 923 K. Oloye *et al.* [13] observed that n-heptane hydroconversion over Mo₂C/SZ did not proceed over a single consecutive pathway. Hence, C₁-C₃ might have been generated through multiple cracking, suggesting high activity towards cracking. The selectivity at carburization temperature of 823 K gave a reasonable selectivity to pentane (C₅), iso-heptane (iC₇) and isopentane (iC₅) compared to carburization at ≥ 923 K; therefore, the surfaces of molybdenum carbide at this temperature were more active in isomerization than cracking. Bouchy *et al.* [14] reported MoO₃ was activated at 623 K, a better temperature, for the n-butane isomerization compared to those activated at 673 K. They pointed out that the catalysts carburized at 623 K with H₂/C₄H₁₀ have similar activity with those reduced at 623 K, but different from those activated at 673 K. Hence, the temperature plays a significant role on the surface species, it invariably affects the catalyst activity [14]. The high selectivity to C₁- C₃ at the expense of C₅, iC₅ and iC₇ might be related to the formation of clean carbide at the carburization temperatures of ≥ 923 K. Unsupported clean carbide has been reported to give predominantly hydrogenolysis products for n-alkane conversion [9,10,15], so this might be the same for supported carbide.

Table 1. The effect of carburization temperatures on conversion and RON.

Temperature (K)	Conversion (%)	Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	RON
823	48	326	40
923	14	75	14
1023	10	53	10
1123	11	58	8

It is generally believed that conversion is the major factor that affects isomers selectivity (i.e. selectivity decreases with increase in conversion), however, other reactions' variables may play a part. Matsuda *et al.* [16] reported iso-heptane selectivity to decrease slightly with the conversion when heptane was converted over $\text{MoO}_{1.5}$, nevertheless, the high selectivity was preserved in the reaction. In a similar way, the activity and iso-heptane selectivity obtained in this research were high considering the catalyst activated at 823 K compared to those carburized at ≥ 923 k, because the surface species play a significant role in the n-heptane conversion and product selectivity. Therefore, we can conclude that it is not just the conversion that affects the product distribution, but also the nature of the catalyst surfaces.

Xiao *et al.* [17] pointed out that the carburization with methane was better in comparison to those with butane, but the carburization with H_2 /butane at 823 K on account of the careful selection of carburization temperature is the most relevant, as it will determine the

activity of the catalyst. They observed that molybdenum carbide prepared between 700 and 900 K do display noble metal and acidic characteristics due to the presence of oxygen and carbon at the interstices of molybdenum [17]. Hence, the presence of oxygen content in the lattices of molybdenum may prove why the catalyst carburized at 823 K showed better activity and isomer selectivity compared to others.

Different types of carbon species could be deposited on the surface of carbide after carburization, depending on the gas mixture and carburization temperature. The common carbon species which could be deposited include amorphous, graphitic carbon (or free carbon), coke, and other aggregates of carbon [2,3]. These additional carbon species play a significant role in the activity and selectivity of a catalyst. Lee *et al.* [2] had reported how to clean the surface of the freshly prepared molybdenum carbide and discovered that a high ratio of hydrogen to hydrocarbon can prevent the unwanted carbon formation. They highlighted the role of surface

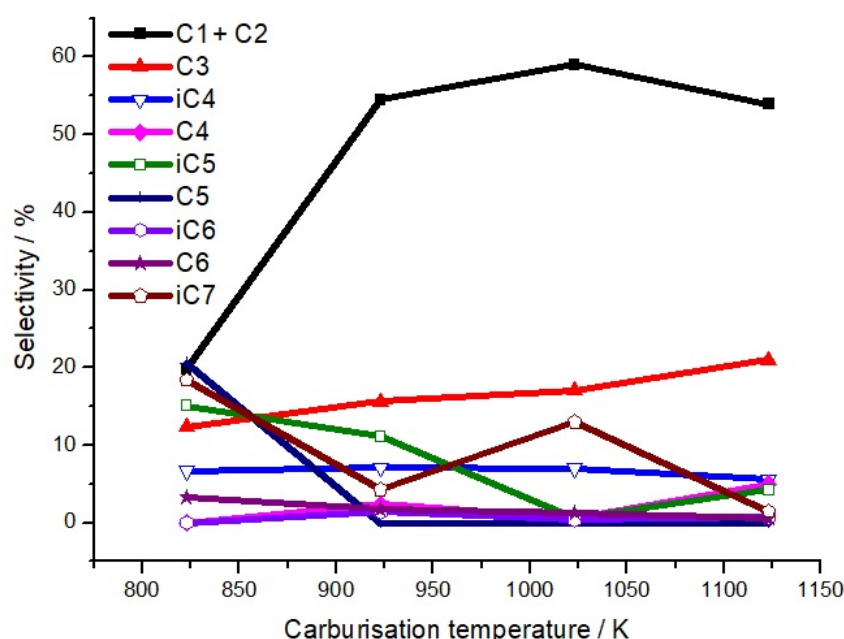


Fig. 1. The effect of carburization temperatures on selectivity (solid circle, ethane; solid upward triangle, propane; open downward triangle, isobutane; solid diamond, butane; open square, isopentane; solid cross, pentane; open hexagon, isoheptane; solid star, hexane; open pentagon, isoheptane).

species most especially oxygen and polymeric carbon. However, they did not elaborate the role of oxygen content in the carbide, nevertheless, Ledoux and co-workers [11,14,18] have done extensive works on the role of oxygen content in the carbide and concluded that oxycarbide is better than pure carbide for n-alkane hydroisomerization. Study on $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ has been reported by Wu *et al.* [3] but the effect of carburization temperature on $\text{Mo}_2\text{C}/\text{SZ}$ has not been investigated. Here, attempts have been made to understand the surfaces of catalysts after *in-situ* temperature program at 823 K and 923 K. It was discovered that the surfaces of molybdenum carbide synthesized at different temperatures were different from each other.

The TPR data (Fig. 2) shows three reduction peaks at 442, 615 and 1154 K when the catalyst was carburized at 823 K. For catalyst carburized at 923 K, peaks were detected at 411, 642 and 1259 K (Fig. 3). Peaks at a temperature around 461 and 493 K were ascribed to CH_4 evolution when $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ was carburized at 1033 K in 60 min [3]. They attributed the methane formation to the reaction of hydrogen with surface carbon atoms of carbide and some deposited carbon atom. Lee *et al.* [2] also reported the formation of methane by removal of surface carbon and this gave methane peak at 735 K. The difference in the number of peaks obtained from bulk Mo_2C , $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, and $\text{Mo}_2\text{C}/\text{SZ}$ might be related to the nature of the supports. Therefore, we can conclude that the first two peaks seen below 700 K in this reaction were due to the removal of surface carbon. At elevated temperature, some carbon atoms of the carbide and some graphitic carbon might be removed. Wu *et al.* [3], observed a strong band at 873 K and concluded that it was possibly due to the removal of graphitic carbon or/and carbon atoms of the carbide,

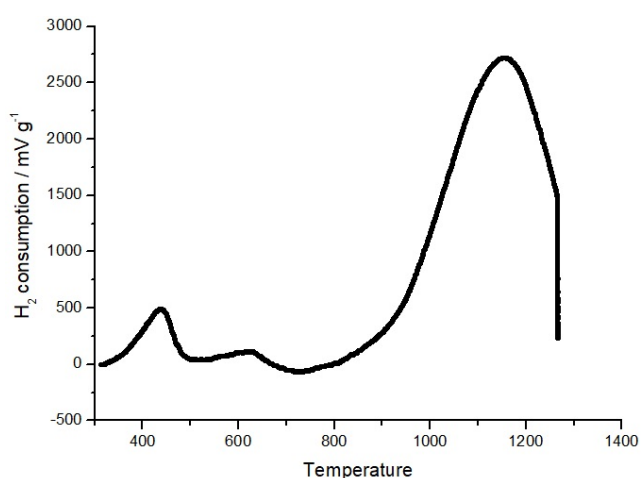


Fig. 2. Temperature program reduction profile after sample *in-situ* carburization at 823 K.

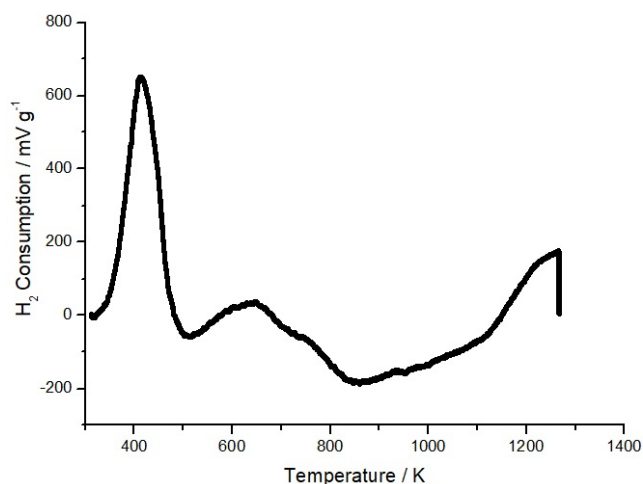


Fig. 3. Temperature program reduction profile after *in-situ* carburization at 923 K.

also they confirmed this observation by TPR-MS assignments. Hence, the third peak at 1154 or 1259 K could be related to carbon atoms of the carbide. The amounts of hydrogen consumed at each of the temperatures corresponding to three peaks in TPR are shown in Table 2. The quantities of hydrogen used up in the first two peaks were slightly greater than that consumed for the catalyst carburized at a lower temperature. Surprisingly the amount of hydrogen consumed at higher temperatures was more in the catalyst carburized at 823 K than that at 923 K. Perret *et al.* [19] measured the resultant C/Mo which was 0.556, 0.588 and 0.667 for Mo_2C , $\text{Au}/\text{Mo}_2\text{C}$, and $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$, respectively. They concluded that the range of C/Mo ratio suggested the full carburization of the sample and that occurrence of excess carbon may be as a result of free surface carbon. In a similar manner, Lee *et al.* [2] believe that C/Mo close to 0.5 suggested the full carburization because this value was close to the ideal stoichiometry of Mo_2C [C/Mo = 0.5]. When the C/Mo ratio was greater than 0.5 [i.e. 6.4], they associate the increase in the ratio with the removal of a multilayer of polymeric carbon deposits. However, they did not support the claim with TPO, since an equal amount of carbon deposits will consume the same amount of oxygen.

Table 2. Quantification of hydrogen consumed during TPR.

Peak	Carburization at 823 K n react ($\mu\text{mol g}^{-1}$)	Carburization at 923 K n react ($\mu\text{mol g}^{-1}$)
1	22.3	30.9
2	6.6	14.1
3	437.3	25.0
C/Mo	3.73	0.56

The C/Mo shown in Table 2 was close to 0.5 for 923 K carburization and greater than 0.5 for 823 K carburization. Hence, it is reasonable to perform TPO experiments to ascertain the amount of carbon present on the surface of the catalysts after the carburization.

The *in-situ* TPO of the catalyst is presented in Fig. 4. The TPO profile for the catalyst shows oxygen consumption at nearly the same temperature and very similar peak area under the curve. The amounts of CO produced were fairly the same. This observation confirmed that it was not only polymeric carbon that affects the C/Mo ratio in Table 3, but also oxygen present in the catalyst carburized at 823 K affects this ratio. This occurs because the material might not be fully reduced at the carburization temperature (823 K). The reduction temperatures for fresh 10 MoO₃/SZ were 724 and 1151 K (Fig. 5). At the first temperature, the catalyst precursor reduced from +6 to +4 while in the second step it reduced from +4 to 0 [20]. Therefore, the carburization at 823 K might have occurred when the catalyst was not fully reduced, hence, the presence of oxygen in the lattices of Mo might help this process. The presence of oxygen in the carburized samples at 823 K was similar to the observation of Xiao *et al.* [8,17], that observed oxygen and carbon in the interstices of molybdenum when the oxides were carburized between 700 and 900 K. Also, the presence of MoO₂ was taken into consideration when calculating the stoichiometry of molybdenum oxycarbohydride by Bouchy *et al.* [14].

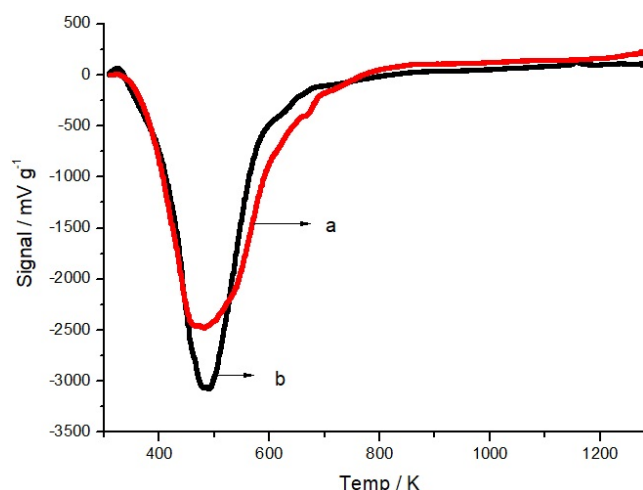


Fig. 4. Temperature program oxidation profile after *in-situ* carburization at [a] 923 K [b] 823 K.

Table 3. Quantification of CO produced during TPO.

Carburization temperature (K)	Peak area (mVs)	CO produced (mmol)
823	-4.435×10^5	0.191
923	-4.750×10^5	0.205

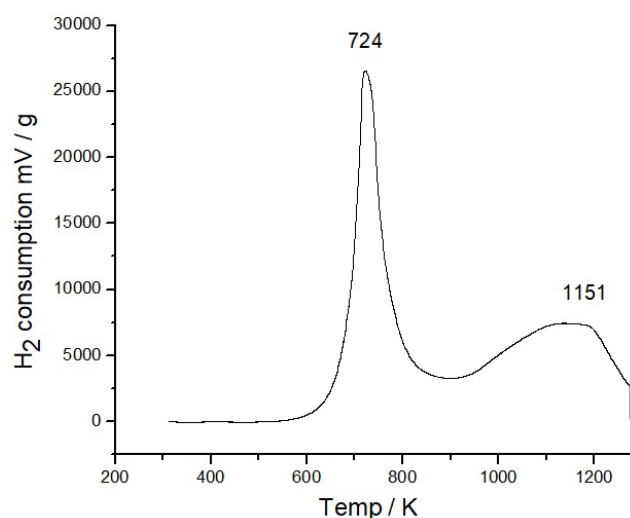
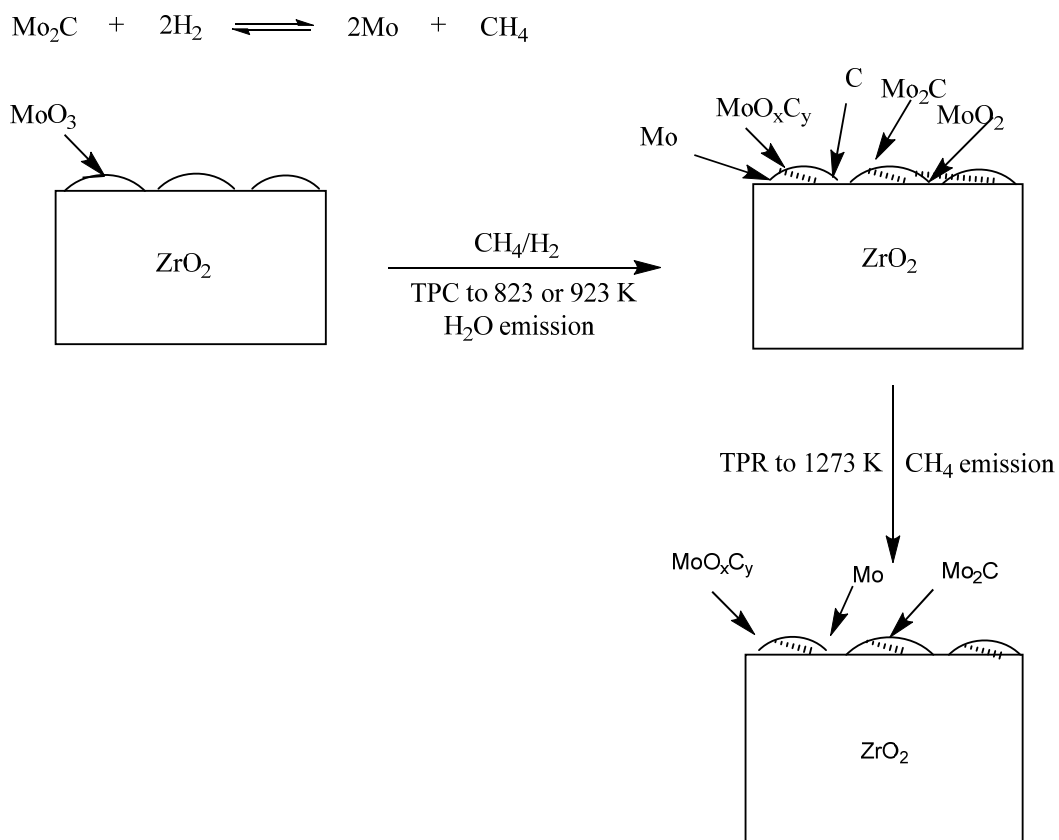


Fig. 5. TPR profile of uncarburized sample.

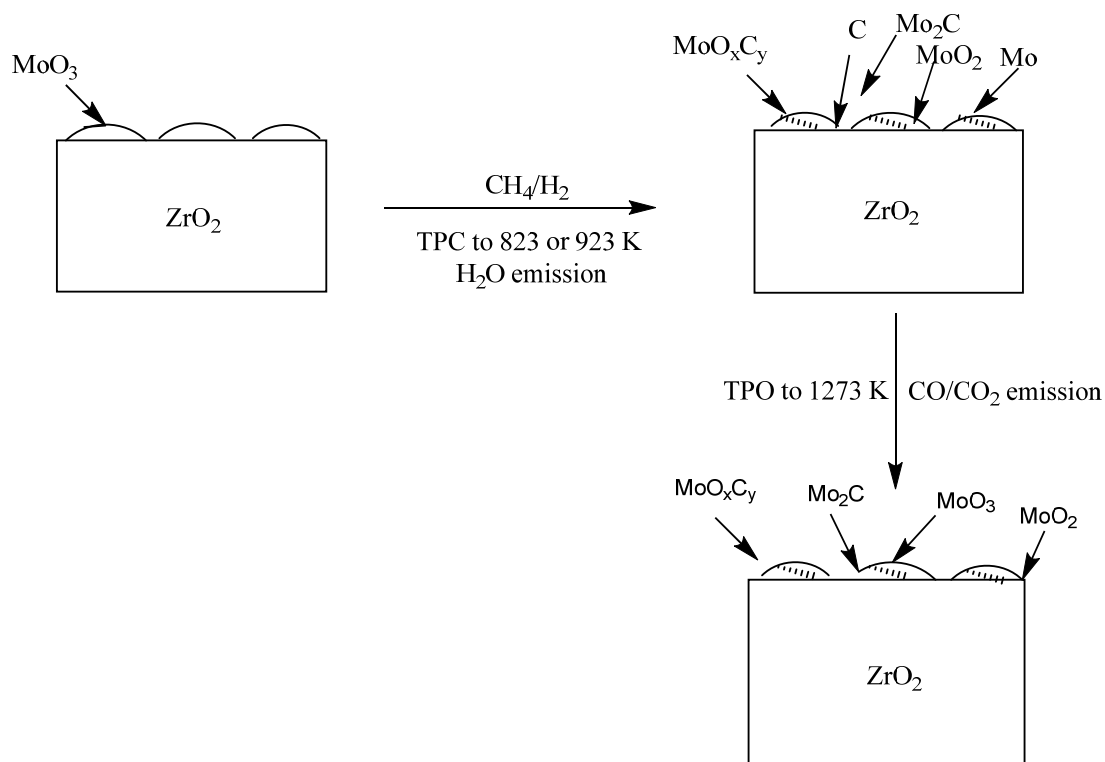
No CO₂ was detected in this experiment, because the H₂S trap used to remove sulfur species from contaminating the detector invariably trapped CO₂, but CO was obtained from TPO at *ca.* 480 K. However, it has been argued that no CO₂ evolved at greater temperatures than 683 K when coke deposition on the catalyst is avoided [14]. Therefore, the surface of the catalyst carburized at ≥ 923 K contains pure carbide and possibly few carbonaceous materials while carburization below 923 K gave oxycarbide with few carbonaceous deposits, which could easily be removed by hydrogen before reaction.

A proposed systematic sequence of the *in-situ* TPC-TPR is described in Scheme 1. This schematic presentation is only for better understanding of the systematic process that occurs during the TPC and the subsequent TPR. The scheme does not represent the real structure for the material. It, however, shows that the catalyst precursor turned into carbide with different amounts of other components at the surface. The nature of the surface is a function of the carburization temperature. The amount of carbon deposit could be quantified by measuring either hydrogen consumption or methane formed. Similarly, Scheme 2 shows *in-situ* TPC-TPO. The amount of CO formed could easily give information about the carbonaceous deposit on the catalyst and insight about the amount of carbon present in the catalyst.

Oxygen vacancy has been known as a common characteristic for many metal oxides [21], and has been reported to be essential for activating molecular H₂ and thus hydrogenate linear olefins, cyclic olefins, and aryl nitro groups [21]. Thus, this feature might be the key factor why oxycarbide was more selective to hydroisomerization compared to pure carbide [10].



Scheme 1. Steps occurring during *in-situ* TPC-TPR of the catalysts.



Scheme 2. Steps occurring during *in-situ* TPC-TPO of the catalysts.

Blekkann *et al.*, [10] have explained the reaction of n-heptane over the oxidized carbide catalyst in terms of a bond-shift mechanism via a metallocyclobutane intermediate. Furthermore, oxidation of metal carbide has been shown to lead to an active and selective material in the isomerization of alkanes [22,10]. Therefore, catalyst carburized at 823 K is catalytically active phase possibly because it produces an oxycarbide consisting of a Mo₂C lattice where oxygen replaces some carbon atoms in the interstitial voids [10]. It can further be deduced that the oxycarbide is capable of producing sites for hydrogenation and dehydrogenation, this may result in forming olefinic intermediates, which can then be isomerized. Hence, the better results were observed when the catalyst was characterized at 823 K.

4. Conclusions

In-situ TPR and TPO were able to differentiate between the surface of catalysts carburized at ≥ 923 K and below 923 K. *In-situ* TPO showed the surfaces of the catalysts to contain the similar amount of carbonaceous deposit, while TPR showed their ability to consume hydrogen in different amounts. These observations suggested the presence of oxygen in the catalyst carburized at 823 K due to the incomplete reduction. The catalyst carburized at 823 K proved to be approximately four times better in both isomer selectivity and conversion compared to catalyst carburized at ≥ 923 K.

References

- [1] J.B. Claridge, A.P.E. York, A.J. Brungs, *J. Catal.* 100 (1998) 85–100.
- [2] J.S. Lee, S.T. Oyama, M. Boudart, *J. Catal.* 133 (1987) 125–133.
- [3] W. Wu, Z. Wu, C. Liang, *J. Phys. Chem. B* 107 (2003) 7088–7094.
- [4] Z. Li, C. Chen, E. Zhan, *Chem. Commun.* 50 (2014) 4469–4471.
- [5] A. Galadima, R.P.K. Wells, J.A. Anderson, *Appl. Petrochem. Res.* 1 (2012) 35–43.
- [6] S.T. Oyama, C.C. Yu, S. Ramanathan, *J. Catal.* 184 (1999) 535–549.
- [7] J.S. Lee, S. Locatelli, S.T. Oyama, M. Boudart, *J. Catal.* 125 (1990) 157–170.
- [8] T.C. Xiao, A.P.E. York, V.C. Williams, *Chem. Mater.* 12 (2000) 3896–3905.
- [9] P. Del Gallo, C. Pham-Huu, A.P.E. York, M.J. Ledoux, *Ind. Eng. Chem. Res.* 35 (1996) 3302–3310.
- [10] E.A. Blekkann, C. Pham-Huu, M.J. Ledoux, *J. Guille, Ind. Eng. Chem. Res.* 33 (1994) 1657–1664.
- [11] C. Pham-Huu, P. Del Gallo, E. Peschiera, M.J. Ledoux, *Appl. Catal. A* 132 (1995) 77–96.
- [12] M.J. Ledoux, C. Pham-Huu, A.P.E. York, *The Chemistry of Transition Metal Carbides and Nitrides*, S.T. Oyama, Ed., Blackie New York, 1996, pp. 373–397.
- [13] F.F. Oloye, A.J. McCue, J.A. Anderson, *Catal. Today* 277 (2016) 246–256.
- [14] C. Bouchy, C. Pham-Huu, B. Heinrich, *Appl. Catal. A* 215 (2001) 175–184.
- [15] M.J. Ledoux, P. Del Gallo, C. Pham-Huu, A.P.E. York, *Catal. Today* 27 (1996) 145–150.
- [16] T. Matsuda, K. Watanabe, H. Sakagami, N. Takahashi, *Adsorption* 242 (2003) 267–274.
- [17] T. Xiao, A.P.E. York, H. Al-Megren, *C.R. Acad. Sci. Ser. II: Chim.* 3 (2000) 451–458.
- [18] C. Bouchy, C. Pham-Huu, B. Heinrich, *J. Catal.* 190 (2000) 92–103.
- [19] N. Perret, X. Wang, L. Delannoy, *J. Catal.* 286 (2012) 172–183.
- [20] F.F. Oloye, A.J. McCue, J.A. Anderson, *Appl. Petrochem. Res.* 6 (2016) 341–352.
- [21] J. Song, Z.F. Huang, L. Pan, J.J. Zou, X. Zhang, L. Wang, *ACS Catal.* 5 (2015) 6594–6599.
- [22] M.J. Ledoux, C. Pham-Huu, H. Dunlop, J. Guille, *Stud. Surf. Sci. Catal.* 75 (1993) 955–967.