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Molybdenum oxycarbide hydrocarbon isomerization catalysts: cleaner fuels for the future

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Abstract

The catalytic behaviour of the molybdenum oxycarbide catalyst, synthesized in situ from molybdenum oxide, is compared with that of a supported bifunctional platinum catalyst for the isomerization of *n*-octane. The main products are the mono- and di-methyl isomers, and almost no aromatics are observed. It is shown that a high selectivity to the isomer products ($> 90\%$) can be obtained over the molybdenum catalyst, even close to the thermodynamic equilibrium (i.e., at high conversion (75%)), while this is not possible over the platinum catalyst. Furthermore, the high resistance of the molybdenum catalyst to sulphur and nitrogen catalyst poisons typically found in crude oil is shown, and the isomerization of *n*-heptane over a supported molybdenum oxycarbide (MoO_3/SiC) catalyst is demonstrated.

Keywords: Molybdenum oxycarbide; Isomerization; *n*-Heptane; *n*-Octane; Sulphur and nitrogen resistance

1. Introduction

Until recently, the enhancement of motor fuel octane rating, allowing the production of high performance automotive fuels and aviation fuels, has been achieved by the addition of lead compounds or aromatics, but both of these methods are now unfashionable and under scrutiny due to their deleterious environmental effects. As a result, the oil industry has been forced to look for new ways of increasing the motor octane number, and the addition of oxygenates (e.g., MTBE), giving ‘unleaded fuels’, is currently preferred since it is thought that this produces cleaner emissions. However, a further alternative is to utilize the isomerization reaction to increase the value of the straight chain alkanes, which are a major constituent in some crude oil fractions, and thus increase the octane rating without the need for additives, as shown in Table 1. This reaction must be carried out with a high selectivity to the branched alkanes, while minimizing the amount of hydrocracking to light hydrocarbons. Furthermore, the aromatization of the alkanes must be avoided for the reasons already mentioned. The isomerization of hydrocarbons $\leq C_6$ is currently carried out very successfully using bifunctional supported platinum catalysts; however, difficulties are encountered with hydrocarbons larger than hexane (i.e., a major constituent of the gasoline fraction) due to the efficiency of industrial platinum catalysts for the cracking reactions [1]. A further

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Table 1
Octane numbers of some hydrocarbons

No. C atoms	Hydrocarbon	M.O.N.
4	Butane	89.1
	Methylpropane	99.0
5	Pentane	61.9
	Methylbutane	90.3
6	Hexane	26.0
	2-Methylpentane	73.5
	3-Methylpentane	74.3
	Benzene	98.0
	2,2-Dimethylbutane	93.4
	2,3-Dimethylbutane	94.3
7	Heptane	0.0
	2-Methylhexane	45.0
	3-Methylhexane	55.8
	3-Ethylpentane	69.3
	2,3-Dimethylpentane	89.0
8	Octane	−15.0
	2-Methylheptane	23.8
	3-Methylheptane	35.0
	2,2,4-Trimethylpentane	100.0

use for the isomerization reaction would be for decreasing the freezing point of gas oil and lubricant oil fractions by conversion of the long straight chain hydrocarbons into their respective methyl-isomers. Once again, this has been achieved with the addition of aromatics, but, since aromatics are now outlawed, a new process must be found. No such process exists with current catalysts and technology.

Recently, it has been found that oxygen modified carbides of the group VI transition metals (Mo and W) are extremely selective for the alkane isomerization reaction. Iglesia and coworkers [2–4] have shown that oxygen treatment of WC or β-W_2C, synthesized by temperature programming carburization of WO_3 under CH_4/H_2 mixtures, results in a highly selective alkane isomerization catalyst. Independent work by Ledoux and his group [5–9] has demonstrated a similar effect using a high specific surface area catalyst synthesized from low surface area MoO_3 or Mo metal, or from high surface area Mo_2C. Ledoux proposed that a new catalytically active 'oxycarbide' phase was formed during the early stages of the reaction, consisting of a MoO_3 lattice with carbon replacing some oxygen atoms in vacancies formed by partial reduction [10].

In this paper, the catalytic behaviour of the molybdenum oxycarbide catalyst is compared with that of a supported bifunctional platinum catalyst for the isomerization of *n*-octane, and the resistance of the molybdenum catalyst to sulphur and nitrogen catalyst poisons is shown. Also, the use of a *supported* molybdenum oxycarbide catalyst is demonstrated for the isomerization of *n*-heptane.

2. Experimental

2.1. Catalyst synthesis

The high specific surface area molybdenum oxycarbide catalyst (145 $m^2\ g^{-1}$) was synthesized in situ from low specific surface area MoO_3 (4 $m^2\ g^{-1}$) at low temperature (350°C) under a hydrocarbon/hydrogen mixture. The SiC, used as a catalyst support, was prepared according to the method described previously [11], and had a surface area of 106 $m^2\ g^{-1}$. MoO_3 was added to SiC using the incipient wetness technique and, after calcination (500°C), the catalyst surface area was 50 $m^2\ g^{-1}$.

A classical bifunctional platinum supported on β-zeolite catalyst was also prepared (see [9]) for comparison with the molybdenum catalysts. Using elemental analysis, the platinum loading was found to be 1.5%. Before use, this catalyst was reduced in situ under hydrogen at 40 ml min^{-1} and 450°C for 3 h, then cooled to the reaction temperature, still under hydrogen, before introduction on the hydrocarbon feed.

n-Heptane and *n*-octane (Prolabo, > 99.5% purity) were used as received. Hydrogen was obtained from Air Liquide (Grade U).

2.2. Apparatus

Reactions were performed in a microreactor consisting of 0.25-in. 316-stainless steel throughout, with the catalyst placed between quartz wool plugs in the centre of a copper-lined steel tube (4 mm i.d. × 300 mm). A Minicor temperature controller was used to regulate the furnace temperature and a second thermocouple, placed alongside the reactor, was installed for careful monitoring of the reactor temperature. The hydrogen flow rate was controlled using a Brooks 5850TR mass flow controller interfaced to a Brooks 5876 control unit, and the liquid hydrocarbon was delivered via a Gilson 302 HPLC pump. The reactor pressure was controlled using a Grove membrane back pressure regulator and a needle valve, and samples were analyzed off-line via a septum. The whole apparatus was heated to avoid condensation of liquids in the system.

2.3. *Product analysis*

Product analysis was carried out on a Hewlett-Packard 5890 II gas chromatograph fitted with a flame ionization detector, and separation of the C_1–C_8 hydrocarbons was achieved using an HP-PONA capillary column coated with methyl-siloxane (0.2 mm i.d. × 50 m, film thickness = 0.5 mm). The major organic impurities in the reactant hydrocarbons were subtracted from the exit gas analysis and response factors for the various products have been taken into account in our calculations. Only traces of alkenes were detected in the reactor exit gas and these have therefore been omitted from the final data analysis. Kinetic data are reported as reaction rates (mol g^{-1} s^{-1}).

3. Results and discussion

3.1. *Isomerization of n-octane over molybdenum oxycarbide and Pt / β-zeolite*

The results for the isomerization of *n*-octane, over the molybdenum oxide (in situ prepared molybdenum oxycarbide) catalyst and the β-zeolite supported bifunctional platinum catalyst at 15 bar, are shown in Table 2.

Table 2

Isomerization of *n*-octane over molybdenum oxycarbide and Pt/β-zeolite catalysts at 15 bar

Catalyst	Mo oxycarbide	Pt/β-zeolite
Reaction temperature	290°C	250°C
Conversion (%)	37	28
Rate (10^{-7} mol g^{-1} s^{-1})	28.3	117.5
C_8 Selectivity (%)	97	93
Isomer products (%) [a]		
TMP + DMH	15.6	18.4
3-EH	5.3	4.0
Σ-MHept	78.9	77.3
Σ-Cyclic	0.1	0.2
Cracked products (%) [b]		
C_7+C_1	30.6	3.2
C_6+C_2	4.9	0.0
C_5+C_3	40.0	51.5
$2\times C_4$	23.9	45.0

[a] TMP + DMH, Σ(tri- and di-methyl isomers); 3-EH, 3-ethylhexane; Σ-MHept, Σ-methylheptanes.

[b] Balance to 100% is C_4 to C_1 not accounted for by a single C–C bond splitting.

Over the molybdenum catalyst, at the start of the reaction, the activity extrapolated to zero, indicating that the starting MoO_3 is inactive for the isomerization reaction. After 5–10 h, under the H_2/*n*-octane reactant feed, a steady state was achieved (not shown). The result given in Table 2 was taken after 24 h (i.e., at the steady state). This increase in the activity with time has been shown before for the isomerization of *n*-hexane and *n*-heptane [6,7,10], and is attributed to the formation of a new catalytically active and selective phase; molybdenum oxycarbide. The structure of this new phase, and the mechanism for its formation, has been extensively studied and was described previously [8–10]. Briefly, the oxycarbide phase is formed by simultaneous reduction along the [010] direction, and substitution of the oxygen atoms by carbon atoms from the gas phase; this results in a blocking of the structure collapse to MoO_2 and the formation of an intermediate phase. No such activation process was observed over the reduced Pt/β-zeolite catalyst, which was stable for the duration of the experiment. Table 2 also shows that the bifunctional Pt/β-zeolite catalyst is much more active than the molybdenum oxycarbide catalyst.

The C_8 isomer selectivity was about 95% for both the catalysts, the main products being the methylheptanes, in the ratio of 2-methyl : 3-methyl : 4-methyl ≈ 3 : 3 : 1, and the dimethylhexanes. Over both the catalysts, the main cracking products were those from mid-molecule cracking (i.e., $(C_5 + C_3)$ and $(2 \times C_4)$), however, over the molybdenum oxycarbide the amount of these molecules decreased with time on stream in favour of the $(C_7 + C_1)$ and $(C_6 + C_2)$ fractions while, in the case of platinum, no change was observed for the duration of the experiment. Only traces of cyclic molecules were detected among the reaction products, and no catalyst deactivation was observed over > 50 h, indicating that coking is not occurring.

The results presented above have shown that the isomerization of *n*-octane can be carried out successfully at low conversion over both the molybdenum oxycarbide and the supported platinum catalysts. However, it has been reported that, over bifunctional platinum catalysts, the isomerization selectivity is dependent on the total conversion, since as the conversion increases, so too does the amount of secondary products (i.e., dimethyl-isomers), which, due to their high reactivity, cleave to give lower molecular weight fractions and thus a lower isomer selectivity [12]. Also, it has been reported that increasing the chain length of the reactant hydrocarbon leads to a more dramatic drop in the isomer selectivity as the conversion is increased [12–15]. In fact, Belloum et al. [1] reviewed the literature and found no commercial process for the isomerization of hydrocarbons larger than hexane.

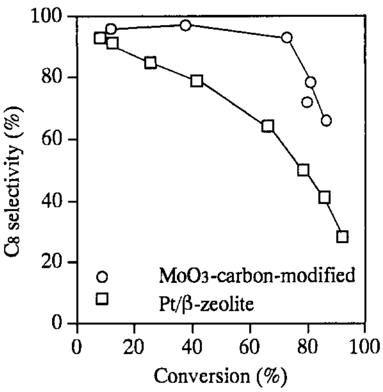

Fig. 1. *n*-Octane isomerization selectivity as a function of total conversion.

Fig. 1 shows a comparison of the isomer selectivity obtained over the Pt/β-zeolite and molybdenum oxycarbide catalysts, at 15 bar and as a function of total conversion. For platinum, as the conversion is increased the selectivity drops steadily (from 95% at about 10% conversion, to 50% at 75% conversion), as discussed above. However, over the molybdenum oxycarbide catalyst, the isomer selectivity remains almost unchanged (about 95%) up to about 75% conversion, with a dramatic drop suddenly occurring as the thermodynamic equilibrium is approached. The reasons for the differences in the behaviour of these two catalysts have been discussed in another publication [9]. *In conclusion, molybdenum oxycarbide provides a possible catalyst for the isomerization of molecules* $> C_6$.

3.2. Resistance of molybdenum oxycarbide and Pt/β-zeolite to catalyst poisons

An important consideration for a catalyst to be implemented successfully in industry is its susceptibility to catalyst poisons present in crude oil, such as thiophene, benzothiophene, thiols and pyridine. In this section, a comparison of the resistance of the molybdenum oxycarbide and the Pt/β-zeolite catalysts against thiophene and piperidine is shown for the *n*-heptane isomerization reaction.

For both catalysts, the steady state was initially achieved using the H_2/*n*-heptane reactant mixture at 20 bar (MoO_3, 350°C, 300 mg catalyst, total flow = 200 ml min^{-1}, $H_2/C_7 = 25$; Pt/β-zeolite, 290°C, 100 mg catalyst, other conditions the same), before the desired concentration of the heterocyclic compound was added to the liquid feed, and the catalyst behaviour followed with time. The organonitrogen compound (piperidine) was a much more potent catalyst poison than the organosulphur compound (thiophene) and therefore a lower concentration of the former was used in the poisoning experiments (10 ppm wt N compared to 120 ppm wt S).

Fig. 2a shows the relative rate (relative rate = rate with poison at time = t/rate without poison at time = 0; steady state position = 1) for the H_2/n-heptane/thiophene reaction over the molybdenum oxycarbide and platinum catalysts as a function of time.

In the case of platinum, an initial rapid decrease in the rate was seen, followed by a plateau where the rate stayed constant over a period of > 20 h. The isomer selectivity was also seen to decrease with time (93 to 80% in 24 h) meaning that the nature of the active sites, as well as the number, has changed. The initial rapid decrease in isomerization activity during the first few hours is attributed to a suppression of adsorption sites on the platinum surface by the formation of surface sulphide. Wang et al. [16] reported that sulphidation occurs with H_2S even at room temperature. The deactivation-plateau trend, seen for Pt/β-zeolite in Fig. 2a, has been observed before by Kao et al. [17], for the Pt/KL hexane aromatization catalyst. Kao et al. suggested that the trend arose from the greater sulphur susceptibility of the Pt particles within the zeolite channels compared with those on the outer surface.

With molybdenum oxycarbide, the relative rate was almost unchanged, dropping from 1 to 0.97 over the course of the experiment (26 h), while the isomer selectivity also remained constant at 90%. The deactivation observed for both the catalysts is attributed to the formation of H_2S by hydrogenolysis of thiophene, which can alter the active phase by the formation of sulphides. Similar results were reported by Dhainaut et al. [18] for the hydrodesulphurization of dibenzothiophene over supported platinum catalysts.

The deactivation trends observed with the H_2/n-heptane/piperidine reactant feed were similar to those with the thiophene, and the results obtained for the two catalysts are shown in Fig. 2b. Again, over the platinum catalyst, a very fast drop in the rate was seen (1.0 to 0.36 in 8 h). However, with piperidine as the poison, the initial rapid drop was followed by slow deactivation over the course of the experiment (to 0.1 after 30 h). A decrease in the rate also occurs with molybdenum oxycarbide as the catalyst; however, in this case, the drop is only 10% of the initial activity after 30 h (i.e., from 1.0 to 0.9).

These results have shown that the molybdenum oxycarbide catalyst exhibits a very high thioresistance, even in the presence of a thiophene concentration much higher than that usually found in industry, while the catalyst also has a higher resistance to organonitrogen compounds compared with the Pt/β-zeolite cata-

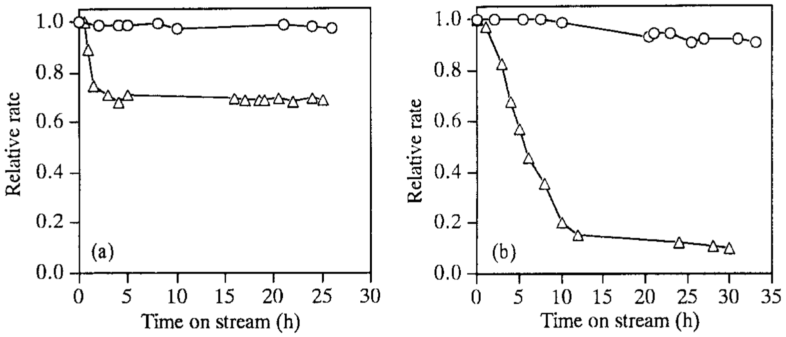

Fig. 2. Effect of catalyst poisons on the activity of molybdenum oxycarbide (○) and Pt/β-zeolite (△) catalysts: (a) thiophene (120 ppm wt S); (b) piperidine (10 ppm wt N).

lyst. Thus, the presence of such common poisons should not pose a problem for the industrial utilization of the molybdenum oxycarbide catalyst.

3.3. Isomerization of n-heptane over SiC supported molybdenum oxycarbide

This paper has described how bulk molybdenum oxycarbide catalysts can be used very efficiently for the isomerization of hydrocarbons larger than hexane. However, in industry, it would be economically more desirable to decrease the amount of the active phase in the reactor, by using a supported catalyst.

In this section, a supported MoO_3 catalyst has been employed for the isomerization of *n*-heptane. MoO_3 supported on SiC (16.1 wt% Mo) was prepared and the isomerization of *n*-heptane carried out at 350°C and 6 bar (300 mg catalyst, $H_2/C_7 = 25$, total flow = 200 ml min^{-1}). The catalytic behaviour was followed with time on stream.

Fig. 3 shows that, as in the case of the bulk molybdenum catalysts, the isomerization rate (shown here per g of MoO_3) increases with time, indicating that the active molybdenum oxycarbide phase is formed in the early part of the reaction. The steady state is reached in about 10 h, with the rate then remaining constant, at about 150×10^{-7} mol (g $MoO_3)^{-1}$ s^{-1}, for the duration of the experiment (50 h).

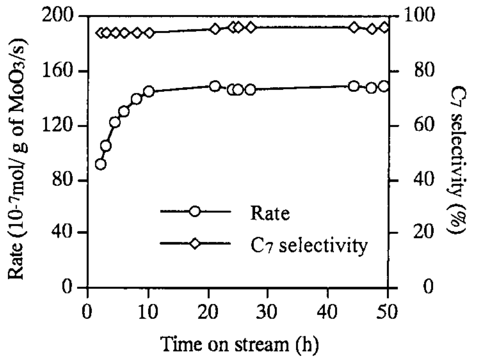

Fig. 3. Isomerization of *n*-heptane over a MoO_3/SiC catalyst (350°C, 6 bar).

Table 3
Isomerization of *n*-heptane over molybdenum oxycarbide as a bulk catalyst and supported on SiC (6 bar and 350°C)

Catalyst	MoO_3 bulk	MoO_3/SiC
Conversion (%)	41.7	23.5
Rate (10^{-7} mol g^{-1} s^{-1})	59.8	149.4
C_7 Selectivity (%)	91	94
Isomer products (%) [a]		
DMP	21.6	8.7
2-MH	35.1	40.2
3-MH	40.1	47.2
3-EP	2.9	3.1
Σ-Cyclic	0.3	0.8
Cracked products (%) [b]		
C_6+C_1	13.0	17.0
C_5+C_2	8.0	19.1
C_4+C_3	75.7	59.9

[a] DMP, Σ-dimethylpentanes; 2- and 3-MH, 2-methyl- and 3-methylhexanes; 3-EP, 3-ethylpentane.

[b] Balance to 100% is C_4 to C_1 not accounted for by a single C–C bond splitting.

The C_7 isomer selectivity also stays constant at about 95%. The results for pure SiC (not given) showed that this material has neither isomerization nor cracking activity and, therefore, the isomerization is due to the supported molybdenum phase.

In Table 3, the results for the SiC supported catalyst are compared with those obtained, under the same conditions, for bulk molybdenum oxycarbide prepared from MoO_3. Both sets of results were taken at the steady state, after 50 h under the reactant feed. No catalyst deactivation was observed during the experiment. The rates given are per g of MoO_3.

It can be seen that the results for the two catalysts do not differ greatly, indicating that a similar active phase is present in both cases. Over both molybdenum catalysts, the C_7 isomer selectivity was > 90%, with 2-methyl and 3-methylhexane as the main products and a significant contribution from the dimethylpentanes. Almost no cyclic products were produced. The main cracking products were the $(C_4 + C_3)$ fraction from mid-molecule cracking, although the amount of these molecules decreased with time in favour of the $(C_6 + C_1)$ and $(C_5 + C_2)$

fractions, particularly in the case of the SiC supported catalyst.

In summary, the isomerization of *n*-heptane over the SiC supported molybdenum oxycarbide catalyst has been successfully demonstrated, with results comparable to those for the bulk molybdenum oxycarbide.

4. Conclusions

In this paper, it is shown that the isomerization of hydrocarbons $> C_6$, with low selectivity to the cracking products and almost no aromatics formation, is now possible, even at very high conversion (close to the thermodynamic equilibrium), using a high specific surface area *molybdenum oxycarbide* catalyst, synthesized by the procedures described in previous publications [5–9], and either as a bulk catalyst or *supported on SiC*. This is extremely important since it provides catalysts which can isomerize hydrocarbons from C_7 to $> C_{20}$ without disastrous cracking occurring. Furthermore, from an economic standpoint, molybdenum is much cheaper and more abundant than platinum, while the molybdenum catalyst is highly resistant to sulphur and nitrogen poisons, and does not deactivate by coking, resulting in a long catalyst lifetime and requiring the extraction of less minerals from the earth. Therefore, this paper shows how *cleaner motor fuels*, with no additives, can be easily produced in the very near future using *molybdenum oxycarbide* catalysts.

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