ELSEVIER

Catalysis Today 27 (1996) 145–150

CATALYSIS TODAY

Molybdenum oxycarbide isomerization catalysts for cleaner fuel production

Marc J. Ledoux *, Pascal Del Gallo, Cuong Pham-Huu, Andrew P.E. York

Laboratoire de Chimie des Matériaux Catalytiques, EHICS, Université Louis Pasteur, 1 rue Blaise Pascal, 67008 Strasbourg Cedex, France

---

Abstract

Isomerization of *n*-heptane and *n*-octane is performed over MoO_3-carbon-modified catalyst with high selectivity even at a conversion of 80%, yielding mainly mono- and dimethyl-isomers. No traces of aromatic molecules are observed among the reaction products.

Keywords: Fuel production; Molybdenum oxycarbide; Isomerization catalysts

---

1. Introduction

In recent years, public concern over the damage being caused to the environment has heightened and the chemical industry has been faced with the need for new, more efficient processes in order to comply with the strict regulations being implemented. In the petroleum industry controls on exhaust pipe emissions have resulted in the search for ways of increasing the octane rating of motor fuel, which in the past has been accomplished using the now unfashionable lead compounds, such as tetraethyl lead, or by the addition of aromatics which are under vigorous scrutiny due to their detrimental environmental effects. The addition of oxygenates such as methyltertiarybutylether, to give unleaded fuels, is currently preferred due to the thought that cleaner emissions are produced.

An alternative is to use 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 additions. It is necessary for this reaction to be carried out with a high selectivity for the branched alkanes while the amount of hydrocracking to light hydrocarbons is minimized. 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 the platinum catalyst for the cracking reaction [1,2]. A further use for the isomerization reaction would be for decreasing the freezing point of gas oil and lubricant oil fractions by conversion of the straight chain hydrocarbons into the methyl-isomers. Again the addition of aromatics has been the solution in the past but, since aromatics are now outlawed, a new process must be found. No

---

* Corresponding author.

0920-5861/96/$32.00
SSDI 0920-5861(95)00182-4

such process exists with current catalysts and technology.

In the last 20 years, a number of researchers have shown that some transition metal carbides, such as those of molybdenum and tungsten, can show similar catalytic behavior to the noble metals [3,4]. Clean carbide surfaces obtained by reductive treatment have been found to be highly efficient alkane hydrogenolysis catalysts [5–7]. However, very selective catalysts for the alkane isomerization reaction can be synthesized by modification of the surface in an oxidative process. Indeed, Iglesia and co-workers [5–7] reported that oxidative treatment of a WC or β-W_2C, prepared by temperature programming carburization of WO_3 under CH_4/H_2 mixtures, gave a catalyst capable of alkane isomerization without extensive hydrogenolysis. Independent work by Ledoux and co-workers [8–10] showed a similar effect for the isomerization of *n*-hexane, using a high specific surface area catalyst synthesized from low surface area molybdenum oxide or molybdenum metal, or from high surface area molybdenum carbide. This was attributed to the formation of a new catalytically active phase formed during the first few hours of the hydrocarbon reaction; an oxycarbide consisting of a MoO_3 lattice where carbon replaces some oxygen atoms in the vacancies formed by partial reduction [11]. It was proposed that over the molybdenum catalyst a metallacyclobutane mechanism was responsible for the alkane isomerization.

The aim of the present study is to report the catalytic behavior of the high specific surface area molybdenum oxycarbide catalyst ($145\ m^2g^{-1}$) for the isomerization of *n*-heptane and *n*-octane molecules at medium pressure.

2. Experimental

2.1. Materials and catalysts

High specific surface area MoO_3-carbon-modified catalyst ($145\ m^2\ g^{-1}$) was synthesized from the low specific surface area MoO_3 ($4\ m^2\ g^{-1}$) at low temperature (623 K) under a mixture of *n*-heptane and hydrogen under medium pressure. For details see Ref. [12].

A classical bifunctional platinum supported on β-zeolite catalyst was also prepared for comparison with the molybdenum catalysts [9]. Elemental analysis was used to confirm the percentage loading of platinum. Before use the catalyst was reduced in situ under hydrogen at 40 ml min^{-1} and 723 K for 3 h and then cooled to the reaction temperature, still under flowing hydrogen, before the introduction of the hydrocarbon feed. Different masses of catalysts were used in order to compare the selectivity at iso-conversion.

The *n*-heptane and the *n*-octane (Prolabo) were used as received with a purity of $> 99.5\%$ and the major organic impurities were subtracted from the exit gas analysis before calculating the product distribution.

2.2. Apparatus

Reactions were performed in a micro-reactor consisting of 1/4 316-stainless steel with the catalyst placed between quartz wool plugs in the center of a copper-lined steel tube (4 mm internal diameter × 300 mm). The tube furnace temperature was controlled by a Minicor temperature controller and the reactor temperature was monitored using a second thermocouple placed alongside the reactor. The hydrogen flow rate was controlled using a Brooks 5850TR mass flow controller controlled from a Brooks 5876 control unit and the hydrocarbon was delivered via a Gilson 302 HPLC pump. The reactor pressure was regulated using a Grove membrane back pressure regulator and a needle valve and samples were analyzed off-line via a septum.

2.3. Product analysis

Product analysis was carried out on a Hewlett-Packard 5890 series II gas chromatograph fitted with a flame ionization detector. Separation of the C_1 to C_8 hydrocarbons was achieved using a HP-PONA capillary column coated with methylsiloxane (50 m × 0.2 mm, i.d., film thickness, 0.5 mm) and the response factors for the various products have been determined and taken into account in our calculations. Only traces of alkenes were detected in the reactor exit gas and these were therefore omitted from the final data analysis.

Kinetic data are reported as reaction rates (mol g^{-1} s^{-1}) calculated assuming a differential reactor (conversion < 10%) or using pseudo first order kinetics for experiments with higher conversions.

3. Results

3.1. MoO_3-carbon-modified catalyst

The results for the isomerization of *n*-heptane and *n*-octane at 15 bar over MoO_3-carbon-modified catalyst are presented in Fig. 1 and Fig. 2. The activity of the molybdenum catalyst develops with time on stream whatever the hydrocarbon used and levels off at a rate of 53.4 and 30.1×10^{-7} mol g^{-1} s^{-1} for *n*-heptane and *n*-octane, respectively.

It should be noted that the isomer selectivity also develops with time. The main products from the isomerization of *n*-C_7 and *n*-C_8 are mono- and dibranched molecules; only traces of cyclic molecules are detected among the reaction products (< 1%) as shown in Table 1 and Table 2. The major cracking products are those from mid-molecule cleavage, i. e., *n*-butane, methylpropane and propane. The amount of these molecules decreases with time on stream in favor of both the ($C_5 + C_2$), ($C_6 + C_1$) for *n*-C_7 and ($C_6 + C_2$), ($C_7 + C_1$) for *n*-C_8.

3.2. Pt/β-zeolite catalyst

In Fig. 3 and Fig. 4 the results are reported obtained over the bifunctional catalyst, Pt (1.5 wt.-%)/β-zeolite, obtained at 15 bar and 523 K (low conversion). The activity and selectivity are stable over the duration of the experiment. The Pt (1.5 wt.-%)/β-zeolite catalyst is more active in

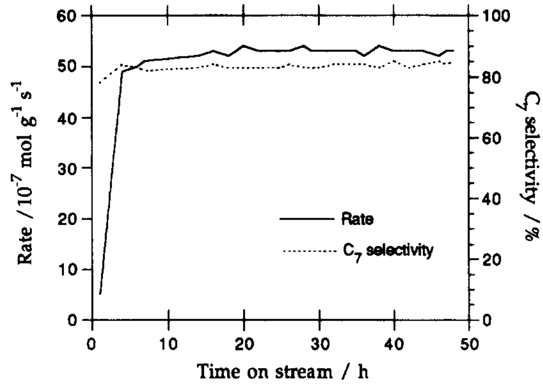

Fig. 1. *n*-Heptane isomerization over MoO_3-carbon-modified catalyst at 623 K.

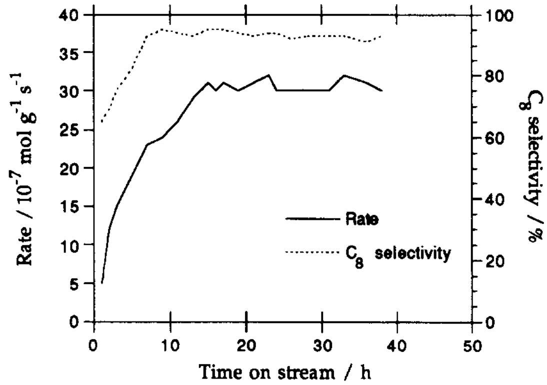

Fig. 2. *n*-Octane isomerization over MoO_3-carbon-modified catalyst at 563 K.

Table 1

Isomerization of *n*-heptane over MoO_3-carbon-modified and Pt (1.5 wt.-%)/β-zeolite catalysts at 15 bar total pressure

Catalyst	MoO_3			Pt/β-zeolite		
Reaction temperature	623 K			538 K		
Tos/h	4	10	24	1	4	24
Conversion/%	38.2	43.3	43.5	22.7	23.0	22.2
Rate/10^{-7} mol/g/s	49.2	53.2	53.4	98.2	99.4	96.3
C_7 selectivity/%	84	83	83	88	88	90
Isomer products/%						
DMP[a]	18.0	19.0	19.3	13.1	13.0	12.8
3EP[a]	3.0	3.2	2.8	2.3	2.3	2.4
MHex[a]	78.4	77.3	77.5	84.1	84.2	84.2
Σ cyclic	0.6	0.5	0.4	0.5	0.5	0.6
Cracked products/%						
$C_6 + C_1$	15.0	16.0	18.0	3.6	3.4	3.0
$C_5 + C_2$	9.0	10.4	12.4	0.3	0.3	0.1
$C_4 + C_3$	73.2	71.3	66.6	91.0	91.3	92.8
Others	2.8	2.3	3.0	5.1	5.0	4.1

[a] DMP = dimethylpentanes, 3EP = 3-ethylpentane, MHex = methylhexanes

Table 2
Isomerization of *n*-octane over MoO_3-carbon-modified and Pt (1.5 wt.-%)/β-zeolite catalysts at 15 bar total pressure

Catalyst Reaction temperature	MoO_3 563 K		Pt/β-zeolite 523 K	
Tos/h	10	24	4	24
Conversion/%	37.2	43.0	27.8	28.0
Rate/10^{-7} mol/g/s	24.4	30.1	116.8	117.5
C_8 selectivity/%	97	94	94	93
Isomer products/%				
DMH[a]	16.3	15.5	18.6	18.4
3EHex[a]	5.0	5.2	4.2	4.0
MHep[a]	78.5	79.2	77.0	77.3
Σ cyclic	0.2	0.1	0.2	0.2
Cracked products/%				
C_7+C_1	16.5	20.3	2.7	3.0
C_6+C_2	5.0	7.1	0	0
C_5+C_3	45.0	40.0	51.8	52.0
$2C_4$	20.5	18.0	45.5	45.0
Others	13.0	14.6	0	0

[a] DMH = dimethylhexanes, 3EHex = 3-ethylhexane, MHep = methylheptanes

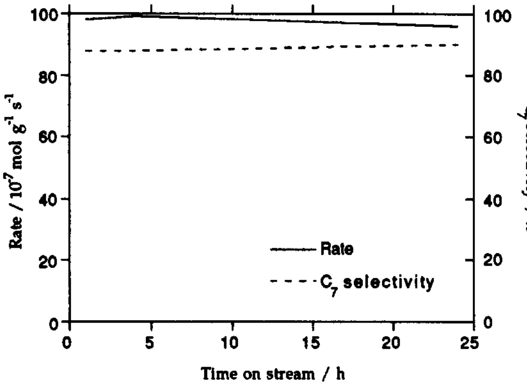

Fig. 3. *n*-Heptane isomerization over Pt/β-zeolite at 538 K.

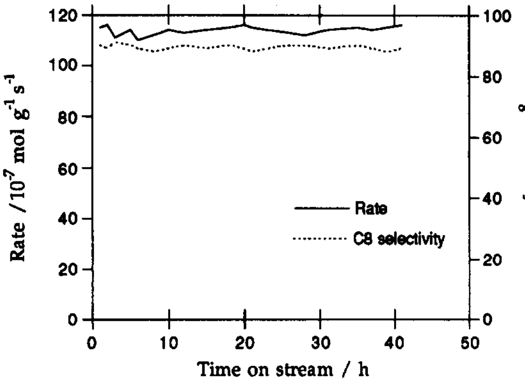

Fig. 4. *n*-Octane isomerization over Pt/β-zeolite at 523 K.

terms of rate compared to the molybdenum catalyst and shows a similar selectivity to isomers at low conversions. The main products from the isomerization of *n*-C_7 and *n*-C_8 are mono and di-branched molecules; only traces of cyclic molecules are detected among the reaction products (< 1%) as shown in Table 1 and Table 2.

3.3. Isomerization selectivity at high conversion

It has been shown in the preceding sections that the isomerization of the linear saturated hydrocarbons used in this study is relatively trivial at moderate conversion over all the catalysts and the catalyst activity is in order: Pt/β-zeolite > MoO_3-carbon-modified. However, it is well known in catalysis that as the reactant conversion increases, competition between the desired products and the reactants for the active sites becomes more and more significant and therefore more secondary products are formed. In the isomerization reaction, the branched products react to give mainly cracked molecules and thus decrease the isomer selectivity of the catalyst. Indeed, the isomerization carried out over the classical bifunctional catalyst is known to be dependent on the total conversion, irrespective of temperature and pressure [1,2]. Belloum et al. [13] reviewed the literature on the isomerization of C_4 to C_7 hydrocarbons and reported no commercial process for heptane isomerization. Therefore, a challenge in catalysis is to be able to carry out the selective isomerization of hydro-carbons, which contain more than 6 carbon atoms, at high conversion

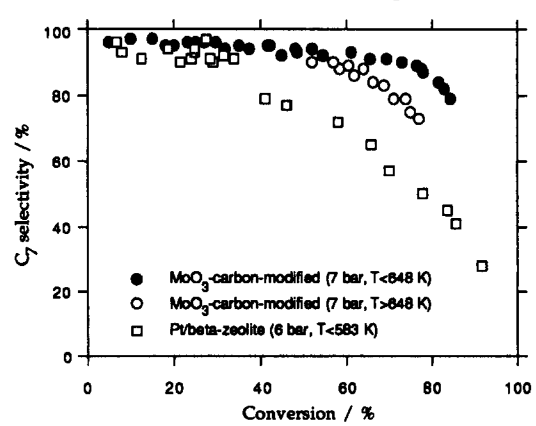

Fig. 5. *n*-Heptane isomerization. Isomer selectivity as a function of the total conversion.

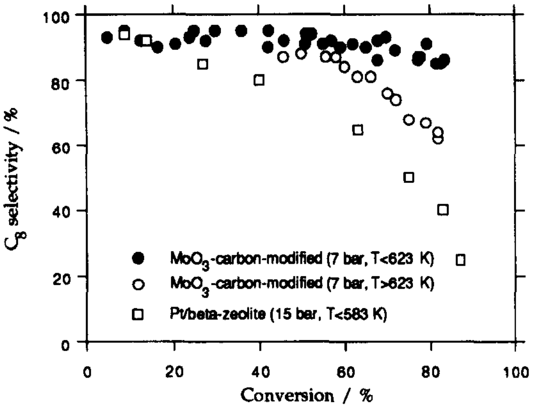

Fig. 6. *n*-Octane isomerization. Isomer selectivity as a function of the total conversion.

without cracking and without formation of a significant amount of aromatic compounds.

Fig. 5 and Fig. 6 show a comparison of the MoO_3-carbon-modified catalyst with the Pt/β-zeolite catalyst, for the isomerization of *n*-heptane and *n*-octane at medium pressure. The results for the isomerization of *n*-heptane and *n*-octane over the molybdenum oxycarbide show that similar isomer selectivities are obtained at low conversion ($\leq 25\%$ conversion gives 90–95% selectivity) to those over the platinum catalyst. However, on increasing the conversion, the isomer selectivity obtained over the MoO_3-carbon-modified catalyst remains almost unchanged up to high conversion (up to about 75%), providing a possible process for the industrial isomerization of molecules $> C_6$; in comparison, the selectivity obtained over the platinum drops dramatically.

4. Discussion

After an activation period under the reactant feed (hydrocarbon + H_2) molybdenum oxide is transformed into a new oxycarbide phase by incorporating carbon atoms in the partially reduced oxide lattice [11]. This is a very active and selective catalyst for the hydrocarbon isomerization reaction. Isomerization is performed over this oxycarbide phase via a methyl shift mechanism involving metallacyclabutane intermediate, giving only mono- and di-methyl-isomers [9,12]. Furthermore, increasing the chain length from C_7 to C_8 leads to an increase in the isomerization rate with the bifunctional mechanism, as shown in Table 1 and Table 2 and in Refs. [1,2,14] for the Pt (1.5 wt.-%)/β-zeolite catalyst. However, the opposite effect is observed for the MoO_3-carbon-modified catalyst, again indicating a difference in the isomerization mechanism. The metallacyclobutane mechanism [9,12] operating over the MoO_3-carbon-modified catalyst allows a high isomer selectivity (85–90%) obtainment at high conversion (75–80%), whereas over the Pt (1.5 wt.-%)/β-zeolite catalyst, a low selectivity (40%) is obtained at high conversion (80%) due to the high reactivity of the isomers, resulting in cracked products.

In addition, almost no cyclic products are formed over the molybdenum catalyst and this is in line with the new regulations which force the industry to decrease the aromatic content of fuels. In addition, the isomerization activity and selectivity are very stable with time on stream meaning that no deactivation due to coke formation is occurring on the catalyst.

5. Conclusion

It has been demonstrated that a highly isomerization selective molybdenum oxycarbide is formed at low temperature from the reaction between the starting MoO_3 and the hydrocarbon/hydrogen mixture. It is selective for the isomerization of a number of *n*-alkanes, with the main products always consisting of mono- and di-methyl-isomers ($> 95\%$) and no traces of cyclic or aromatic products among the reaction products. A high isomerization selectivity can be obtained even close to the thermodynamic equilibrium (i.e., isomer selectivity is independent of total conversion) for the isomerization of *n*-heptane and *n*-octane. These reactions are impossible over the classical bifunctional catalyst Pt/β-zeolite. This is extremely important industrially since it provides catalysts which can isomerize hydrocarbons from C_7 to $> C_{20}$ without disastrous cracking occurring. The relative high temperature required by this new catalyst (573–623 K) is not in favor of multibranched isomers, however it is still better to have monobranched than linear in the gasoline fraction and largely enough for improving diesel gas-oil and lubes.

Acknowledgements

This work was supported by the Pechiney Co. APEY wishes to thank the Royal Society for an ESEP fellowship. Dr. S. Hantzer of Exxon (Baton Rouge, LA, USA) is acknowledged for the donation of the zeolite support material.

References

[1] H. Vansina, M.A. Baltanas and G.F. Froment, Ind. Eng. Chem. Prod. Res. Dev., 22 (1983) 526.
[2] M. Steijns, G.F. Froment, P. Jacobs, J. Uytterhoeven and J. Weitkamp, Ind. Eng. Chem. Prod. Res. Dev., 20 (1981) 654.
[3] J.M. Muller and F.G. Gault, Bull. Soc. Chim. Fr., 2 (1970) 416.
[4] R.B. Levy and M. Boudart, Science, 181 (1973) 547.
[5] F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J. Baumgartner and E. Iglesia, J. Catal., 130 (1991) 86.
[6] F.H. Ribeiro, M. Boudart, R.A. Dalla Betta and E. Iglesia, J. Catal., 130 (1991) 498.
[7] E. Iglesia, F.H. Ribeiro, M. Boudart and J. Baumgartner, Catal. Today, 15 (1992) 307.
[8] M.J. Ledoux, C. Pham-Huu, H. Dunlop and J. Guille, in L. Guczi, et al. (Editors), Proc. 10th ICC, New Frontiers in Catalysis, Akadémiai Kiado Pub., Budapest, 1992, p. 955.
[9] E.A. Blekkan, C. Pham-Huu, M.J. Ledoux and J. Guille, Ind. Eng. Chem. Res., 33 (1994) 1657.
[10] M.J. Ledoux, C. Pham-Huu, A.P.E. York, E.A. Blekkan, P. Delporte and P. Del Gallo, Proc. Transition Metal Carbides and Nitrides: Preparation, Properties and Reactivity, Int. Chem. Congr. of the Pacific Basin Soc., Honolulu, 1995, in press.
[11] P. Delporte, F. Meunier, C. Pham-Huu, P. Vénnégues, M. J. Ledoux and J. Guille, Catal. Today, 23(3) (1995) 251.
[12] M.J. Ledoux, J. Guille, C. Pham-Huu, E.A. Blekkan and E. Peschiera, Eur. Pat. Appl. 9314199, 1993.
[13] M. Belloum, C. Travers and J.P. Bournonville, Rev. de l'Ins. Fra. du Pétrole, 46(1) (1991) 89.
[14] J.P. Franck, M. El Malki and R. Montarnal, Rev. de l'Ins. Fra. du Pétrole, 36(2) (1981) 211.