low Pt loadings (0.2 wt.%, R035), the predicted yields of i-C16 and cracked C5-C13 were much higher than the experimental ones. The higher yields at low Pt loadings may be due to the fact that when Pt was low, olefinic products obtained from cracking could not be hydrogenated to a sufficient extent so that some of active sites might be blocked, decreasing catalytic activity. At high hydrogen pressures (1600 psig, R048), the predicted yield of cracked products C5-C13 was much lower than the experimental one, probably due to severe secondary cracking occurring at high conversions of n-C16. Based on these results, the kinetic model can be used to predict product fractions at intermediate conversion levels of n-C16 (< 70 wt.%) if catalyst deactivation does not occur.

Table 18. Experimental Yields vs. Predicted Yields Using the Kinetic Model (n-C16: 0.0256 mole; Catalyst: $Pt/ZrO_2/SO_4$; Temperature: 433 K)

Run No.	Pt (wt.%)	Time (min)	P_{H2} (psig)	n-C16		i-C16		C5 - C13	
				Expt.	Pred.	Expt.	Pred.	Expt.	Pred.
R035	0.2	60	360	0.015	0.0043	0.0037	0.011	0.015	0.022
R040	5.0	10	360	0.0069	0.0076	0.0042	0.0017	0.034	0.034
R041	0.5	50	300	0.0088	0.0045	0.0040	0.0083	0.030	0.027
R048	0.5	30	1600	0.00011	0.0012	0.00010	0.00079	0.065	0.049

The results show that the model predicts the yield of cracked products better than that of isohexadecanes under all conditions. The yield of isomerized products should not be extrapolated using this model. The predicted yields at high Pt loading (5 wt.%, R040) or hydrogen pressure (300 psig, R041) were close to the experimental ones. However, at low Pt loadings (0.2 wt.%, R035), the predicted yields of i-C16 and cracked C5-C13 were much higher than the experimental ones. The higher yields at low Pt loadings may be due to the fact that when Pt was low, olefinic products obtained from cracking could not be hydrogenated to a sufficient extent so that some of active sites might be blocked, decreasing catalytic activity. At high hydrogen pressures (1600 psig,

R048), the predicted yield of cracked products C5-C13 was much lower than the experimental one, probably due to severe secondary cracking occurring at high conversions of n-C16. Based on these results, the kinetic model can be used to predict product fractions at intermediate conversion levels of n-C16 (<70 wt.%) if catalyst deactivation does not occur.

8.5 Summary

A kinetic model for the hydrocracking and hydroisomerization of a long chain n-alkane (n-hexadecane) over $Pt/ZrO_2/SO_4$ based on a simplified reaction network was developed in this work to describe the amounts of lumped n-C16, i-C16 and cracked products as a function of reaction time. A derivative free nonlinear regression program, AR, from the BMDP library was successfully employed to optimize the nonlinear differential equations. The predicted product fractions obtained under various hydrogen pressures or platinum loadings agreed with the experimental data with an average relative error 25%. The model can be used to predict the effect of initial hydrogen pressure or platinum loading on the reactivity and product distributions for the hydrocracking and hydroisomerization of n-hexadecane. It should also provide quantitative guidance for control of product selectivities by varying reaction parameters.

9.0 CONCLUSIONS

The primary objective of this work was to explore the use of sulfated metal oxides in general, and zirconium oxide in particular, as a catalyst for the hydrocracking and hydroisomerization of long chain hydrocarbons including FT waxes. The main conclusions from this work are listed as follows:

(1) The $Pt/ZrO_2/SO_4$ exhibits a high activity for the hydrocracking and hydroisomerization of long chain paraffins (n-C16 and n-C32) as well for Sasol waxes under relatively mild reaction conditions (< 453 K and 360 psig hydrogen pressure) to yield liquid products. No methane, ethane or olefins are detected in the cracked products.

(2) Addition of a hydrogenation metal greatly modifies the catalytic activity and acid properties of sulfate promoted zirconium oxide. Three hydrogenation metals (platinum, palladium and nickel) were used. $Pt//ZrO_2/SO_4$ gave 30% higher conversion of n-hexadecane than $Pd/ZrO_2/SO_4$. $Ni/ZrO_2/SO_4$ was inactive for the conversion of n-hexadecane due to the poor hydrogenation capability of Ni under given reaction conditions (433 K and 360 psig of H_2 (cold)).

(3) In hydrocracking and hydroisomerization of n-hexadecane catalyzed by $Pt/ZrO_2/SO_4$ catalyst, at a given hydrogen pressure and reaction temperature, the conversion of n-hexadecane increases significantly with increasing Pt loading with a concomitant increase in selectivity to cracked products and a decrease in selectivity to isohexadecanes. The cracked product distribution shifts to shorter chain hydrocarbons.

(4) In hydrocracking and hydroisomerization of n-hexadecane catalyzed by $Pt/ZrO_2/SO_4$ catalyst, an increase in hydrogen pressure results in an increase in the conversion of n-hexadecane at given reaction temperature (433 K). Selectivity to cracked products also increases with a concomitant decrease in selectivity to isohexadecanes. The distribution of cracked products is not affected greatly by hydrogen pressure.

(5) In hydrocracking and hydroisomerization of n-heptane and n-hexadecane catalyzed by $Pt/ZrO_2/SO_4$ catalyst, addition of an olefin (1-heptene, 5-decene or 1-hexadecene) reduces the

conversions of n-heptane and n-hexadecane. The negative effect of olefins with a terminal double bond on the catalytic activity is greater than that of olefins with an internal double bond.

(6) Addition of a hydride transfer agent (adamantane or methylcyclopentane) increases the conversions of n-hexadecane and n-dotricontane. Selectivity to cracked products decreases and selectivity to isomerized hexadecane or dotriacontane increases

(7) The $Pt/HfO_2/SO_4$ catalyst showed a much lower activity than $Pt/ZrO_2/SO_4$ prepared at the same conditions due to a lower number of acid sites and acid strength. A sulfate-promoted and Pt doped mixture of zirconium and hafnium oxides, $Pt/ZrO_2{\cdot}HfO_2/SO_4$ with a molar ratio of Zr to Hf of one, had an activity higher than the $Pt/ZrO_2/SO_4$ catalyst. An increase in the molar fraction of HfO_2 reduced the selectivity to cracked products and increased selectivity to isomerized products.

(8) The long-term performance of $Pt/ZrO_2/SO_4$ (0.5 wt.% of Pt) catalyst for the hydrocracking and hydroisomerization of n-hexadecane in a continuous fixed-bed reactor was good: this catalyst maintained its initial activity after 96 hours. It was also very active at high hydrogen pressures (1600 psig) at 433 K and the sulfate group was not reduced.

(9) A novel zirconia precursor $Zr(SO_4)_2{\cdot}4H_2O$, instead of conventional materials such as $ZrOCl_2$ and $ZrO(NO_3)_2$, was used successfully to prepare the $Pt/ZrO_2/SO_4$ catalyst. The main advantage is that this zirconia precursor eliminates the need to thoroughly wash the precipitates to remove undesirable ions such as Cl^{-1} and NO_3^{-1}.

(10) The catalytic activity and acidic properties of the $Pt/ZrO_2/SO_4$ catalyst were similar regardless of the nature of zirconia precursor employed ($Zr(SO_4)_2{\cdot}4H_2O$, $ZrOCl_2$ or $ZrO(NO_3)_2$). They were affected by preparation procedures such as the precipitation method, the concentration of the sulfuric acid solution used, and the calcination temperature. A $Pt/ZrO_2/SO_4$ catalyst sample prepared by heterogeneous precipitation with addition of 1 N of sulfuric acid for sulfation and calcination for three hours at 873 K gave the highest activity for hydrocracking and hydroisomerization of n-hexadecane.

(11) Sulfate, tungstate and molybdate groups were used to treat zirconium oxides which

were then doped with platinum. The number of acid sites, acid strength and catalytic activity of the sulfate-promoted zirconium oxides were much greater than those promoted by either of the other two groups.

BIBLIOGRAPHY

1. Ansorge, J. and Hoke, A., Conversion of Natural Gas to Transportation Fuels via the Shell Middle Distillates Synthesis Process (SMDS) (The Hague, Netherlands: Shell International Petroleum Maatschappij, 1990), unpublished.
2. MacDougall, L.V., "Methanol to Fuels Routes-The Achievements and Remaining Problems", Catalysis Today, Vol.8 (1991), pp. 337-369 .
3. Sie, S.T., Senden, M.M.G., Van Wechem, H.M.H., "Conversion of Natural Gas To Transportation Fuels Vis The Shell Middle Distillate Process (SMDS)", Catalysis Today, Vol.8 (1991), pp. 371-394.
4. Emmett, P.H., ed., Catalysis, " Kinetics and Reaction Mechanism of the Fischer-Tropsch Synthesis, by Anderson, R.B." (2nd edition; New York: Reinhold, 1961), pp. 350-450.
5. Proc. 9th Int. Cong. on Catalysis, Calgary, Alberta, Canada, 1988, "Consequences of Fischer-Tropsch Chain Growth Kinetics For Process Mode Selection and Product Selectivity, by Sie, S.T., Eilers, J. and Minderhout, J.K.", (Canada: Chem.Inst., 1989), pp. 743-750.
6. Kuo, J.C., Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels, DOE Contract No.DE-AC22-83PC60019 (NJ: Mobil Res.Dev.Corp., October, 1985).
7. Eilers, J., Posthuma, S.A. and Sie S.T., "The Shell Middle Distillates Synthesis Process (SMDS)", Catal.Lett., Vol.7 (1990), pp. 253-270 .
8. 5th Synfuels Worldwide Symposium, Washington, D.C., November 11-13, 1985, "The Shell Middle Distillate Synthesis Process, by M.J.van der Burgt, J.van Klinken and Sie, S.T.", (Preprint).
9. Wen, M.Y., Wender, I. and Tierney, J.W., "Hydroisomerization and Hydrocracking of n-Heptane and n-Hexadecane on Solid Superacids" Energy & Fuels, Vol.4, No.4 (1990), pp. 372-379.
10. Tanabe, K., Misono, M., Ono, Y. and Hattori, H., New Solid Acids and Bases, (Amsterdam: Elsevier Science Publishers B.V., 1989), pp. 300-302.
11. Mohanty, S., Kunzru, D. and Saraf, D.N., "Hydrocracking: A Review", Fuel, Vol.69 (1990) pp. 1467-1473 .
12. Choudhary, N. and Saraf, D.N., "Technology Review, Hydrocracking: A Review" Ind.Eng.Chem.Prod.Res.Dev., Vol.14, No.2 (1975), pp. 74-83.
13. Archibald, R.C., Greensfelder, B.S., Holzman, G., Rowe, D.N., "Catalytic Hydrocracking of Aliphatic Hydrocarbons", Ind.Eng.Chem., Vol.52, No.9 (1960), pp. 745-750.
14. Shah, P.P., Sturtevant, G.C., Humbach, M.J., Padrta, F.G. and Steigleder, K.Z., Fischer-Tropsch Wax Characterization and Upgrading, DOE/PC/80017-T1 (UOP and Allied-Signal EMRC, June 6, 1988).

15. Ward, J.W. and Qader, S.A., Hydrocracking and Hydrotreating (Washington DC: Am.Chem.Soc.Symp.Ser., Vol.20, 1975), " The Influence of Chain Length in Hydrocracking and Hydroisomerization of n-Alkanes, by J. Weitkamp", pp. 1-27.
16. Greensfelder, B.S., Voge, H.H. and Good, G.M., "Catalytic and Thermal Cracking of Pure Hydrocarbons", Ind.Eng.Chem., Vol.41, No.11 (1949), pp. 2573-2584.
17. Nenitzescu, C.D. and Dragan, A., "Über die Einwirkung von Aluminiumchlorid auf n-Hexan und n-Heptan, Allein und in Gegenwant von Halogenderivatten Eine Überführung von Paraffin-in Cycloparaffin-Kohlenwasserstoffe" Ber.Dtsch.Chem.Ges., Vol.66 (1933) pp. 1892-1993.
18. Kuchar, P.J., Bricker, J.C., Reno, M.E. and Haizmann, R.S., "Paraffin isomerization Innovations", Fuel Proc.Tech., Vol.35 (1993), pp. 83-200.
19. Ward, J.W., Catalysis 1987, "Octane Enhancement by Selectively Reforming of Light Paraffins, by P.W. Tamm, D.H.Mohr and C.R.Wilson" (New York: Elsevier Science Publishers B.V., 1988), pp. 335-353.
20. Asinger, F., Paraffins Chemistry and Technology (New York: Pergamon Press, 1968), Chapter 8, pp. 693-730.
21. Schobert, H.H., The Chemistry of Hydrocarbon Fuels (London: Butterworth & Co Ltd, 1990), pp. 172-209.
22. Seddon, Duncan, "Reformulated Gasoline, Opportunities For New Catalyst Technology", Catalysis Today, Vol.15 (1992), pp.1-21.
23. Abad-zade Kh.I. and M.I.Rustamov, "Destructive Hydroisomerization of Napha Cuts Over Zeolite Nickel", Chem.Tech.Fuels & Oils, Vol.22 (1986), pp. 475-477.
24. Orkin, B.A., "Hydroisomerization of Normal Paraffins over Fluorided Platinum-Alumina Catalysts", Ind.Eng.Prod.Res.Dev., Vol.8, No.2 (1969), pp. 154-159.
25. Gibson, J.W., Good, G.M. and Holzman, G., "Isomerization of High Molecular Weight n-Paraffins", Ind.Eng.Chem., Vol.52, No.2 (1960), pp. 113-116.
26. Weltkamp, J., "Isomerization of Long-Chain n-Alkanes on a Pt/caY Zeolite Catalyst", Ind.Eng.Chem.Prod.Res.Dev., Vol.21, (1982), pp. 550-558.
27. Ward, J.W. and Qader, S.A., Hydrocracking and Hydrotreating (Washington DC: Am.Chem.Soc.Symp.Ser., Vol.20, 1975), "Catalyst Effects on Yields and Product Properties in Hydrocracking, by R.F.Sullivan and J.A.Meyer", pp. 20-51.
28. Clough, H., "Gasoline Production From Coal Tar Oils", Ind.Eng.Chem., Vol.49, No.4 (1957), pp. 673-679.
29. Flinn, R.A., Larson, O.A. and Beuther, H., "The Mechanism of Catalytic Hydrocracking", Ind.Eng.Chem., Vol.52, No.2 (1960), pp. 153-156.
30. Coonradt H.L. and Garwood, W.E., "Mechanism of Hydrocracking", Ind.Chem.Proc.Des.Dev., Vol.3, No.1 (1964) pp. 38-45.
31. Schulz, H.F. and Weitkamp, J.H., "Zeolite Catalysts", Ind.Eng.Chem. Prod.Res.Dev., Vol.11, No.1 (1972), pp. 46-53.
32. Steijns, M., Froment, G., Jacobs P. and Uytterhoeven, J., "Hydroisomerization and

Hydrocracking 2. Product Distributions From n-Decane and n-Dodecane", Ind.Eng.Chem.Prod.Res.Dev., Vol.20, No.4 (1981), pp. 654-660.

33. Weitkamp, J., Jacobs, P.A. and Martens, J.A., "Isomerization Hydrocracking of C9 Through C16 n-Alkanes on Pt/HZSM-5 Zeolite", Appl.Catal., Vol.8 (1983), pp. 123-141.
34. Martens, J.A., Jacobs P.A. and Weitkamp, J., "Attempts to Rationalize the Distribution of Hydrocracked products. I Qualitative Description of the Primary Hydrocracking Modes of Long Chain Paraffins in Open Zeolites", Appl.Catal., Vol.20 (1986), pp. 239-281.
35. Proceedings of the 13th North American Meeting of the Catalysis Society, Pittsburgh, May "Hydrocracking Model Studies Over Zeolite Supported Transition Metal Sulfide Catalysts, by W.J.J. Welters, O.H.van der Waerden and V.H.J. de Beer" (Preprint).
36. Cookson, D.J., Lloyd, C.P. and Smith, B.E., "Investigation of the Chemical Basis of Kerosene (Jet Fuel) Specificative Properties", Energy & Fuels, Vol.1 (1987), pp. 438-447.
37. Proceeding of the Tenth World Petroleum Congress, London, 1980, "Lube Oil Manufacture By Severe Hydrotreatment, by S.Bull and A.Marmin", (London: Heyden & Son, Vol.4, 1980).
38. Plank, C.J., Sibbett, D.J. and Smith, R.B., "Comparison of Catalysts in Cracking Pure Methylcyclohexane and n-Decane", Ind.Eng.Chem., Vol.49, No.4 (1957), pp. 742-750.
39. Nace, D.M., "Catalytic Cracking Over Crystalline Aluminosilicates", Ind.Eng.Chem.Prod.Res.Dev., Vol.8, No.1 (1968), pp. 31-38.
40. Ward, J.W., Catalysis 1987, "Effect of Sulfur on The Performance of Zeolite Isomerization Catalysts, by A.S.Zarchy and E.S.Shamshoum" (New York: Elsevier Science Publishers B.V., 1988), pp. 355-366.
41. Olah, G.A., Prakash, G.K.S. and Sommer, J., Superacids (New York: Wiley & Sons, 1985), pp. 243-335.
42. Olah, G.A., Prakash, G.K.S., and Sommer, J., "Superacids" Science, Vol.206 (1979), pp.13-20.
43. Petro, A.A., Petroleum Hydrocarbons (New York: Spring-Verlag 1987), pp.40-41.
44. Gillespie, R.J., "Fluorosulfric Acid and Related Superacid Media", Accts.Chem.Res., Vol.1 (1968), pp. 202-209.
45. Ymaaguchi, T., "Recent Progress in Soiid Superacid", Appl.Catal., Vol.61 (1990), pp. 1-25.
46. Arata, K., "Solid Superacids", Adv.Catal., Vol.37 (1990), pp. 165-211.
47. Hammett L.P., and Deyrup, A.J., "A Series of Simple Basic Indicators. I. The Acidity Functions of Mixtures of Sulfuric Acid Perchloric Acids with Water", J.Am.Chem.Soc. Vol.54 (1932), pp. 2721-2739.
48. Basila, M.R., Kantner, T.R. and Rhee, K.H., "The Nature of the Acidic Sites on a Silica-Alumina. Characterization by Infrared Spectroscopic Studies of Trimethylamine and Pyridine Chemisorption", J.Phy.Chem., Vol.68 (1964), pp. 3197-3199.
49. Bourdillon, G. and Gueguen, C., "Characterization of Acid Catalysts by Means of Model Reactions", Appl.Catal., Vol.61 (1990), pp. 123-139.

50. Aguayo, A.T., Arandes, J.M., Olazar, M. and Bilbao, J., "Study of Temperature-Programmed Desorption of tert-Butylamine To Measure the Surface Acidity of Solid Catalysts", Ind.Eng.Chem.Res., Vol.29 (1990), pp. 1621-1626.
51. Ingemar Odenbrand, C.U., Brandin, Jan G.M. and Busca, G., "Surface Acidity of Silica-Titania Oxides", J.Catal., Vol.135 (1992) pp. 505-517.
52. Schwarz, J.A., Russell, B.G. and Harnsberger, H.F., "A Study of Pyridine Adsorbed on Silica-Alumina Catalysts by Combined Infrared Spectroscopy and Temperature-Programmed Desorption", J.Catal., Vol.54 (1978) pp. 303-317.
53. Coster, D.J., Bendada, A., Chen, F.R. and Fripiat, J.J., "Relation Between the Scaling of the Acid Strength of Lewis Sites by EPR and NMR Probes", J.Catal., Vol.140 (1993), pp. 497-509.
54. Chen, F.R., G.Coudurier, J.F.Joly and J.C.Vedrine, "Superacid and Catalytic Properties of Sulfated Zirconia", J.Catal., Vol.143 (1993), pp. 616-626.
55. Fărcaşiu, D., Ghenciu, A. and Miller , G., "Evaluation of Acidity of Strong Acid Catalysts I. The Strength of Boron Trifluoride-Water Systems", J.Catal., Vol.134 (1992), pp. 118-125.
56. Fărcaşiu, D. and Ghenciu, A., "Evaluation of Acidity of Strong Acid Catalysts II. The Strength of Boron Trifluoride-Water Systems", J.Catal., Vol.134 (1992), pp. 126-133.
57. Conversion of Hydrocarbons on Heterogeneous Acid Catalysts, "Conceptual Background for the Conversion of Hydrocarbons on Heterogeneous Acid Catalysts, by J.A.Martens and P.A.Jacobs" (New York: Van Nostrand Reinhold, 1990), Chapter 2, pp. 52-110.
58. Fabre, P.L., Devynck, J. and Tremillon, B., "Thermodynamic Behavior of Alkanes in Superacid Media", Chem.Rev., Vol.82, (1982), pp. 591-614.
59. Shendye, R.V. and Rajadhyaksha, R.A., "Analysis of Product Selectivity in Cracking of Long Chain Hydrocarbons by Simulation of the Molecular Processes", Chem.Eng.Sci., Vol.47, No.3 (1992), pp. 661-672.
60. Nakamo, Y., Izuka, T., Hattori, H. and Tanabe, K., "Surface Properties of Zirconium Oxide and Its Catalytic Activity For Isomerization of 1-Butene", J.Catal., Vol.57 (1979), pp. 1-10.
61. Tanabe, K., Ishiya, C., Matsuzaki, I., Ichikawa, I. and Hattori, H., "Acidic Property and Catalytic Activity of Ti_2-ZnO", Bull.Chem.Soc.Japan., Vol.45 (1972), pp. 47-51.
62. Kayo, A., Yamaguchi, T. and Tanabe, K., "The Effect of Preparation Method on the Acidic and Catalytic Properties of Iron Oxide", J.Catal., Vol.83 (1983), pp. 99-106.
63. Arata, K. and Hino, M., "Reaction of Butane to Isobutane Catalyzed by the Solid Superacid of HfO_2 Treated with Sulfate Ion", React.Kinet.Catal.Lett., Vol.25, Nos.1-2 (1984), pp. 143-145.
64. Matsuhashi, H. Hino, M., and Arata, K., "Solid Catalyst Treated with Anion, XIX. Synthesis of the Solid Superacid Catalyst of Tin Oxide treated with Sulfate Ion", Appl.Catal., Vol.59 (1990), pp. 205-212.
65. Baba, Shibata, Kawamura, Takaoka, Kimura, Minato, Yoshihiro, Yokoyama, Lida.Imai,

"Solid Acid Catalysts", Europ.Pat.Appl., EP 0 174 836 A2 (1985).

66. Arata, K., "Preparation of Superacids by Metal Oxides and Their Catalytic Action", Mater.Chem.Phys., Vol.26 (1990), pp. 213-237.
67. Tanabe, K., Hattori, H. and Yamaguchi, T., "Surface Properties of Solid Superacids", Critical Review in Surface Chemistry, Vol.1, Issue 1 (1990) pp. 1-25.
68. Jin, T., Machida, M., Yamaguchi, T. and Tanabe, K., "Infrared Study of Sulfur-Containing Iron Oxide, Behavior of Sulfur during Reduction and Oxidation", Inorg.Chem., Vol.23 (1984), pp. 4396-4398.
69. Yamaguchi, T., Jin, T. and Tanabe, K., "Structure of Acid Sites on Sulfur-Promoted Iron Oxide", J.Phys.Chem., Vol.90 (1986), pp. 3148-3152.
70. Tanabe, K., Kayo A. and Yamaguchi, T., "Enhanced Catalytic Activity of Specially Prepared Fe_2O_3 for the Isomerization of 1-Butene and Cyclopropane and the Dehydration of 2-Butanol", J.Chem.Soc., Chem.Commun. (1981), pp. 602-603.
71. Jin, T., Yamaguchi, T. and Tanabe, K., "Mechanism of Acidity Generation on Sulfur-Promoted Metal Oxides", J.Phys.Chem., Vol.90 (1986), pp. 4794-4796.
72. Tanabe, K. and Yamaguchi, T., "Activity of Complex Metal Oxides For Direct Coal Liquefaction", Fuel Proc.Tech., Vol.17 (1986), pp. 99-110.
73. Parera, J.M., "Promotion of Zirconia Acidity By Addition of Sulfate Ion", Catalysis Today, Vol.15 (1992), pp. 481-490.
74. Hino, M. and Arata, K., " Reaction of Butane and Isobutane Catalyzed by Titanium Oxide Treated with Sulfate Ion. Solid Superacid Catalyst", J.Am.Chem.Soc. Chem.Commun. (1979), pp. 1148-1149.
75. Hino, M., Arata, K., "Synthesis of Solid Superacid Catalyst with Acid Strength of $H_o \leq$ 16.04", J.Am.Chem.Soc.Chem.Commun. (1980), pp. 851-852.
76. Yamaguchi, T. and Tanabe, K., "Preparation and Characterization of ZrO_2 and SO_4^{2-} Promoted ZrO_2", Mater.Chem.Phys., Vol.16 (1986), pp. 67-77.
77. Hino, M., Kobayashi, S. and Arata, K., "Reactions of Butane and Isobutane Catalyzed by Zirconium Oxide Treated with Sulfate Ion. Solid Superacid Catalyst", J.Am.Chem.Soc., Vol.101 (1979), pp. 6439-6441.
78. Tanabe, K., Yamaguchi, T., Akiyama, K., Mitoh, A., Iwabuchi, K. and Isogai, K., "The Catalytic Synthesis of Acylated Compounds by Using Solid Superacid", Proc.8th Int.Congr.Catal., Vol.5 (1984) pp. 601.
79. Fujisawa, H. and Yamaguchi, T., "Catalytic Disproportionation of Alkylsilanes over Sulfated ZrO_2", Chem.Lett., No.3 (1993), pp. 593-596.
80. Hino, M. and Arata, K., "Dehydrocyclization of Hexane to Benzne Catalyzed by Reduced Zirconium Oxide Treated with Sulfate, Selenate, and Tellurate Ions", Chem.Lett., No.10 (1985), pp. 1483-1486.
81. Hino, M. and Arata, K., "Catalytic Activity of Iron Oxide Treated with Sulfate Ion For Dehydration of 2-Propanol and Ethanol and Polymerization of Isobutyl Vinyl Ether", Chem.Lett. No.5 (1979), pp. 477-480.

82. Wang, G.W., Hattori, H. and Tanabe, K., "The Enhancement of Acid Strength and Catalytic Activity of SnO_2 by Addition of Sulfate Ion", Chem.Lett., No.3 (1983), pp. 277-280.
83. Hino, M. and Arata, K., "Dehydrogenation of Cyclohexanol to Cyclohexanone Catalyzed by Tin Oxide and the Sulfated Tin Oxide", Chem.Lett., No.9 (1990), pp.1737-1740.
84. Matsuhashi, H., Hino, M. and Arata, K., "Synthesis of the Solid Superacid of SnO_2 with Acid Strength of $H_o \leq 16.04$", Chem.Lett., No.6 (1988), pp. 1027-1028.
85. Hino, M. and Arata, K., "Reaction of Butane to Isobutane Catalyzed by Iron Oxide Treated with Sulfate Ion. Solid Superacid Catalyst", Chem.Lett., No.10 (1979), pp. 1259-1260.
86. Hino, M. and Arata, K., "Conversion of Pentane to Isopentane and Isopentane to Isobutane Catalyzed by a Solid Superacid in the Vapor Phase", React.Kinet.Catal.Lett., Vol.19 (1982), pp. 101-104.
87. Scurrell, M.S., "Conversion of Methane-Ethylene Mixtures Over Sulfate-Treated Zirconia Catalyst", Appl.Catal., 34, 109-117 (1987).
88. Rajadhyaksha R.A. and Chaudhari, D.D., "Alkylation of o-Xylene with Styrene by Superacid Catalysts", Ind.Eng.Chem.Prod.Res., Vol.26 (1987), pp. 1743-1746.
89. Arata K. and Hino, M., "Solid Catalyst Treated with Anion. XVIII. Benzoylation of Toluene with Benzoyl Chloride and Benzoic Anhydride Catalyzed by Solid Superacid of Sulfate-Supported Alumina", Appl.Catal., Vol.59, (1990), pp. 197-204.
90. Hino, M. and Arata, K., "Acylation of Toluene with Acetic and Benzoic Acids Catalyzed by a Solid Superacid in a Heterogenous System", J.C.S.Chem.Commun. (1985), pp. 112-113.
91. Hino, M. and Arata, K., "Synthesis of Esters From Acetic Acid with Methanol, Ethanol, Propanol, Butanol and Isobutyl Alcohol Catalyzed by Superacid", Chem.Lett., No.12 (1981), pp. 1671-1672.
92. Hino, M. and Arata, K.,"Synthesis of Esters From Terphthalic and Phthalic Acids with n-Octyl and 2-Ethylhexal Alcohol,Acrylic Acid with Ethanol and Salicylic and with Methanol Catalyzed by Solid Superacid", Appl.Catal., Vol.18 (1985) pp. 401-404.
93. Hino, M. and Arata, K., "Polymerization of Ethyl and Methyl Vinyl Esters Catalyzed by Iron Oxide Treated with Sulfate Ion. Synthesis of Stereospecific Polymer", Chem.Lett., No.8 (1980), pp. 963-963.
94. Hollstein, E.J., Wei, J.T. and Hsu, C.Y., U.S. Catalyst For Hydrocarbon Conversion and Conversion Process Utilizing the Same, Patent No. 4, 918, 041 (1990).
95. Hsu, C.Y., Heinbuch, C.R., Armes, C.T. and Gates, B.C., "A Highly Active Solid Superacid Catalyst For n-Butane Isomerization: a Sulfated Oxide Containing Iron, Manganese and Zirconium", J.C.S.Chem.Commun. (1992), pp. 1645-1646.
96. Lin, C.H. and Hsu, C.Y., "Detection of Superacidity on Solid Superacids; A New Approach", J.C.S.Chem.Commun. (1992), pp. 1479-1450.
97. Sohn, J.R.and Jang, H.J., "Characterization of ZrO_2-SiO_2 Unmodified or Modified with

H_2SO_4 and Acid Catalysts", J.Molecl.Catal., Vol.64, (1991), pp. 349-360.

98. Yamaguchi, T., Morita, T., Salama T.M. and Tanabe, K., "Surface Properties of ZrO_2 Dispersed on SiO_2", Catal.Lett., Vol.4 (1990), pp. 1-6.
99. Ishida, T., Yamaguchi, T. and Tanabe, K., "Acid Property of Sulfur-Promoted Zirconium Oxide on Silica as Solid Superacid", Chem.Lett., No.11 (1988), pp. 1869-1872.
100. Luy, J.C., Yori, J.C., Castro A.A. and Parera, J.M., "Skeletal Isomerization of 1-Butene on ZrO_2/Al_2O_3 Treated with Sulfate Ion", React.Kinet.Catal.Lett., Vol.36 (1988), pp. 275-279.
101. Symposium on Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts, New York, Agu. 25-30,1990 "Sulfate-Containing Solid Superacids for Acid-Catalyzed Hydrocarbon Conversions, by Rodriguez-Ramos, A. Guerrero-Ruiz and J.L.G. Fierro" (New York: ACS, 1990), pp. 804-812.
102. Wang, G.W., Hattori, H. and Tanabe, K., "Pronounced Effect of Sulfate Ion on Catalytic Activity of ZrO_2-SnO_2 For Isomerization of Cyclopropane", Chem.Lett., No.7 (1983), pp. 959-960.
103. Proc.9th Int.Conge.Catal., Ottawa, 1988, "Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and Its Catalytic Action, by Arata K. and Hino, M." (Ottawa: The Chemical Institute of Canada, 1988), pp.1727.
104. Hino, M., Arata, K., "Synthesis of Solid Superacid of Molybdenum Oxide Supported on Zirconia and Its Catalytic Action", Chem.Lett., No.5 (1989), pp. 971-972.
105. Proc.10th Int.Conge.Catal., Bydapest, Hungary, 1992, "ZrO_2/SO_4 Catalysts. Nature and Stability of Acid Sites Responsible For N-Butane Isomerization, by Nascimento, P., Akratopoulou C., Oszagyan, M., Coudurier, G., Travers, C., Joly, J.F. and Vedrine, J.C." (Bydapest: New Frontiers in Catalysis, 1992).
106. Symposium on Preparation and Characterization of Catalysts, Loa Angeles, Sept. 25-30, 1988, "Characterization and C5/C6 Isomerization Activity of Solid Superacid ($Pt/SO_4^{2-}/ZrO_2$), by T.Hosoi, T.Shimidzu, S.Itoh, S.Baba and H.Takaoka" (Loa Angeles: Division of Petroleum Chemistry, ACS, 1988), pp. 562-567.
107. Inui.T., ed., Successful Design of Catalysts, "Design of Sulfur-Promoted Solid Superacid Catalyst, by K.Tanabe and T.Yamaguchi" (Amsterdam: Elsevier, 1989), pp. 99-110.
108. Yori, J.C., Luy J.C. and Parera, J.M., " Deactivation of H-Mordenite and ZrO_2/SO_4^{2-} During n-Butane Isomerization", Appl.Catal., Vol.46 (1989), pp. 103-112.
109. Baba, S., Shibata, Y., Takaoka, H., Imai. T. and Yokoyama, T., "Isomerization of Pentane Over $PtSO_4^{2-}/ZrO_2$", Disc.Meet.Petrol.Chem., preprint 2-i (1986), pp. 17.
110. Tanabe, K., Hattori, H., Yamaguchi T. and Tanaka, T., ed., Acid-Base Catalysts "Effects of Pt Loading on SO_4^{2-}/ZrO_2 Upon Catalytic Activity and Surface Acidity, by K.Ebitani, J.Konishi, A.Horie, H.Hattori and K.Tanabe" (Kodansha, Tokyo, Verlag-Chemie, Weinheim, 1989).
111. Ebitani, K., Konishi, J. and Hattori, H., "Skeletal Isomerization of Hydrocarbons over Zirconium Oxide Promoted by Platinum and Sulfate Ion", J.Catal., Vol.130 (1991), pp.

257-267.

112. Ebitani, K., Tsuji, J., Hattori H. and Kita, H., "Dynamic Modification of Surface Acid Properties with Hydrogen Molecule for Zirconium Oxide Promoted by Platinum and Sulfate Ion", J.Catal., Vol.135 (1992), pp. 609-617.
113. Ebitani, K., Konno, H., Tanaka T. and Hattori, H., "In-Situ XPS Study of Zirconium Oxide Promoted by Platinum and Sulfate Ion", J.Catal., Vol.135 (1992), pp. 60-67.
114. Paàl, Z., Muhler, M. and Schlögl, R., "The Possible Interpretation of XP Spectra of Supported Pt Catalysts in the Oxidized and Sulfided States", J.Catal., Vol.143 (1993), pp. 318-321.
115. Zhao, J., Huffman G.P. and Davis, B.H., "XAFS Study of the State of Platinum in a Sulfated Zirconia Catalyst", unpublished.
116. Sayari, A. and Dicko, A., "The State of Platinum in Pt on Sulfated Zirconia Superacid Catalysts", J.Catal., Vol.154 (1994), pp. 561-564.
117. Martens, J.A., Jacobs, P.A. and Weitkamp, "Attempt to Rationalize the Distribution of Hydrocracked Products II. Relative Rates of Primary Hydrocracking Modes of Long Chain Paraffins in Open Zeolites", Appl.Catal., Vol.20 (1986), pp. 283-303.
118. Giannetto, G.E., Perot, G.R. and Guisnet, M.R., "Hydroisomerization and Hydrocracking of n-Alkanes 1. Ideal Hydroisomerization PtHY Catalysts", Ind.Eng.Chem.Prod.Res.Dev., Vol.25 (1986), pp. 481-490.
119. Giannetto, G.E., Alvarez, F.B. and Guisnet, M.R., "Hydroisomerization and Hydrocracking of n-Alkanes 3. n-Heptane Transformation on PtH Offretite Catalysts", Ind.Eng.Chem.Prod.Res.Dev., Vol.27 (1988), pp. 1174-
120. P.B.Weisz, " Adv.Catal. ", Vol.13, 137 (1962).
121. Sie, S.T., "Acid Catalyzed Cracking of Paraffinic Hydrocarbons. 1. Discussion of Existing Mechanism and Proposal of a New Mechanism", Ind.Eng.Chem.Res., Vol.31 (1992), pp. 1881-1889.
122. Sie, S.T., "Acid-Catalyzed Cracking of Paraffinic Hydrocarbons. 3. Evidence for the Protonated Cyclopropane Mechanism from Hydrocracking /Hydroisomerization Experiments", Ind.Eng.Chem.Res., Vol.32 (1993), pp. 403-408.
123. Sie, S.T., "Acid-Catalyzed Cracking of Paraffinic Hydrocarbons. 2. Evidence for the Protonated Cyclopropane Mechanism from Catalytic Cracking Experiments", Ind.Eng.Chem.Res., Vol.32 (1993), pp. 403-408.
124. Cullity, B.D., Elements of X-Ray Diffraction, 2nd Edition (Reading, MA: Addison-Wesley, 1978), pp. 1-30, 81-106.
125. Morterra, C., Cerrato, G., Emanuel, C. and Bolis, V., "On the Surface Acidity of Some Sulfate-Doped ZrO_2 Catalysts", J.Catal., Vol.142 (1993), pp. 349-367.
126. Symposium on Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts, New York, Agu. 25-30.1990 "Superacid and Catalytic Properties of Sulfated Zirconia, by Chen, F.R., Coudurier, G. Joly, J.F. and Vedrine, J.C." (New York: ACS, 1991), pp. 878-886.

127 Umland, J.B., General Chemistry (New York: Westing Publishing Comp., 1993), pp. 1026-1029.

128. Robert, A.K., Scott, L., Sparks, D., Hu, J.L., Wender, I., Tierney, J.W., Wang, W. and Davis, B.H., "Hydroisomerization and Hydrocracking of Hexadecane Over Platinum Promoted Sulfated Zirconium Catalyst", Energy & Fuel, Vol.8 (1994), pp. 755-762.

129. Chokkaram, S., Srinivasan, R., Milburn, D.R. and Davis, B.H., "Ion Exchange and Thermal Studies of Sulfated Zirconia" (1993), unpublished.

130. Iglesia, E., Soled, S.L. and Kramer, G.M., "Isomerization of Alkanes on Sulfated Zirconia: Promotion by Pt and by Adamantyl Hydride Transfer Species", J.Catal., Vol.144 (1993), pp. 238-253.

131. Soled, S.L., Iglesia, E., Kramer, G.M., Heights, B., Gates, W.E., Ernst, R.H. and Glen, G., Isomerization of Paraffins with Strong Solid Acid Catalyst and Adamantane, U.S. Patent No. 5,157,199 (1992)

132. Olah, G.A., ed., Cage Hydrocarbons, "The Superacid Route to 2-Adamantyl Cation, by T. S. Sorensen and S. T. Whitworth" (New York: John Wiley & Sons, Inc., 1990), Chapter 3.

133. Seminar, University of Pittsburgh, April 12, 1991 "Fischer-Tropsch Wax Production and Upgrading, by J.C. Kuo" (NJ: Mobil Res.Dev.Corp., 1991).

134. Steijns, M. and Froment, G.F., "Hydroisomerization and Hydrocracking. Kinetic Analysis of Rate Data for n-Decane and n-Dodecane", Ind.Eng.Chem.Res.Dev., Vol. 20 (1981), pp. 660-668.

135. Steijns, M. and Froment, G.F., "Hydroisomerization and Hydrocracking. 5. Kinetic Analysis of Rate Data for n-Octane", Ind.Eng.Chem.Res.Dev., Vol.22 (1983), pp. 531-539.

136. Degnan, T.F. and Kennedy, C.R., "Impact of Catalyst Acid/Metal Balance in Hydroisomerization of Normal Paraffins", AIChE J., Vol. 39, No.4 (1993), pp. 607-614.

137. Wark, K., Thermodynamics (2nd edition; New York: McGraw-Hill Comp., 1971), Appendix A-3, pp. 748-749.0

138. BMDP Statistic Software Manual, Vol. 1, (University of California Press, 1992), pp. 427-466.

139. Voge, H.H., ed., Catalysis, "Catalytic Cracking, by P.H. Emmett", (Reinhold: New York, 1958), Vol. VI, Chapter 5, pp. 407-492.

140. Problem-Solving Software System, Math/Library, IMSL version 1.0 (1987), pp. 640-651

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