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Transformation of *n*-Heptane by Brønsted Acidic Sites Over 12-Tungstosilicic Acid

AHMED AOUISSI
Departement of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia
E-mail: aouissed@yahoo.fr

Catalytic transformation of *n*-heptane over $H_4SiW_{12}O_{40}\cdot13H_2O$ as a solid acid catalyst was investigated. The prepared heteropolyacid $H_4SiW_{12}O_{40}\cdot13H_2O$ was characterized by means of XRD and IR. Catalytic tests were carried out in a continuous flow system under atmospheric pressure. The effect of the reaction temperature and the support on the *n*-heptane transformation was investigated. It has been found that Brønsted acidic sites play an important role in *n*-heptane reaction. The lack of protons on the heteropolyacid owing to the collapse of the Keggin structure observed at 320 ºC led to a decay of the activity of $H_4SiW_{12}O_{40}\cdot13H_2O$. The decrease of the number of protons through a heteropolyacid-support interaction favored the cracking reaction to the detriment of cyclization reaction.

Key Words: *n*-Heptane transformation, Heteropolyanion, Solid acid catalyst, Keggin structure Skeletal rearrangement, Bifunctional catalyst.

INTRODUCTION

Transformation of *n*-alkanes is of great importance in the petroleum refining industry[1-3]. Transformation through cracking to light alkanes, isomerization to increase the research octane number (RON) of the feed and cyclization are some of the interesting processes. Among *n*-alkane transformation, the process involving the skeletal rearrangement of *n*-heptane has been investigated[4-7]. It has been found that the transformation reaction can lead to various components depending on both the condition reaction and the nature of the catalyst's sites. This skeletal rearrangement process, which requires acidic properties, was first investigated using liquid-phase systems such as HF, H_2SO_4 and halogen-containing solids. These catalysts exhibited good catalytic performance, but they generated many problems, including corrosion and storage issues. The need for materials are in agreement with environmental concerns and regulations has led to the preparation of solid acid catalysts with particular capacities, including high conversion and selectivity toward isomerization, high stability under reaction condition and easy regeneration. A number of reports have described the skeletal transformation of *n*-alkanes in the presence of hydrogen over bifunctional catalysts[8-11]. The *n*-alkane undergo primary reaction which lead to the formation of olefin on the metallic site and then of alkyl carbocation on the acidic site. The following step includes competitive reactions of isomerization and cracking[12].

Heteropolyacids are characterized by their stronger acid strength than conventional liquid and solid acids. Due to this character, heteropolyacids exhibit high activity and selectivity to various acid-catalyzed reactions such as alkylation, esterification and acylation, as summarized in review articles[13,14] and other reports[15-17]. Since acid sites were found to be an important parameter, it was decided to study the role of Brønsted acid sites in the skeletal rearrangement of *n*-heptane. In order to achieve this aim we have synthesized and tested $H_4SiW_{12}O_{40}\cdot 13H_2O$, looking for the effect of reaction temperature and the support on the conversion and on the reaction orientation.

EXPERIMENTAL

Preparation of the catalysts: The 12-tungstosilicic acid ($H_4SiW_{12}O_{40}\cdot 13H_2O$) was prepared according to known method[18]. The alumina supported 12-tungstosilici acid, $H_4SiW_{12}O_{40}/Al_2O_3$ with a loading of $H_4SiW_{12}O_{40}$ on Al_2O_3 fixed at 15 wt %, was prepared by incipient-wetness impregnation of Al_2O_3 (GF 254 type 60/E Merck) with an aqueous solution of $H_4SiW_{12}O_{40}\cdot 13H_2O$ at high enough concentration to avoid its degradation[19]. The slurry of alumina and impregnation solutions was constantly stirred at 323 K until dryness evaporation. The catalyst was then dried under vacuum at 100 °C for several hours.

Physico-chemical techniques: The purity, the Keggin structure and the thermal stability of the sample was checked by IR and X-ray diffraction. IR spectra were recorded with an infrared spectrometer GENESIS II-FTIR (4000-400 cm^{-1}) as KBr pellets. The XRD powder patterns were recorded on a PHILIPS X PERT, PRO diffractometer using Cu Kα radiation.

Catalytic measurements: Catalytic tests were carried out at atmospheric pressure using a fixed-bed continuous-flow reactor made of a Pyrex tube. The catalysts (250 mg) packed in the reactor, was preconditioned under H_2 flow for 2 h with a rate of 80 mL/min at 300 ºC. After the pretreatment, the *n*-heptane was admitted in the reactor (admission of *n*-heptane was carried out automatically and continuously by micro-injection through a syringe). The reaction was conducted at 300 ºC. Reaction products were analyzed by gas-phase chromatography with FID type Pye Unicam PU 4500 connected to an integrator-recorder Perkin Elmer LCI-100. The hydrocarbons were separated by SE-30 packed column of 1.5 m of length.

RESULTS AND DISCUSSION

The infrared spectrum of $H_4SiW_{12}O_{40}\cdot 13H_2O$ is shown in Fig. 1. The main characteristic features of the Keggin structure are observed at 917 cm^{-1} (γ_{as} Si-Oa), at is 970 cm^{-1} (γ_{as} Mo-Od), at 850 cm^{-1} (γ_{as} Mo-Ob-Mo) and at 767 cm^{-1} (γ_{as} Mo-Oc-Mo). This result is in agreement with those reported in the literature[18,19] for this heteropoly acid.

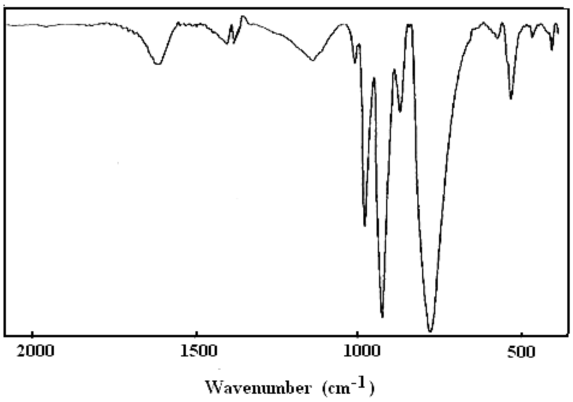

Fig. 1. Infrared spectra of $H_4SiW_{12}O_{40}\cdot 13H_2O$

The X-ray diffraction patterns of $H_4SiW_{12}O_{40}\cdot 13H_2O$ catalyst, is presented in Fig. 2. The characteristic peaks of Keggin structure of this heteropolyacid are observed[20-24]. The four main diffraction peaks that appeared at 10.38, 25.58 and 34.78 can be assigned to the diffraction characteristic peaks of crystalline $H_4SiW_{12}O_{40}\cdot 13H_2O$ Keggin structure[25].

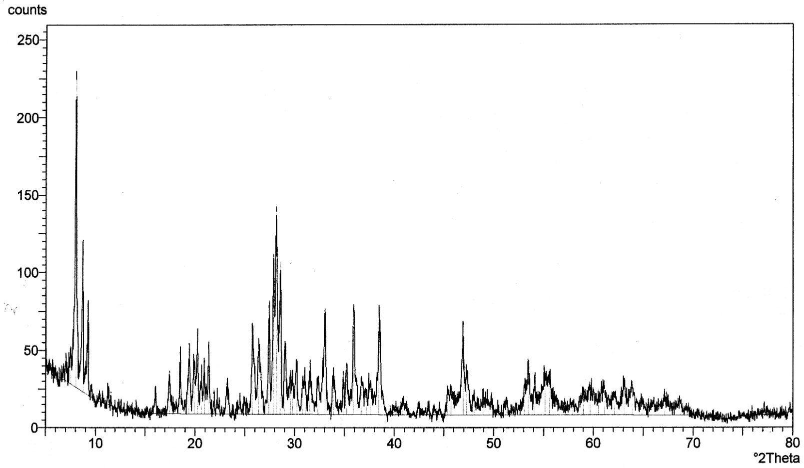

Fig. 2. XRD patterns of $H_4SiW_{12}O_{40}\cdot 13H_2O$

Catalytic reaction

Effect of temperature: The reaction was studied at different temperatures ranging from 240-320 °C. The evolution of the total conversion with time on stream for each reaction temperature is represented in the Fig. 3. Under these experimental conditions $H_4SiW_{12}O_{40}\cdot 13H_2O$ showed almost a stable activity with time on stream for all reaction temperatures. The changes in the conversion were small for all cases.

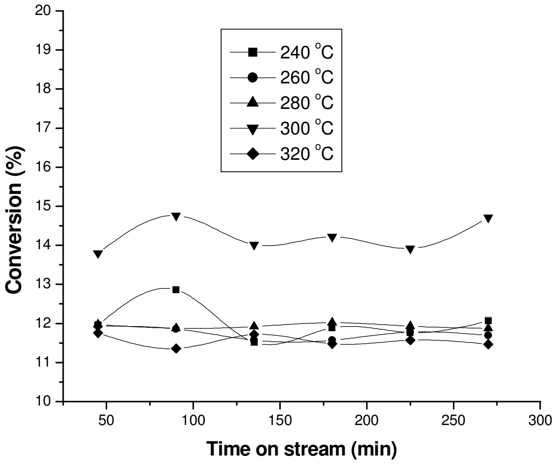

Fig. 3. Conversion *versus* time on stream obtained over $H_4SiW_{12}O_{40}\cdot 13H_2O$ at different reaction temperature

Fig. 4 shows the evolution of total conversion, isomerization (S_{isom}), cyclization (S_{cycl}) and cracking (S_{crack}) product selectivities for each reaction temperature. With respect to the conversion and the selectivity of cyclic products these go through a maximum when increasing reaction temperature. Considering both, the catalytic activity and the selectivity of cyclic products, the optimal reaction temperature is around 300 ºC. $H_4SiW_{12}O_{40}\cdot 13H_2O$ seems to perform better at this temperature than those with too high or too low temperature. This significant change in the conversion and the product selectivity beyond 300 ºC is mainly due to the modification of the nature of the active phase. In fact, it has been reported[26] that the Keggin structure

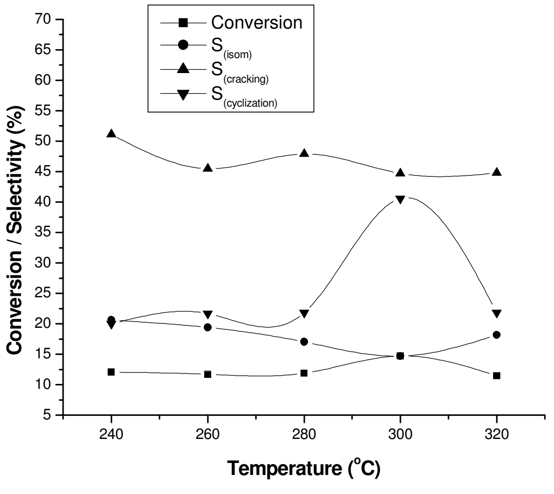

Fig. 4. Effect of reaction temperature on the catalytic activity and the selectivity of products for the conversion of heptane over $H_4SiW_{12}O_{40}\cdot 13H_2O$

collapses at temperatures higher than 300 ºC. This result is consistent with the thermal stability of heteropolyacids. It is now well established that deprotonation of heteropolyacids occurs when thermal treatment is realized at too high temperature leading to lower activity in reaction sensitive to the protonic density as *n*-alkane isomerization[27-29].

Effect of support: The evolution of the *n*-heptane conversion with time on stream on the unsupported and alumina-supported $H_4SiW_{12}O_{40}\cdot 13H_2O$ is given in Fig. 5. It can be seen from this figure that the conversion is stable along the time on stream when the reaction was catalyzed by the unsupported $H_4SiW_{12}O_{40}$, whereas a decrease of the conversion was observed after 3 h on time on stream when the reaction was catalyzed by the supported $H_4SiW_{12}O_{40}\cdot 13H_2O$. These results suggest the possibility of deactivation by coke formation through pore blockage and limitation to access to the active sites[30].

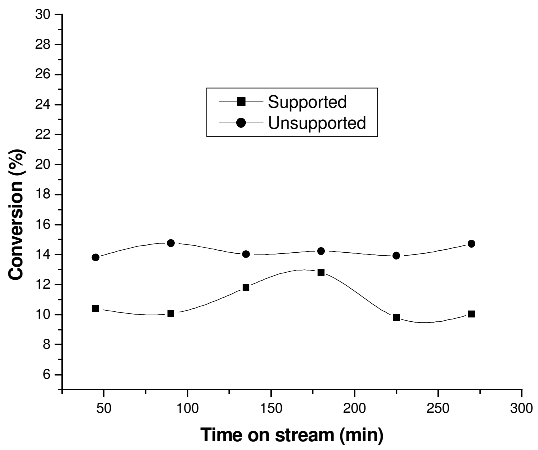

Fig. 5. Conversion of *n*-heptane *versus* time on stream over unsupported and alumina-supported $H_4SiW_{12}O_{40}\cdot 13H_2O$

The value of the conversion and the products selectivity at the steady state are reported in the Table-1. The results indicate that the support decreases both the conversion and the formation of cyclic products in favour of cracking products. The conversion decreased from 14.71-10.04 % and the selectivity of the cyclic products from 40.60-24.54 % when the heteropolyacid was supported on alumina. This result can be explained by a decrease of Brønsted acidic sites number. In fact, at lower coverages (< 15 %) all the protons are more and more trapped through an heteropolyacid-support interaction and the number of Brønsted acid decreases, inducing the decrease of the Brø nsted-acid character[26] leading to a decrease in the activity and in the cyclic products in favour of cracking. This results are in agreement with those reported in the literature where it was mentioned that higher conversion selectivity of cyclic products were obtained in the presence of a maximum number of strong acid sites in this sample[31].

TABLE-1
CONVERSION AND SELECTIVIES AT THE STEADY STATE FOR THE UNSUPPORTED AND ALUMINA-SUPPORTED $H_4SiW_{12}O_{40}\cdot 13H_2O$

Catalyst	Conv (%)	S_{isom}	S_{crack}	S_{accliz}
$H_4SiW_{12}O_{40}$	14.71	14.70	44.72	40.60
$H_4SiW_{12}O_{40}/Al_2O_3$(10%)	10.04	22.27	53.25	24.54

Conclusion

In this work, the transformation of *n*-heptane was studied over $H_4SiW_{12}O_{40}\cdot 13H_2O$ as a solid acid catalyst. The role of Brønsted acidic sites in the *n*-heptane transformation was investigated by studying both the effect of the temperature and the support. The best activity of the heteropolyacid was observed at 300 ºC owing both to the temperature effect and to the preservation of Brønsted acid sites on this catalyst. At 320 ºC the collapse of the Keggin structure was observed. Consequently a decay of the activity occurred owing to the lack of protons of the resulting oxides from the heyteropolyacid. When $H_4SiW_{12}O_{40}\cdot 13H_2O$ was supported on alumina, the number of the available protons decreased leading to a decrease of the activity and to an increase in cracking products. Thus, this work demonstrates that Brønsted acidity plays an important role in *n*-heptane reaction.

REFERENCES

1. I.E. Maxwell, *Catal. Today*, **1**, 385 (1987).
2. J.G. Sikonia, W.L. Jacobs and S.A. Gembieki, *Hydrocarbon Process*, **57**, 117 (1978).
3. S.D. Light, R.V. Bertram and J.U. Ward, *Hydrocarbon Process*, **60**, 93 (1981).
4. V. Keller, F. Barath and G. Maire, *J. Catal*., **189**, 269 (2000).
5. A. Katrib, D. Mey and G. Maire, *Catal. Today*, **65**, 179 (2001).
6. C. Castro, A. Corma and J. Primo, *J. Mol. Catal. A*, **177**, 273 (2002).
7. K. Liu, S.C. Fung. T.C. Ho and D.R. Rumschitzki, *J. Catal*., **206**, 188 (2002).
8. M. Busto, V.M. Benitez, C.R. Vera, J.M. Grau and J.C. Yori, *Appl. Catal. A*, **117**, 347 (2008).
9. M. Occhiuzzi, D. Cordischi, De S. Rossi, G. Ferraris, D. Gazzoli and M. Valigi, *Appl. Catal. A*, **29**, 351 (2008).
10. J.C. Yori, R.J. Gastaldo, V.M. Benitez, C.L. Pieck, C.R. Vera and J.M. Grau, *Catal. Today*, **133**, 339 (2008).
11. T. Okuhara, *Catal. Today*, **116**, 179 (2006).
12. E. Iglesia, F.H. Ribeiro, M. Boudart and J.E. Baumgartner, *Catal. Today*, **15**, 307 (1992).
13. Y. Ono, J.M. Thomas, K.I. Zamaraev, Perspectives in Catalysis London, p. 431 (1992).
14. T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal*., **41**, 113 (1996).
15. J. Mao, T. Nakajo and T. Okuhara, *Chem. Lett*., **31**, 1104 (2002).
16. A. Miyaji, T. Echizen, K. Nagata, Y. Yoshinaga and T. Okuhara, *J. Mol. Catal. A*, **201**, 145 (2003).
17. K. Sano, H. Uchida and S. Wakabayashi, *Catal. Surv. Jpn*., **3**, 55 (1999).
18. C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.*, **22**, 207 (1983).
19. C. Rocchiccioli-Deltcheff and M. Fournier, *J. Chem. Soc. Faraday Trans*., 3913 (1991).
19. J. Gong, X.J. Cui, Z.W. Xie, L.Y. Wang and S.G. Qu, *Synth. Metals*, **129**, 187 (2002).
20. H. Atia, U. Armbruster and A. Martin, *J. Catal*., **258**, 71 (2008).
21. Q.D. Zhang, Y.S. Tan, C.H. Yang and Y.Z. Han, *Chin. J. Catal.*, **27**, 916 (2006).
22. N. Bhatt and A. Patel, *J. Mol. Catal. A: Chem*., **264**, 214 (2007).
23. X. Zhao, H.M. Xiong and J.S. Chen, *Mater. Chem. Phys*., **80**, 537 (2003).

24. Q.Y. Wu and G.Y. Meng, *Solid State Ionics*, **273**, 136 (2000).
25. Z.O. Kraus, *Kristallogr Kristallgeometrie Kristallphys Kristall Chem*., **91**, 402 (1935).
26. C. Rocchiccioli-Deltcheff, A. Aouissi, M.M. Bettahar, S. Launay and M. Fournier, *J. Catal*., **164**, 16 (1996).
27. K. Na, T. Okuhara and M. Misono, *J. Chem. Soc., Faraday Trans*., **91**, 367 (1995).
28. T. Okuhara, T. Nishimura and M. Misono, *Chem. Lett*., **55**, 28 (1995).
29. N. Essayem, Y.Y. Tong, H. Jobic and J.C. Vedrine, *Appl. Catal. A*, **109**, 194 (2000).
30. F.J. Maldonado-Hodar, M.F. Ribeiro, J.M. Silva, A.P. Antunes and F.R. Ribeiro, *J. Catal*., **178**, 1 (1998).
31. S.K. Sahoo, N. Viswanadham, N.J. Ray, K. Gupta and I.D. Singh, *Appl. Catal. A*, **205**, 1 (2001).

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