4.24 Modification of Isomerization Activity and Selectivity over Sulfated Zirconia Catalysts

S. L. Soled[a], E. Iglesia[b], and G. M. Kramer[a]
[a]Corporate Research, Exxon Research and Engineering Co., Rt. 22 East, Annandale, NJ. 08801
[b]Department of Chemical Engineering, University of California, Berkeley, California 94720

Abstract

Alkane isomerization over $Pt/ZrO_2/SO_4^=$ shows a positive hydrogen kinetic order, suggesting the reaction proceeds via chain transfer pathways, rather than by conventional bifunctional (metal-acid) sequences. Adamantane, a molecular hydride transfer agent, when added in small quantities to n-heptane feeds increases isomerization rates while inhibiting cracking reactions. The faster hydride transfer rates and accompanying shorter carbocation surface residence times decrease secondary cracking. This effect differs significantly from acid site poisoning by aromatic molecules, which decreases both isomerization and cracking rates.

1. INTRODUCTION

Branched C_6-C_{10} paraffins are important components in motor fuels; they are produced by processes such as alkylation, isomerization, and oligomerization, all of which require strong acid catalysts. Environmental concerns about halide-containing solids and about strong liquid acids continue to drive the search for new oxide-based solid acids.

Holm and Bailey in 1962 discovered the unusual strong acidity of a sulfate-modified zirconia gel[1], but this class of anion modified oxides was not examined in detail until the 1980's [2,3,4,5,6,7,8,9,10]. Hammett indicators suggested that sites with $H_0 < -16$ exist[2]. These sites are much stronger than 100% sulfuric acid ($H_0 \sim -12$) or acidic zeolites. Jin et al. proposed that the strong acidity of these materials arises from the electron donation to the $SO_4^=$ ligand, which creates a coordinatively unsaturated and electron deficient metal center acting as a strong Lewis acid[5]. Ebitani and coworkers suggested the interaction of H_2 with Pt forms hydride ions that titrate Lewis acid sites, and protons that form OH groups acting as new Bronsted acid sites[11,12]. Hall et al. have recently questioned Hammett acidity measurements on $ZrO_2/SO_4^=$ [13], but these acids catalyze n-hexane isomerization at room temperature for several turnovers; in the presence of hydrogen and with supported platinum, they isomerize light alkanes (C_4-C_9) for long periods of time at 200°C[14].

Here, we show that the addition of adamantane increases isomerization rate and decreases cracking selectivity during n-C_7+ paraffin isomerization over $Pt/ZrO_2/SO_4^=$ [15]. Isomerization proceeds through a hydride transfer chain mechanism and adamantane, because of its unique ability to easily form tertiary carbocations at bridgehead carbon atoms, increases the intermolecular hydride transfer rate. In effect, the lifetime of carbocation intermediates decreases because of faster hydride transfer rates. Isomerized surface chains desorb more rapidly, and sites for ionizing new reactant molecules turnover more frequently. The lower surface residence times of carbocation intermediates leads to fewer opportunities for cracking side reactions.

2. EXPERIMENTAL METHODS

$Pt/ZrO_2/SO_4^=$ was prepared by precipitating zirconium hydroxide from the nitrate salt using a 28% ammonium hydroxide solution. Ten grams of $Zr(OH)_4$ dried at 110°C were slurried into 20 cm^3 of an aqueous chloroplatinic acid solution containing 0.05 g Pt. After stirring for 5 min, the solids were filtered and dried overnight at 110°C. They were then placed into 22 cm^3 of the 1N sulfuric acid solution, stirred for 5 min, filtered, dried overnight at 110°C, and calcined at 600°C for 3 h in air. Chemical analysis of the resulting solids showed that about 75% of the platinum in the solution exchanges onto the support (i.e. ~0.4% Pt content and 4.5 wt% $SO_4^=$).

The catalyst was pressed into a wafer, crushed and sieved to retain the 0.25 to 0.50 mm fraction and then recalcined at 600°C in air for 1 hour immediately prior to being loaded into the reactor. The catalyst was reduced in flowing hydrogen at 200°C for 1 h. n-Pentane, n-hexane, n-heptane, n-octane and n-decane (Fluka, puriss grade, >99% purity) were introduced into the H_2 stream and the flow rates were adjusted to obtain the desired space velocity and H_2/hydrocarbon ratio. Catalytic tests were carried out between 180 and 240°C at total pressures between 300 and 2500 kPa. Reaction products were analyzed by on-line capillary chromatography using flame ionization and mass spectrometric detection.

3. RESULTS AND DISCUSSION

3.1. Catalytic Reactions of n-Hexane

At 200°C, isomerization rates resemble those on Pt/mordenite catalysts reported at 250-270°C. n-Hexane isomerization selectivities exceed 98% and depend weakly on conversion. The cracking products consist primarily of isobutane, isopentane, and propane. From the observed selectivities, cracked products must arise predominantly from polymerization/cracking cycles rather than from direct hexane cracking.

Both thermodynamic and kinetic barriers limit isomerization to multibranched alkanes. Thermodynamic constraints require low temperatures to favor multibranched isomers, which in turn necessitates strong acidity to obtain the desired activity. The approach to thermodynamic isomer concentrations is usually kinetically limited. In practice, this translates into extensive recycle of unconverted reactants and monobranched products. Our isomerized products contain a dibranched/monobranched ratio of 0.23 (at 200°C, 780 kPa, and 17% conversion), much lower than the equilibrium value (1.10). The 2,2 dimethylbutane isomer, which contains a quaternary carbon atom, forms substantially below equilibrium level. This quaternary isomer requires the strongest acidity and the longest surface residence time; its formation apparently requires transformation from the stable tert-2,3 dimethylbutyl cation to the less stable and sterically hindered sec-2,2 dimethyl-3 butyl cation. Hence, kinetic factors limit the approach to equilibrium on all but the strongest acids because of the slow carbocation rearrangements required to produce these quaternary isomers. Therefore, although $Pt/ZrO_2/SO_4^=$ shows isomerization activity at lower temperatures than other oxide catalysts, multibranched isomer formation remains kinetically limited.

3.2 Catalytic Reactions of n-Heptane and C_7+

C_7^+ paraffin isomerization presents additional challenges. The presence of stable leaving groups containing tertiary carbons (e.g. isobutane) promotes cracking; thus, commercial isomerization practice is limited to C_4-C_6 feeds. Both desired (isomerization) and undesired (cracking) reactions occur on strong acid sites; thus control of cracking during C_7+ paraffin isomerization remains a difficult challenge. Table 1 shows how cracking/isomerization ratios on a platinum/sulfated zirconia catalyst increase markedly with increasing size of paraffin reactants.

Cracking selectivities increase from a few percent for n-hexane reactants to nearly 50% for n-heptane. This abrupt change reflects the availability of stable (non-primary carbon) decomposition products, isobutane and propane, formed by β-scission of 2-methylhexyl carbocations (Table 2).

Table 1. Cracking/Isomerization Ratio For Different n-Paraffins over $Pt/ZrO_2/SO_4^=$

n-paraffin	cracking/isomerization (wt ratio)
n-pentane	0.05
n-hexane	0.02
n-heptane	0.71
n-octane	2.01

conditions: 200°C, 780 kPa, conv <30%, 6.2/1 H_2/n-paraffin

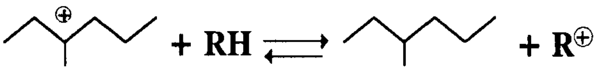
Table 2. Cracked Products Formed During n-Heptane Isomerization over $Pt/ZrO_2/SO_4^=$

Product	Mole (%) in C_5^- Fraction
methane	2.0
ethane	0.1
propane	43.6
n-butane	1.1
i-butane	48.1
n-pentane	0.7
i-pentane	4.0

conditions: 200°C, 6.2/1 H_2/n-C_7, 780kPa, 10.1% conversion

Therefore, in contrast with the oligomerization/cracking sequence required for cracking of n-hexane and isohexanes, n-heptane feeds easily form C_3 and C_4 leaving groups by direct β-scission and hydride transfer steps. Consequently, the isomerized reaction products crack more easily than the linear feed molecules and cracking selectivity increases with increasing conversion (Fig. 1). In analogy with n-C_6, the quaternary isomers 2,2 and 3,3 dimethylpentane form below equilibrium values during n-C_7 isomerization.

A plot of n-heptane reaction rate divided by H_2 partial pressures over a range of hydrogen (0.8-2.9 MPa) and n-heptane (0.033-0.2 MPa) partial pressures is nearly horizontal (Fig. 2); thus the total reaction rate is approximately first order in hydrogen and zero order in heptane. Ebitani et al[11] also found a positive H_2 rate order and suggested that it was not consistent with a conventional bifunctional isomerization mechanism. In the latter case, negative H_2 rate order normally reflects rate-limiting nature of the acid-catalyzed rearrangement of olefin intermediates (with the metal catalyzed dehydrogenation/hydrogenation at equilibrium). However, a bimolecular chain mechanism involving hydride transfer can account for the positive order kinetics of the isomerization reaction. If the chain isomerization mechanism is operating here, we might expect addition of hydride transfer agents to promote the isomerization rate.



(1)

3.3 Adamantane Addition to C_7^+ Feeds

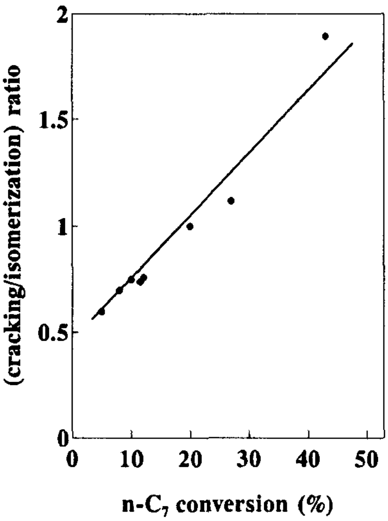
Adamantane was previously reported to act as a hydride transfer agent and to inhibit cracking during paraffin isomerization on Friedel Craft acids[16] On $Pt/SO_4/ZrO_2$, adamantane also decreases cracking selectivity during isomerization of n-heptane and n-octane. Other cracking inhibitors, such as toluene, also decrease cracking selectivity, but concurrently decrease paraffin isomerization rates.

Table 3. Selectivity Ratio (cracking/isomerization) for n-paraffins with adamantane addition

n-paraffin	no additive	0.8% adamantane	1% toluene
n-heptane	0.73	0.14	0.53
n-octane	2.1	0.28	

200°C, 6.2/1 H_2/n-C_7, 780 kPa, 12-22% conversion

Fig. 1. Cracking/Isomerization Ratio as a Function of Conversion



200°C, 780kPa, H_2/n-C_7 = 6.2

Isomerization rate enhancements by adamantane can occur only if catalytic reactions on $Pt/ZrO_2SO_4^=$ proceed by carbocation chain reactions. With 0.8 wt% adamantane addition, we observe a substantial increase in n-heptane conversion rate. Figure 3 compares the rate of n-C_7 conversion (moles C_7/sulfur atom/sec) with either 0.8% adamantane or 1% toluene added to n-heptane reactants. Addition of toluene decreases C_7 reaction rate. Both toluene and adamantane decrease the average lifetimes of carbocation intermediates. However, toluene titrates the strongest acid sites, thereby decreasing both the cracking/isomerization ratio and the C_7 conversion rate. In contrast, adamantane decreases carbocation surface lifetimes by enhancing the hydride transfer rate, so that reaction turnovers occur faster, and the cracking/isomerization ratio decreases.

These kinetic data and the effects of adamantane addition on isomerization rate and selectivity suggest that acid sites on $Pt/ZrO_2/SO_4^=$ are sufficiently strong and metal sites sufficiently poisoned by sulfate that the isomerization of n-alkanes occurs by carbocation chain mechanisms rather than by bifunctional metal/acid sequences.

It has also been shown that n-heptane isomerizes first to methyl hexanes; rapid methyl shifts equilibrate methyl positions before subsequent conversion to dimethylpentanes[17]. The path to dibranched quaternary ions (2,2 and 3,3 dimethylpentanes) involves initial formation of 2,3 dimethylpentyl cations. Adamantane decreases the lifetime of all cations (including methyl hexyl and 2,3 dimethylpentyl), so that the yield of multibranched-isomers (Table 4) decreases.

Table 4. Percent of Monobranching in Isomerate During n-Heptane Isomerization over $Pt/ZrO_2/SO_4^=$ with Added Adamantane

wt % adamantane added	% dibranched isomers
0	28
0.1	26
0.4	25
0.8	24

conditions: 200°C, 6.2/1 $H_2/n\text{-}C_7$, 780kPa, 20-25% conversion

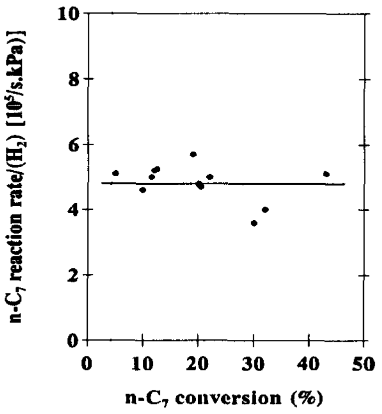


Fig. 2. H_2 Rate Order for C_7 Isomerization

200°C, 0.8-3 MPa H_2, 0.1-0.2 MPa $n\text{-}C_7$

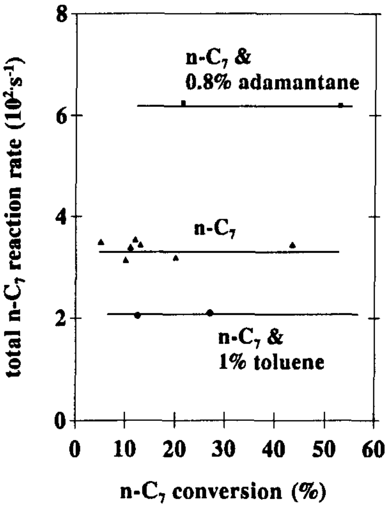


Fig. 3. Adamantane and Toluene Addition Effect C_7 Conversion Rate

200°C, 780kPa, $H_2/n\text{-}C_7$ = 6.2

These results suggest that quaternary isomers and cracked products probably share a common intermediate and both require longer surface lifetimes than monobranched isomers. The decrease in carbocation lifetimes caused by adamantane addition and resulting in higher isomerization turnover rates also limits the selectivity to multibranched isomers.

ACKNOWLEDGMENTS

The authors would like to thank William E. Gates, Sal Miseo and Richard Ernst for their experimental assistance, and Gary McVicker for discussions on solid acid chemistry.

REFERENCES

1 V. C. F. Holm and G. C. Bailey, U.S. Patent 3,032,599(1962)
2 M. Hino and K. Arata, Chem Comm., **1980**, 851.
3 T. Jin, M. Machida, K. Tanabe, Inorg. Chem., **1984**, 23, 4396.
4 T. Yamaguchi, T. Jin, and K. Tanabe, J. Phys. Chem., **1986**, 90, 3148.
5 T. Jin, T. Yamaguchi, and K. Tanabe, J. Phys. Chem., **1986**, 90, 4794.
6 T. Yamaguchi, T. Jin, T. Ishida, and K. Tanabe, Mat. Chem. Phys., **1987**, 17, 3.
7 H. Matsuhashi, M. Hino, and K. Arata, Chem. Lett., **1988**, 1027.
8 M. Hino and K. Arata, J. Chem. Soc. Chem. Commun., **1987**,1259.
9 T. Ishida, T. Yamaguchi, and K. Tanabe, Chem Lett., **1988**, 1869.
10 K. Tanabe, Crit. Rev. Surf. Chem., **1990**, 1(1),1.
11 K. Ebitani, J. Konishi, and H. Hattori, J. Cat. **1991**, 130, 257.
12 K. Ebitani, J. Tsuji, H. Hattori, and H. Kita, J. Cat. **1992**, 135, 609.
13 B. Umansky, J. Engelhardt, and W. K. Hall, J. Cat. **1991**, 127, 128.
14 T. Hosoi, T. Shimidzu, S. Itoh, S. Baba, H. Takaoka, T. Imai, and N. Yokoyama, Prepr. -Am. Chem. Soc., Div. Pet. Chem., **1988**, 33(4), 562.
15 E. Iglesia, S. L. Soled, and G. M. Kramer, J. Cat. **1993**, 144,238.
16 G. M. Kramer, U.S. Patent 4,357,484(1984); U.S. Patent 4, 424, 387(1984).
17 G. M. Kramer and A. Schriesheim, J. Phys. Chem., **1961**, 65, 1283.