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Evidence for Alkylcarbenium Ion Reaction Intermediates from Intrinsic Reaction Kinetics of C_6–C_9 *n*-Alkane Hydroisomerization and Hydrocracking on Pt/H–Y and Pt/USY Zeolites

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A quaternary mixture of hexane, heptane, octane, and nonane was hydroconverted on Pt/H–Y with a Si/Al ratio of 2.7 and two Pt/USY catalysts with Si/Al ratios of 13 and 30, respectively. Although these zeolite catalysts have largely different activities, they show unique yield curves of monobranched isomers, multibranched isomers, and cracked products versus conversion. Intrinsic reaction rate constants were obtained from the modeling of experimental conversions with a combined adsorption–reaction model assuming alkylcarbenium ion reactions as rate-determining steps, and independently determined multicomponent adsorption equilibrium expressions. On the three catalysts, the relative intrinsic reactivities of the different *n*-alkanes are constant. The relative intrinsic reaction rates of skeletal branching and cracking reaction steps are also catalyst independent. With respect to the reaction mechanism, this independence of relative reaction rates of the nature of the zeolite favors the occurrence of the classic reaction mechanism with alkylcarbenium ions as true reaction intermediates rather than as transition states not completely separated from the acid site. The dependence on carbon number of the intrinsic rate constants is consistent with branching reactions of alkylcarbenium ions via protonated cyclopropanes.

Key Words: **alkylcarbenium ions; *n*-alkanes; hydroconversion; hydrocracking; hydroisomerization; reaction mechanism; modeling; bifunctional catalysis; Y zeolite.**

INTRODUCTION

Isomerization and hydrocracking, or hydroconversion for the short, of hydrocarbons in the presence of hydrogen over bifunctional zeolite catalysts is a key process in the production of hydrocarbon fuels (1). In the modeling of hydroconversion reactions of alkanes catalyzed by bifunctional zeolites, it is accepted that alkylcarbenium ions are formed as reaction intermediates (2). These alkylcarbenium ions are formed through dehydrogenation of the alkane on the noble metal followed by protonation of the alkene on a Brønsted acid site (3). According to this model, the acidity of the zeolite influences the rate of formation of alkylcarbenium ions, but has no influence on the relative reactivities of different molecules nor on the selectivity of their transformations.

A totally different view of this catalytic chemistry evolves from quantum chemical studies concerning the interaction of short alkenes with aluminosilicate clusters representing the zeolite (4, 5). These studies predict the formation of an alkoxide in the ground state having a covalent bond between a carbon atom of the hydrocarbon and an oxygen atom of the catalyst. The transformations of alkoxides into the reaction products proceed through concerted mechanisms with ringlike positively charged transition states not completely separated from the acid site. Whereas variations in acidity do not greatly influence the relative stability of the covalent ground states, they do affect the energy of the transition state (5). According to this quantum chemical model, the activation energy is influenced by the basicity of the framework oxygen atoms stabilizing the positively charged transition state. The basicity of the framework oxygen atoms is dependent on the chemical composition of the zeolite (6). The quantum chemical models predict the relative reactivity of molecules and the selectivity of the catalytic conversions to change with the zeolite composition.

The key experiment to evaluate the rival models is an investigation of the dependence of the selectivity of the hydrocarbon conversion on the acid–base properties of the zeolite. The zeolite catalyst for such an experiment must have pores that are wide enough to avoid product and transition-state shape-selective phenomena. The acid and metal functions must be balanced in order to suppress side reactions such as hydrogenolysis on the metal and dimerization–cracking on acid sites (7, 8). Based on these requirements, we selected the hydroconversion of C6–C9 *n*-alkanes on Pt-on-Y-type zeolites. Zeolite Y samples with Si/Al ratios of 2.7, 13, and 30, representing the largest possible variation of acid–base properties of hydrogen faujasites, were selected.

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TABLE 1

Zeolite Properties

	Y	USY (Si/Al 13)	USY (Si/Al 30)
Source	Zeocat	PQ (CBV720)	PQ (CBV760)
Bulk Si/Al ratio	2.7	13	30
Crystal dimensions (μm)	0.45	0.2	0.2
Micropore volume (cc/g)[a]	0.34	0.29	0.28
Mesopore volume (cc/g)[a]	0.04	0.15	0.16
Acid site concn (mmol/g)[b]	n.d.	0.62	0.24
Weak	n.d.	0.06	0.05
Strong	n.d.	0.54	0.19
Ammonium CEC (mmol/g)[c]	4.1	0.60	0.37
Al(IV) content (mmol/g)[d]	4.6	0.60	0.22
Al(VI) content (mmol/g)[d]	0.0	0.06	0.08

[a] A determined with nitrogen adsorption at 77 K.

[b] Determined with ammonia TPD (16); data from Refs. (17) and (18); Weak sites, $\Delta H = 90$–95 kJ mol^{-1}; strong sites, $\Delta H = 115$–127 kJ mol^{-1}.

[c] Ammonium cation exchange capacity, determined as the ammonium content of the sample determined with Micro Kjeldahl analysis (18).

[d] Determined with ^{27}Al MAS NMR (19).

EXPERIMENTAL

The hydrocracking of a quaternary mixture of hexane (10 wt%), heptane (30 wt%), octane (35 wt%), and nonane (25 wt%) was performed in a tubular vapor-phase flow reactor at an inlet pressure of hydrocarbons and hydrogen of 32 and 418 kPa, respectively, and a temperature of 506 K. Zeolite properties are given in Table 1. Ammonium forms of the zeolites were loaded with 0.5 wt% platinum metal by incipient wetness impregnation with $Pt(NH_3)_4Cl_2$ in aqueous solution. The zeolite powder was compacted into discs by applying a pressure of ca. 20 Pa, and the discs were broken into fragments and sieved. For the catalytic experiments the 300–500-μm fraction was used. The catalysts were activated in flowing oxygen, under increasing temperature from room temperature to 673 K at 6 K/min, and at 673 K for 1 h. After a purge with nitrogen, the platinum was reduced in a flow of hydrogen for 1 h at 673 K. Reaction product analysis was carried out online with a HP 5890 gas chromatograph and a FID detector. During the experiments, no catalyst deactivation was observed.

The weighed conversion is defined as

$$\bar{x} = \sum_{i=1}^{4} f_i x_i \Big/ \sum_{j=1}^{4} f_j \qquad [1]$$

in which x and f represent the fractional conversion and the molar fraction in the feed, respectively.

The yield of cracked products from an individual n-alkane, y_{CRi}, was calculated from the difference between the conversion and the yield of monobranched (y_{MBi}) and multibranched (y_{MTBi}) isomers from that n-alkane:

$$y_{\mathrm{CRi}} = x_{\mathrm{i}} - y_{\mathrm{MBi}} - y_{\mathrm{MTBi}} \qquad [2]$$

RESULTS AND DISCUSSION

The conversion of the feed was changed by changing the space time by altering the amount of catalyst and/or the inlet flow rate while keeping the reaction temperature at 506 K. The hydrocarbon space time ranges used to evaluate the Pt/H–Y, Pt/USY(Si/Al 13), and Pt/USY(Si/Al 30) catalysts were 70–1500, 250–5500, and 200–3500 kg s mol^{-1}, respectively. For the three catalysts, the hydroconversion of hexane, heptane, octane, and nonane in their quaternary mixture is plotted against the weighed conversion in Fig. 1. The data points obtained on the different catalysts fall on the same curves. The evolution with the weighed conversion of the yield of monobranched isomers, multibranched isomers, and cracked products of the different n-alkanes from the feed is shown in Fig. 2. Linear alkanes are first isomerized into monobranched alkanes. Due to the further isomerization of the monobranched alkane fraction into multibranched alkanes, the yield of monobranched alkanes starts to decrease beyond a certain weighed conversion. At high conversions, the multibranched alkanes are cracked into shorter alkanes. Again, the data points obtained with the three catalysts can be fitted with the same curves. The superposition of the conversion and yield curves indicates that on a relative basis, the rates of the different reactions are not influenced by the nature of the zeolite. This is strong evidence for a reaction mechanism in which the transition states are not influenced by the nature of the zeolite such as in the classic mechanism with alkylcarbenium ion intermediates and with rearrangements of these intermediates as rate-determining steps.

Apparent reaction rates in zeolite-catalyzed reactions are strongly influenced by physisorption (9). Under the present specific reaction conditions, the adsorption competition of the alkanes is almost the same on the three

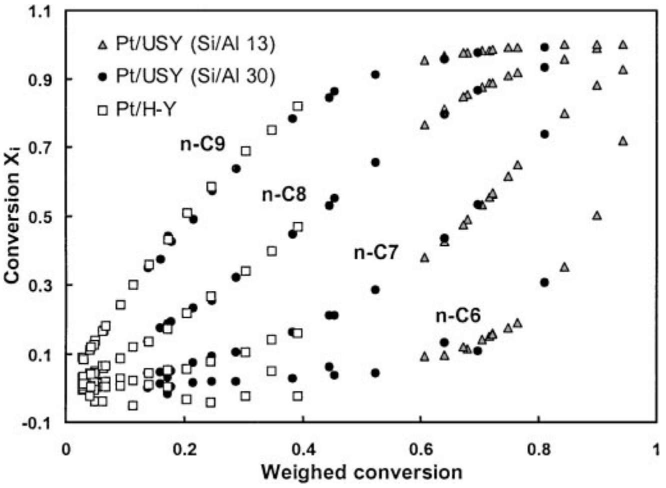

FIG. 1. Conversion of a mixture of hexane, heptane, octane, and nonane on Pt/H–Y (Si/Al 2.7), Pt/USY (Si/Al 13), and Pt/USY (Si/Al 30) at 506 K.

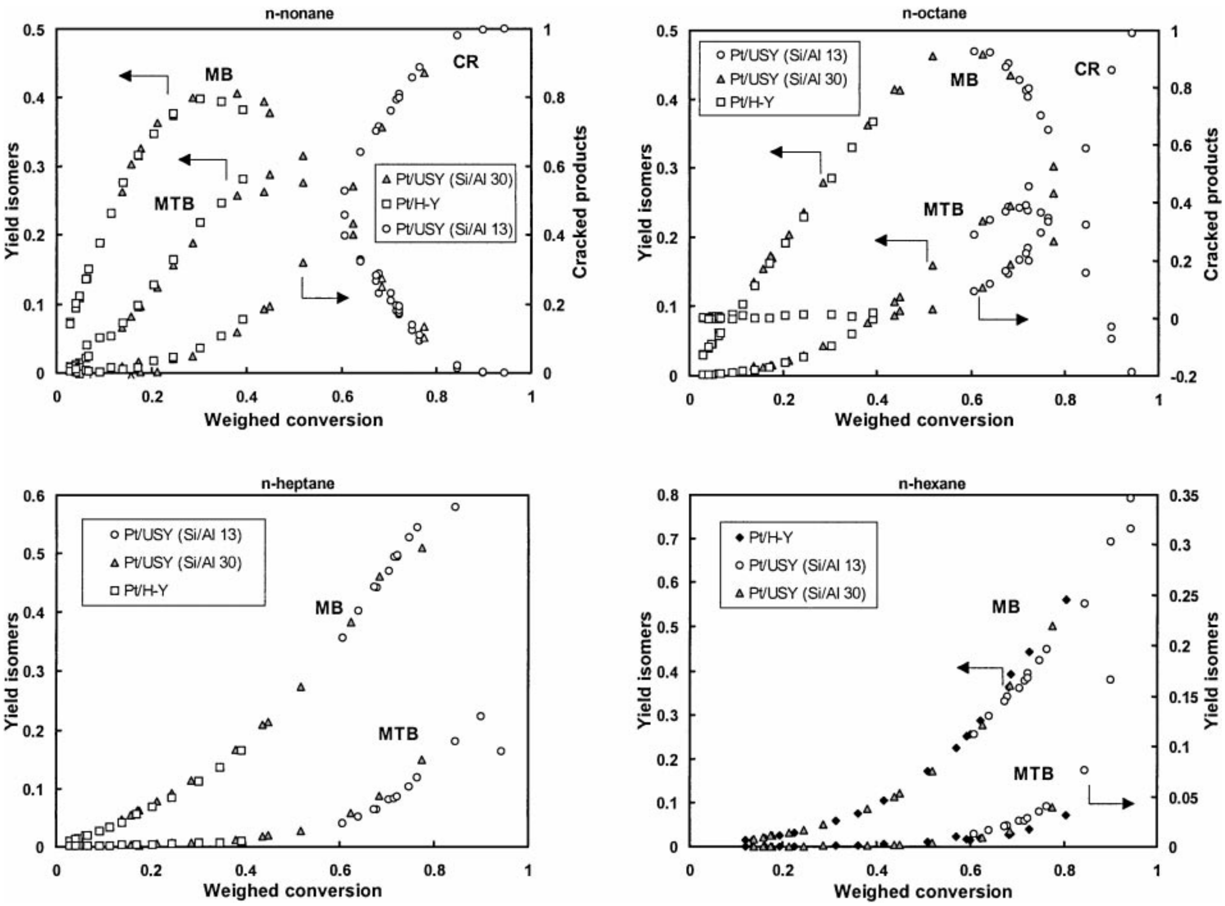

FIG. 2. Yield of monobranched isomers (MB), multibranched isomers (MTB), and cracked alkanes (CR) in the hydroconversion of a mixture of hexane, heptane, octane, and nonane on Pt/H–Y (Si/Al 2.7), Pt/USY (Si/Al 13), and Pt/USY (Si/Al 30) at 506 K.

investigated zeolite Y samples (10). Extraction of intrinsic rate constants from the experimental data necessitates the incorporation of accurate adsorption isotherm expressions in the reaction rate equations. Adsorption isotherms of normal and branched alkanes as pure compounds and as mixtures at the temperature and the pressures of the present hydroisomerization–hydrocracking experiments were previously determined using perturbation chromatographic techniques on catalyst samples that were inactivated by omitting the noble metal (10). A multicomponent Langmuir + interaction equation with specific Henry, Langmuir, and interaction parameters for each zeolite was found to be a suitable expression for these multicomponent competitive adsorption equilibria (10). The expression accounts reasonably well for variations of the separation factors with adsorbate concentration and the simultaneous adsorption of *n*-alkanes in micropores and mesopores of USY zeolites.

Intrinsic kinetic constants were determined using Langmuir + interaction isotherm expressions and a combined reaction scheme comprising monobranching, multibranching, and cracking steps:

$$n\text{-alkane} \underset{\longleftarrow}{\overset{k_{\mathrm{MB}}}{\longrightarrow}} \mathrm{MB} \underset{\longleftarrow}{\overset{k_{\mathrm{MTB}}}{\longrightarrow}} \mathrm{MTB} \overset{k_{\mathrm{CR}}}{\longrightarrow} \mathrm{CR} \qquad [3]$$

These rate equations assume that the rate-limiting steps in the reaction scheme are the rearrangement and cracking reactions of alkylcarbenium ions, and that the adsorption and desorption and hydrogenation and dehydrogenation steps are in quasi equilibrium; their solution and the fitting procedure are reported elsewhere (10). The intrinsic kinetic reaction rate constants for monobranching, multibranching, and cracking for the different *n*-alkanes and the three catalysts are listed in Table 2. These constants reveal large activity differences among the three catalysts and maximum activity for the sample with intermediate Si/Al ratio. Such “volcano”-type variation in activity with Si/Al has been observed for many reactions (11–13) and reflects the combination of a decreasing number of acid sites with a concomitant increase in their strength. When the intrinsic reaction rate constants are presented on a relative basis

TABLE 2

Intrinsic Kinetic Constants for Monobranching, Multibranching, and Cracking on Pt/H–Y, Pt/USY (Si/Al 13), and Pt/USY (Si/Al 30) at 506 K

	Pt/H–Y	Pt/USY (Si/Al 13)	Pt/USY (Si/Al 30)
		k_{MB} (1/s)	
Hexane	100	2600	530
Heptane	110	4100	650
Octane	220	5800	1100
Nonane	340	8100	1500
		k_{MTB} (1/s)	
Hexane	—	—	—-
Heptane	61	2100	350
Octane	150	3900	730
Nonane	280	6500	1300
		k_{CR} (1/s)	
Hexane	—	—	—
Heptane	39	—	220
Octane	81	2200	410
Nonane	150	3700	720

(Table 3), within the error margin, the ratio of kinetic constants is catalyst independent.

The kinetic constants reported here quantify the transformation of one combined group to another group, such as the isomerization of the linear octane molecules to all monobranched octane isomers. Such a rate constant thus contains the contribution of all individual steps participating in the global conversion. The dependence of the intrinsic kinetic constants for branching on the carbon number can be rationalized by considering the mechanism of skeletal isomerization. In the classic model for the bifunctional hydroconversion of *n*-alkanes, the alkylcarbenium ions are rearranged through formation of protonated cyclopropanes (PCP) (14).

The formation of a methyl side branch occurs through a proton jump in the protonated cyclopropane ring toward a ring carbon atom free of alkyl substituents and further ring opening (15). Depending on the position of the positively charged carbon atom in the chain, different PCPs can be formed. Not all of these possible PCP structures give rise to skeletal branching upon ring opening, since part of them would lead to the formation of very unstable primary alkylcarbenium ions. The number of effective PCP structures increases with increasing carbon number. The relative kinetic constants for monobranching were divided by the number of possible effective PCP structures (Table 4). Despite this simplification, it is observed that PCP rearrangements of alkylcarbenium ions occur at very similar rates, independent of the carbon number.

TABLE 3

Ratio of Intrinsic Rate Constants

	Pt/H–Y (Si/Al 2.7)	Pt/USY (Si/Al 13)	Pt/USY (Si/Al 30)
		k_{MB}/k_{MTB}	
n-C6	—	—	—
n-C7	1.9	1.9	1.9
n-C8	1.5	1.5	1.5
n-C9	1.2	1.3	1.2
		k_{MB}/k_{CR}	
n-C6	—	—	—
n-C7	2.9	—	2.9
n-C8	2.7	2.6	2.8
n-C9	2.3	2.2	2.1

TABLE 4

Relative Intrinsic Rate Constants for Monomethyl-Branching through a PCP

	Pt/H–Y (Si/Al 2.7)	Pt/USY (Si/Al 13)	Pt/USY (Si/Al 30)
n-C6	1	1	1
n-C7	0.8	1.1	0.8
n-C8	1.1	1.1	1.1
n-C9	1.3	1.3	1.2

CONCLUSIONS

The selectivity of the hydroconversion of *n*-alkanes on bifunctional Y zeolites is not influenced by the Si/Al ratio of the Y zeolite. This observation is in agreement with a reaction mechanism involving free alkylcarbenium ions rather than alkylcarbenium ion-like transition states not completely separated from the acid site. The conversions can be modeled with rearrangements of the alkylcarbenium ions not influenced by their chemical environment. Consequently, models developed for one Y zeolite with a particular framework composition can be extrapolated to Y zeolites with other compositions, provided a correction is made for the adsorption behavior and the absolute activity, which can be determined, for example, in a simple experiment with one single hydrocarbon compound.

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