Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 113 (2006) 174–177

CATALYSIS TODAY
www.elsevier.com/locate/cattod

Palladium–sulfated zirconium pillared montmorillonite: Catalytic evaluation in light naphtha hydroisomerization reaction

Rachid Issaadi [a,*], François Garin [b], Chems Eddine Chitour [c]

[a] *Laboratoire de génie de la réaction chimique et des procédés catalytiques, Département de chimie industrielle, Faculté des sciences de l'ingénieur, Université Saad Dahleb, B.P. 270 Blida, Algeria*
[b] *Laboratoire des matériaux, surfaces et procédés pour la catalyse, UMR 7515 CNRS, ECPM, Université Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France*
[c] *Laboratoire de valorisation des énergies fossiles, Département de génie chimique, Ecole Nationale Polytechnique, Alger, Algeria*

Abstract

The present work is an evaluation of 1 wt.% Pd/sulfated zirconium pillared montmorillonite catalyst in the hydroisomerization reaction of two fractions of light naphtha composed mainly of C_5 and C_6 paraffins (feeds 1 and 2). Catalyst activity test was carried out in a fixed-bed flow reactor at reaction temperature of 300 °C, under atmospheric hydrogen pressure and weight hourly space velocity of $0.825\ h^{-1}$.

The reaction products showed high isomer and cyclane selectivity. Monobranched and multibranched isomers were formed as well as C5 and C6 cyclane products. After the catalytic reaction, the total amount of benzene and cyclohexane decreased by 30% for the ‘‘feed 1’’ and by 40% for the ‘‘feed 2’’ leading to methylcyclopentane formation in the products. A long-term performance test catalyst for the two light naphtha fractions was also performed and we observed an improving of the research octane number (RON) by 15–17 for, respectively, feeds 1 and 2.

Keywords: Zr-pillared montmorillonite; Isomerization; Naphtha; Research octane number

---

1. Introduction

The challenge, now at dawn of the 21st century, for the internal combustion engines is in the reduction of pollutant-exhausted gases coupled with a low CO_2 emission and the production of a high quality of fuels. This requirement is compulsory and has to be applied urgently all over the world. The reformulated gasoline should have a low content of carbon–carbon double bonds, either aromatics and olefins and should have octane components.

The skeletal isomerization of *n*-paraffins and olefins to their branched isomers fits well with the reformulation trend of gasoline since the octane number is improved. A catalyst with both a (de)hydrogenation function and an acid function in the case of paraffins is required. The most widely applied alkane isomerization catalysts are chlorinated alumina supported platinum and mordenite supported Pt or Pd. This zeolite type catalyst came into wide application, for these reactions, because of their levels of sophisticated structures able to ‘‘guide’’ to the desired products via shape selectivity [1]. Such materials can also be prepared by intercalating inorganic polyoxycations into the interlayer region of abundant minerals (usually montmorillonite) followed by oxidation [2–4]. The resulting microporous pillared clays have also shown catalytic aptitude in variety of acid mediated reactions like isomerization [5,6]. In recent works [7,8], we have shown by dispersing a metallic function, e.g. palladium on three pillared clays: aluminium-pillared-sodium-montmorillonite, aluminium-pillared-acid-activated-montmorillonite and sulfated-zirconium-pillared-sodium-montmorillonite that a bifunctional catalyst is obtained, able to catalyse such reactions as hydroisomerization of alkanes. The sulfated-zirconium-pillared-sodium-montmorillonite catalyst is two to three times more active than the two other catalysts mentioned above and acts as an excellent *n*-paraffin hydroisomerization catalyst giving high isomer selectivities.

---

[*] Corresponding author. Tel.: +213 25 43 36 31; fax: +213 25 43 36 31.
E-mail address: rachidissaadi@yahoo.fr (R. Issaadi).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.063

In this study, we investigated with the sulfated-Zr-pillared-montmorillonite supported 1 wt.% Pd as catalyst in the hydroisomerization of two light naphtha (feeds 1 and 2) obtained from ASTM distillation of catalytic reforming unit feedstock of the Algerian refinery. It will give information about the catalyst behaviour in relation to time on stream and on the evolution of the research octane number (RON).

2. Experimental

The starting clay mineral is an Algerian bentonite and the preparation of the sulfated zirconium pillared montmorillonite has been described elsewhere [7]. To the sodium montmorillonite fraction (<2 μm) obtained from the raw bentonite, $ZrOCl_2 \cdot 8H_2O$ solution is added. After filtration, washing and drying at 110 °C, 0.1N H_2SO_4 is brought together, dried and oxidised at 400 °C for 6 h. The catalyst was prepared by impregnating the sulfated zirconium pillared clay with the required volume of palladium tetraamine chloride to load support with 1 wt.% of palladium. The mixture was stirred for 2 h and then dried in an oven for 12 h. The dried catalyst was packed into a tubular reactor, calcined again in air at 400 °C for 6 h and reduced in flowing hydrogen at 300 °C for 6 h prior to start the catalytic experiments.

The support, calcined at 400 °C, and the catalyst, calcined at 400 °C and reduced at 300 °C, were characterized by different methods. The basal spacing was measured by X-ray diffraction using a Philips vertical goniometer with nickel filtered Cu Kα radiation. Nitrogen adsorption experiments were performed at 77 K using a home made volumetric surface area analyser. Specific surface areas were calculated by the BET method. The total pore volumes were estimated from the liquid volume of N_2 adsorbed at a relative pressure of 0.98. De-Boer "*t* plot" method was used to determine the micropore volumes and areas. The surface acidity of the samples were evaluated by temperature programmed desorption (TPD) of ammonia adsorbed at 100 °C.

Catalytic activity test was carried out in fixed-bed flow reactor using two light naphtha as feed. The experiments were carried out at atmospheric pressure in a fixed-bed pyrex glass tubular reactor which was heated by an electric furnace at 300 °C. The amount of catalyst loading (0.4 g) is diluted with an inert matrix (inactive silica) to minimize the thermal effects. A stream of hydrogen saturated with the feed vapour was generated by passing hydrogen through a thermostated glass saturator filled with the light naphtha and kept at constant temperature (78 °C). The total flow (hydrogen + naphtha) was adjusted to keep the weight hourly space velocity (WHSV) equal to 0.825 h^{-1}. The products of reaction were analysed on a capillary silicon column CPSil5CB (length 50 m, diameter 0.53 mm).

The hydroisomerization performance of the catalyst was evaluated from the various ratios: isomers over *n*-paraffins and cyclo C5 over ΣcycloC6, determined before and after the catalytic test. These ratios are: isopentane/*n*-pentane (iC_5/C_5), 2,2 + 2,3-dimethylbutane/*n*-hexane (2,2 + 2,3-DMB/n-C_6), dimethylpentanes/*n*-heptane (DMP/n-C_7) and methylcyclopentane/benzene + cyclohexane (MCP/Bz + cC_6).

3. Results and discussion

For the 1 wt.% Pd/Zr–M/SO_4^{2-}, we got the following physico-chemical characterizations: Basal spacing $[d_{0\,0\,1}]$ = 1.29 nm, surface area = 128 m^2/g, pore volume = 0.130 cm^3 -liq./g and micropore volume = 0.085 cm^3 liq./g and the acidity of the catalyst is equal to 450 μmol NH_3/g or 3.52 μmol NH_3/m^2.

In general, the acidity developed with sulfated compounds may be attributed to the electron withdrawing of the anion groups (SO_4^{2-}) tending to get electron deficient centers which may behave as strong Lewis acid sites [9–12]. In the case of the 1 wt.% Pd/Zr–M/SO_4^{2-} catalyst, this strong Lewis acid sites are in part still present and we must also take into account the Brønsted acid sites which can be formed in the presence of palladium and dihydrogen dissociation on the metallic sites followed by spill over of hydrogen atoms as suggested by some authors [13,14].

The physical properties and chemical composition of the feeds are given in Table 1. As can be seen, the feeds 1 and 2 of the light naphtha used have respectively a boiling point ranging between 50–90 and 90–105 °C, a specific gravity of 0.659 and 0.702 g/cm^3 and a RON around 63.9 and 57.6. Their chemical

Table 1
Physical properties and chemical compositions of the feeds 1 and 2

Specifications	Feed 1	Feed 2
Boiling point range (°C)	50–90	90–105
Specific gravity (g/cm^3)	0.659	0.702
RON	63.9	57.6
Composition (wt.%)		
Butane	2.24	0.13
Isopentane	4.85	0.34
Pentane	14.02	1.74
2,2-Dimethylbutane	0.94	0.33
2,3-Dimethylbutane	4.23	2.10
2-Methylpentane	16.90	11.37
3-Methylpentane	9.25	7.55
Hexene	0.30	0.53
n-Hexane	24.60	27.26
Dimethylpentane	1.50	3.09
Methylcyclopentane	3.90	6.16
Benzene	3.46	4.96
Cyclohexane	3.06	5.67
2-Methylhexane	2.00	5.00
3-Methylhexane	1.92	5.00
Heptene	1.38	3.60
n-Heptane	2.60	8.35
Methylcyclohexane	1.24	3.94
Toluene	0.24	1.00
C_7+	1.37	1.88
iC_5/n-C_5	0.35	0.20
2,2 + 2,3-DMB/n-C_6	0.21	0.09
MCP/Bz + cC_6	0.60	0.58
DMP/n-C_7	0.58	0.37

n-C_5: *n*-pentane; n-C_6: *n*-hexane; DMB: dimethylbutane; Bz: benzene; cC_6: cyclohexane; MCP: methylcyclopentane; n-C_7: *n*-heptane.

Table 2
Physical properties and chemical compositions of the products 1 and 2

Specifications	Product 1	Product 2
Specific gravity (g/cm^3)	0.650	0.689
RON	79.2	74.4
Composition (wt.%)		
Butane	7.17	5.35
Isopentane	17.24	3.21
Pentane	0.53	0.23
2,2-Dimethylbutane	3.80	3.04
2,3-Dimethylbutane	6.89	5.55
2Methylpentane	21.21	23.41
3Methylpentane	14.41	14.49
Hexene	0	0
n-Hexane	6.68	7.81
Dimethylpentane	3.60	4.07
Methylcyclopentane	5.07	8.13
Benzene	2.12	1.79
Cyclohexane	1.78	2.08
2-Methylhexane	3.01	7.07
3-Methylhexane	2.49	4.48
Heptene	0	0.50
n-Heptane	1.29	3.21
Methylcyclohexane	1.04	2.61
Toluene	0.33	1.07
C_7+	1.36	1.90
iC_5/*n*-C_5	32.5	13.8
2,2 + 2,3-DMB/*n*-C_6	1.60	1.10
MCP/Bz + cC_6	1.30	2.10
DMP/*n*-C_7	3.1	3.60
ΔRON/feed[a]	15.3	16.8

n-C_5: *n*-pentane; *n*-C_6: *n*-hexane; DMB: dimethylbutane; Bz: benzene; cC_6: cyclohexane; MCP: methylcyclopentane; *n*-C_7: *n*-heptane.

[a] ΔRON/feed values determined between the difference $RON_{product} - RON_{feed}$.

compositions showed respectively a relative high concentration in *n*-pentane and *n*-hexane.

Table 2 gives the product distributions after 1 h on stream as well as isomers/*n*-alkanes and cycloC5/cycloC6 ratios. In reference respectively to the feeds 1 and 2, the fraction of *n*-alkanes (*n*-pentane, *n*-hexane and *n*-heptane) decreased from 41.22 to 8.50 wt.% and from 37.36 to 11.25 wt.% with a concomitant increase in the fraction of mono and multi-branched isomers from 45.49 to 72.45 wt.% and from 40 to 65.32 wt.%. The fraction of MCP is more important in the products than in the feeds to the detriment of benzene and cyclohexane fractions. In Table 2, we calculated the ΔRON/feed determined from $[RON_{product} - RON_{feed}]$. We can clearly see that the catalyst performed a good hydroisomerization reaction as characterized by the increase of the isomers/*n*-alkanes ratios improving the RON by 15 and 17, respectively.

The product selectivity obtained suggests the participation of a bifunctional mechanism in which the acid character is more pronounced than the metallic one. Single branched isomers like isopentane, methylpentanes and methylhexanes are selectively formed from *n*-pentane, *n*-hexane and *n*-heptane, respectively. This is similar to the selectivity of Pt/H-mordenite or Pt/Y-zeolite [15,16] where a bifunctional mechanism is thought to operate. On the other hand, multibranched isomers are formed. This result suggests an acid mechanism like the one proposed by Ribiero et al. [17] where multibranched isomers are obtained on HY zeolite and acid alumina.

We have shown [7,8] that the 1–5 dehydrocyclization of *n*-hexane does not occur on acidic catalyst. This statement was based on the fact that no methylcyclopentane was formed on such catalyst. On the contrary, such reaction can occur on metallic catalyst via a selective or a non-selective dehydrocyclization process which corresponds to the reverse reaction of a selective or a non-selective cyclic mechanism [18–20]. By the use of cyclohexane as a reactant, we pointed out the competition of the two possible reactions: dehydrogenation leading to benzene formation and 1–5 ring contraction leading to methylcyclopentane formation which takes place respectively on metallic and acid sites.

As shown in the chemical composition of the product, the methylcyclopentane fraction increases while the cyclohexane and benzene fractions decreases. So, methylcyclopentane is formed from cyclohexane or benzene via a bifunctional mechanism with an associative first adsorption step and when active site is a metal-proton adduct $[Pd–H]^+$ [21,22]. These collapsed bifunctional sites should be responsible of the reactivity of the catalyst which shows more pronounced acid character. Such explanation was also given by Manoli et al. [23] to explain the behaviour of $Pt/ZrO_2/SO_4^{2-}$ which was different from traditional bifunctional metal catalyst on acid support. They proposed the name of compressed bifunctional sites for the centers of acid–metal co-operation. In both cases a ‘‘concerted metal–acid catalysis’’ may prevail.

In order to investigate the life time of 1 wt.% Pd/Zr–M/SO_4^{2-} catalyst for longer terms, the reaction of the feed 1 has been run at 300 °C continuously for 90 h. The results of this long-term test are shown in Fig. 1. The iC_5/ΣC_5, DMB/ΣC_6, DMP/ΣC_7, MCP/ΣcycloC6 ratios and the RON are reported in this figure. After an initial stabilization period, the different ratios and the RON remained stable without any further observable decrease trend.

The high steady state of this catalyst can be associated to the relative strength and to the amount of active sites as well as to the hydrogenation power of palladium which avoids the (hydro)carbon residues to block the active sites.

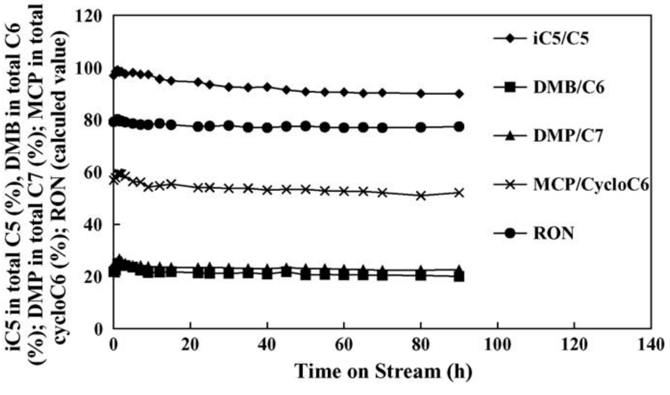

Fig. 1. Results obtained during a long-term catalytic reaction on stream.

4. Conclusion

The sulfated zirconium montmorillonite supported 1 wt.% palladium is an active catalyst able to catalyse such reactions as hydroisomerization of light naphtha. Its relative high activity and selectivity can be related on one hand, to the relative strength of the acid sites and, on the other hand, to the hydrogenation power of palladium which avoids the (hydro)-carbon residues to block the actives sites. This catalyst, applied to the hydroisomerization of two light naphtha fractions, showed a high isomer selectivity improving the research octane number by 15 and 17, moreover, its live time is important.

References

[1] S.M. Csicsery, Zeolites 4 (1984) 202.
[2] T.J. Pinnavaia, Science 220 (1983) 365.
[3] D.E.W. Vaughan, R. Lussier, in: L.C. Rees (Ed.), Proceeding of the Fifth International Conference in Zeolites Naples 1980, Heyder Press, London, 1980, p. 84.
[4] J. Shabtai, N. Fydmann, R. Lazar, in: G.C. Bond, P.B. Wills, F.C. Tompkins (Eds.), Proceeding of the Sixth International Congress on Catalysis London 1976, Chemical Society, London, 1977.
[5] R. Burch, C.I. Warburton, J. Catal. 97 (1996) 367.
[6] M.L. Occelli, Catal. Today 2 (1988) 339.
[7] R. Issaadi, F. Garin, C.E. Chitour, G. Maire, Appl. Catal. 207 (2001) 323.
[8] R. Issaadi, F. Garin, Appl. Catal. 243 (2003) 367.
[9] E.M. Farfan-Torres, P. Grange, Catal. Sci. Tech. 1 (1991) 103.
[10] H.L. Castillo, A. Gil, P. Grange, Catal. Lett. 43 (1997) 133.
[11] M. Tanabe, M. Itoh, K. Morishige, H. Hattori, in: B. Delmon, G. Poncelet, G. Jacobs (Eds.), Preparation of Catalysts I, Elsevier, 1975, p. 65.
[12] M. Hino, K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.
[13] K. Ebitani, J. Konishi, H. Hattori, J. Catal. 135 (1991) 357.
[14] K. Ebitani, J. Tsuji, H. Hattori, H. Kita, J. Catal. 135 (1992) 609.
[15] D.J. Chick, J.R. Katzer, B.C. Gates, in: J.R. Katzer (Ed.), Molecular Sieves II ACS Symposium Seire 40,, American Chemical Society, Washington, 1977, p. 517.
[16] H. Vansina, M.A. Baltanas, G.F. Fremont, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 526.
[17] R. Ribiero, C. Marcilly, M. Guisnet, J. Catal. 78 (1982) 267.
[18] Z. Paàl, Adv. Catal. 29 (1980) 273.
[19] F.G. Gault, Adv. Catal. 30 (1981) 1.
[20] F. Garin, G. Maire, Acc. Chem. Res. 22 (1989) 100.
[21] U.B. Demirci, F. Garin, Catal. Lett. 76 (2001) 45.
[22] U.B. Demirci, F. Garin, J. Mol. Catal. A: Chem. 188 (2002) 233.
[23] J.M. Manoli, C. Potvin, M. Muhler, U. Wild, G. Resofszki, T. Buchlolz, Z. Paal, J. Catal. 178 (1998) 338.