

Influence of zeolite pore structure on catalytic reactivity

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Influence Of Zeolite Pore Structure On Catalytic Reactivity

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The influence of zeolite pore-size and shape on the hydro-isomerization of n-hexane was studied. Computer simulations and kinetic measurements, in combination with Positron Emission Profiling (PEP) experiments have been performed. Results showed that, for zeolites with a Al/Si molar ratio of less than 0.1 acidic protons had the same activity. Differences in reactivity are due to differences in the heat of adsorption. Smaller pores result in a higher steady state concentration of adsorbed substrate and adsorbed alkoxy species. Based on a kinetic model, and using experimental heats of adsorption and theoretical protonation energies, the activation energy of hydro-isomerization of n-hexane was found to be approximately 127 kJ/mol. This is consistent with results of a recent quantum chemical model of reactions catalysed by a zeolite proton.

1. INTRODUCTION

One of the major questions still unanswered in zeolite catalysis is concerned with the influence of the pore-size and shape on acid catalysed reactions. One type of effect is shape selectivity [1]. A second effect arises from interactions between the zeolite pore walls and sorbates [2]. This effect influences adsorption and diffusion properties of reactants, intermediates and products.

In this study the influence of the heat of adsorption of the reactant was investigated. The hydro-isomerization of n-hexane over platinum loaded acidic zeolites was chosen as a model reaction. The mechanism, as proposed by Weisz in 1963 [3], is given schematically in Figure 1. In this mechanism, a noble metal performs hydrogenation-dehydrogenation on the reactant and products. The rate determining step is the actual isomerization on Brønsted acid sites.

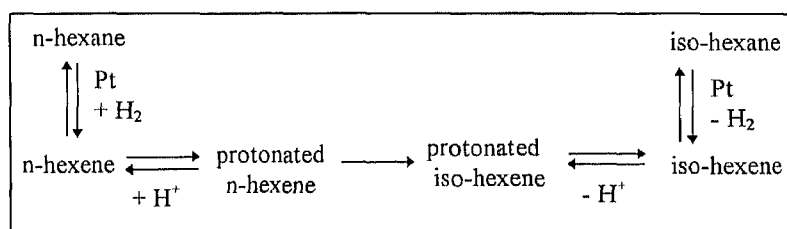


Figure 1. Schematic representation of Weisz' bifunctional mechanism for the hydro-isomerization of n-hexane on platinum loaded acidic catalysts

The pore size and shape influence on this reaction was determined by performing catalytic measurements, computer simulations and PEP experiments on different zeolites. Zeolites showing different heats of adsorption for n-hexane were used.

2. EXPERIMENTAL

2.1. Catalyst preparation

Na-ZSM-5 was obtained from Exxon Chemicals, Machelen, Belgium. Na-Mordenite was obtained from Shell Laboratories in Amsterdam. Conversion to the protonated form was carried out via the following procedure. Zeolites were exchanged with an aqueous ammonium nitrate solution, stirring overnight at room temperature. This was repeated three times with a fresh solution. The zeolites were washed, dried and calcined. The calcination procedure consisted of a drying period in nitrogen at 120 °C after which the temperature was increased at a rate of 5 K/min to 500 °C. This temperature was then held for 1 hour. The sample was cooled to 250 °C and an oxygen flow (20 volume %) was added to the nitrogen flow. After stabilisation of the temperature, the calcination was completed by reheating to 500 °C.

Platinum loading of the zeolites was performed by an overnight ion exchange at room temperature with a platinum tetra-ammonium hydroxide solution. Both *in situ* and *ex situ* pretreatments were used. The dried sample was pressed for 1 minute at 5 tons in an infra-red press. After crushing and sieving, a sieve fraction of 125-500 µm was used.

2.2. Catalyst characterisation

The intrinsic proton acidity of both H-Mordenite (Si/Al 10) and H-ZSM-5 (Si/Al 28) was measured. The chemical shift of ¹H MAS NMR was the same for both samples (4.1 ppm with respect to TMS). The OH stretching vibration in the IR was also constant (~ 3610 cm⁻¹). Thus, both H-Mordenite and H-ZSM-5 had similar Brønsted acid strengths. Titration of the acid sites using ammonia was performed to establish the amount of sites.

2.3. Equipment

Hexane (Janssen Chimica 99+% purity), delivered by a HP1050 HPLC pump, was evaporated into flowing hydrogen. The gas flows were controlled by a mass-flow controller. The mixture was flowed through a fixed-bed reactor at atmospheric pressure. A quartz reactor with an internal diameter of 4 mm was used, typically filled with 200 mg of catalyst. Reaction products were analysed on-line using a HP5995 gas chromatograph equipped with a FID detector and a Chrompack fused silica column with a Al₂O₃/KCl coating.

The temperature range employed was 220-260 °C. A WHSV range of 4-17 h⁻¹ was used. When necessary, nitrogen was used as diluting gas. A hydrogen/n-hexane molar ratio of above 20 was used so that deactivation by coking was minimised. Following an ageing period (see next paragraph), the activity reached a stable plateau. The catalysts could then be used for up to 1000 hours on stream without further loss of activity. The reaction was found to be free from both internal and external diffusion limitations.

2.4. *In situ* and *ex situ* pre-treatment

Each catalyst was subjected to the following pre-treatments:

1). Calcination: heating at 0.5 K/min in a 50 ml/min 80/20 nitrogen/oxygen flow to 450 °C, a 2 hour dwell period and subsequent cooling in nitrogen to room temperature.

- 2). Reduction: heating at 5 K/min in a 50 ml/min hydrogen flow to 400 °C, a 2 hour dwell period and subsequent cooling to room temperature.
- 3). Ageing: after a hydrogen pre-treatment of 400 °C the catalyst was submitted to 20 hours of standard reaction conditions. These conditions are: 0.03 ml/min liquid flow of n-hexane, 145 ml/min flow of hydrogen, a temperature of 240 °C. During this treatment, after an initial deactivation period, a stable level of activity was reached.

Between measurements Mordenite catalysts were re-activated by an *in situ* hydrogen treatment at 450 °C, ZSM-5 catalysts at 250 °C.

2.5. Computer simulations

In addition to the reactor studies, the kinetics of the hydro-isomerization reaction were simulated based on the microkinetics method as developed by Dumesic [4]. In this method, the steady state concentrations of gas phase and surface species are calculated as a function of distance along the reactor. The rates of elementary steps, both forward and reverse, are calculated from fundamental data such as pre-exponential factors and activation energies. No step was *a priori* assumed to be rate determining or equilibrated. Thermodynamic energy diagrams were used to ensure that each reaction cycle was closed, i.e. conservation of energy was maintained.

The mechanism was divided into elementary steps, based on the Weisz mechanism. These steps consisted of the following groups.

- 1). Adsorption/desorption on the zeolite
- 2). Transport to and from adsorption sites to platinum sites
- 3). Hydrogenation/dehydrogenation in one step
- 4). Protonation/deprotonation on Brønsted acid sites
- 5). Isomerization on Brønsted acid sites
- 6). Adsorption/desorption of hydrogen onto platinum sites

A total of 23 gas phase, 24 platinum site, 15 acid site and 23 adsorption site species were used. The species involved are all hexane and hexene isomers and hydrogen. The model therefore consists of a system of 210 differential equations, to be solved simultaneously. At steady state conditions this system reduces to one of 210 algebraic equations. The applied simulation routine uses a zero finder to obtain surface coverages from gas phase concentrations. Gas phase concentrations along the length of the plug flow reactor were calculated applying equations for a cascade of CISTR's (Continuously Ideally Stirred Tank Reactors). Input for these equations are gas phase concentrations and surface coverages at z , leading to concentrations at a point somewhat further in the reactor ($z + \Delta z$).

Other input parameters are reaction conditions, such as temperature and flow, concentrations of sites and other catalyst characteristics. So although surface coverages are used, the site balance can still be accounted for. Further details about the simulation will be presented elsewhere [5].

The pre-exponential factors and activation energies, needed to describe the elementary steps, were either taken from the literature, estimated from theory or deduced from experimental characterisation data. The most important of the elementary steps is the acid catalysed isomerization (step 5). The activation energies of this step were calculated using a mechanism in which an intermediate alkoxy species is formed by protonation of an olefin by a zeolite proton [6]. Isomerization then occurs in a transition state with respect to the stable alkoxy intermediate. Kazansky *et al.* calculated a value of 120-130 kJ/mol for the activation energy of desorption of an alkoxy species to an adsorbed alkene [7]. To estimate the

isomerization activation energies this value must be added to the liquid phase isomerization energies as found by Brouwer [8]. The activation energies used are somewhat lower than the full sum since a complete desorption is not necessary for isomerization to occur. The order of magnitude of the corresponding pre-exponential factor was restricted for one catalyst and set of conditions to obtain a conversion level close to that found experimentally. The same value was then used for all other calculations.

2.7. Positron Emission Profiling

Positron emitting ^{11}C labelled CO has been used earlier by Jonkers *et al.* [9] to study elementary reaction rate constants and surface concentrations of intermediates of catalytic reactions at steady state conditions. The half-life of a ^{11}C atom is approximately 20 minutes. An emitted positron, once it has annihilated with an electron, will produce two γ photons. These photons travel at an 180° angle of each other. When the reactor is placed in an array of the appropriate detectors, the labelled atom can be pinpointed at the moment of decay. A schematic representation of the set-up is given in Figure 2.

In the PEP experiments, the concentrations of labelled molecules can be determined *in situ* as a function of position and time under actual operating conditions. Under steady state reaction conditions, these labelled molecules include both reactants and products. The retention time distribution is therefore due to reaction, adsorption and diffusion. Experiments were also performed on zeolites without platinum loading under identical conditions so that the effects of adsorption and diffusion could be studied independently.

We are using this technique to study the isomerization of n-hexane. The ^{11}C labelled n-hexane was produced using a special procedure [10]. This procedure involves an on-site production of ^{11}C labelled CO which is adsorbed on a vanadium promoted ruthenium on silica catalyst at high temperature (350°C). The deposited carbon is then coupled to 1-pentene using a lower temperature (110°C). The products are hydrogenatively desorbed and collected. The labelled n-hexane is separated from the other products and concentrated by trapping at liquid nitrogen temperature. Then the hexane can be pulsed into a steady state stream without disturbing this stream. The pulse contains only a few pico-moles of labelled substrate and approximately 2 micro-moles of non-labelled n-hexane. The retention time distribution of the pulse is then measured by the PEP detector.

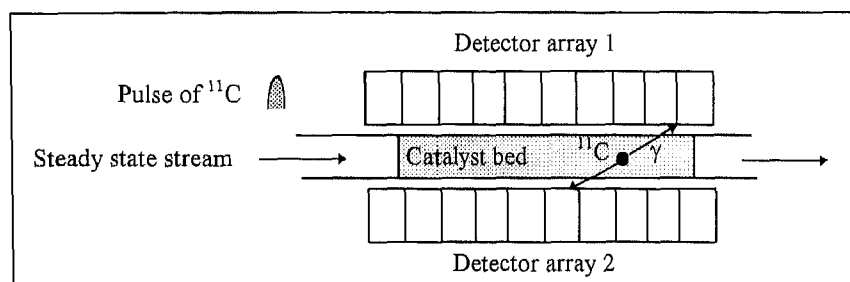


Figure 2. Schematic representation of the PEP set-up

3. RESULTS AND DISCUSSION

3.1. Experiments

When the platinum function is sufficiently active to establish the hexane/hexene equilibrium, the rate determining step in the hydro-isomerization is the acid catalysed isomerization (step 5). Under these conditions and using the ideal bi-functional mechanism shown in Figure 1, one calculates that the order of the reaction in hydrogen should be negative (between 0 and -1). At high absolute hydrogen pressure, a 0.015 platinum to acid sites molar ratio is sufficient to obtain this situation [11]. However, we have found that at atmospheric pressure this ratio resulted in a positive order in hydrogen. This anomaly can be explained in two ways:

1. a two-step dehydrogenation in which dissociated hydrogen is needed to abstract the first hydrogen atom from the alkane [12]
2. direct hydrogenation of the alkoxy species from the acid sites [13], in this case the hydrogenation on the platinum has become the rate determining step

It was found that at atmospheric pressure a higher Pt/H⁺ ratio of 0.04 was needed to ensure that the isomerization step was rate determining.

The Turn Over Frequency (TOF) of a catalyst is defined here as the number of moles of n-hexane converted per mole of acid sites per hour. Experiments showed that a ZSM-5 catalyst was a factor of 5 more active than a Mordenite catalyst (see Table 1). This may be due to an enhanced surface coverage of hexane in case of ZSM-5, caused by a higher adsorption energy of the substrate molecule. Since the acidity of both zeolites was shown to be the same the enhanced activity can not be attributed to a difference in intrinsic acid activity.

Adsorption energies and orders of reaction in hydrogen and n-hexane are given in Table 2 on the next page.

Table 1

TOF as a function of zeolite

Catalyst	TOF [h ⁻¹]	WHSV [g/gh]
2 wt.% Pt/HMOR	5.4	8.05
0.5 wt.% Pt/HZSM-5	27.4	16.4

T = 240 °C, p_{H₂}/p_{nC₆} = 28, Pt/H⁺ = 0.04

The main kinetic data of interest are the intrinsic activation energy of isomerization (E_{act,intr}) and the heat of adsorption of an alkene to form an alkoxy species. The former can be calculated from the experimental data, according to equation (1) [14].

$$E_{act,iso} = E_{act,app} + n \cdot [\Delta H_{prot,gas} + \Delta H_{hydr}] \quad (1)$$

E_{act,iso} = activation energy of isomerization from the alkoxy species

E_{act,app} = apparent activation energy

n = order of the reaction in hexane

ΔH_{prot,gas} = theoretical protonation enthalpy of hexene from the gas phase

ΔH_{hydr} = enthalpy needed for dehydrogenation (from thermodynamics)

The protonation energy of hexene from the gas phase can be calculated from the adsorption energy of hexene added to the protonation energy from the adsorbed phase. The assumption is made that the adsorption energy of hexene is equal to the adsorption energy for hexane. In this way one obtains:

$$\Delta H_{\text{prot,gas}} = \Delta H_{\text{prot,ads}} + \Delta H_{\text{ads,nC6}} \quad (2)$$

$\Delta H_{\text{prot,gas}}$ = protonation enthalpy of hexene from the gas phase

$\Delta H_{\text{prot,ads}}$ = protonation enthalpy of hexene from the adsorbed phase

$\Delta H_{\text{ads,nC6}}$ = measured adsorption energy of hexane [15]

The protonation enthalpy from the adsorbed state is taken from quantum chemical calculations by Kazansky *et al.* [7]. The results are summarised in Table 2.

Table 2

Kinetic results							
Zeolite	n	m	$E_{\text{act,app}}$	$\Delta H_{\text{prot,ads}}$	$\Delta H_{\text{ads,nC6}}$	ΔH_{hydr}	$E_{\text{act,iso}}$
			[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]	[kJ/mol]
ZSM-5	0.54	-0.24	104	80	82	-114.8	129.5
MOR	0.42	-0.18	111	80	71.9	-114.8	126.6

m = order of the reaction in hydrogen

n = order of the reaction in n-hexane

In Table 2 an activation energy for isomerization on zeolites of approximately 127 kJ/mol is calculated. This value is much higher than the values of around 30 kJ/mol, as given for liquid phase isomerization [8]. A value of approximately 160 kJ/mol is deduced for the protonation energy of hexene with respect to the gas phase.

3.2. Simulations

In general, the computer generated data are showing the same trends as those obtained experimentally. In Table 3 the surface coverages as a function of temperature are given. Table 4 contains the corresponding simulated activities of Mordenite and ZSM-5.

The simulations showed a strong influence of surface coverage on the activity of the catalyst. Higher temperature leads to lower surface coverage (Table 3) but higher rates. The influence of temperature on the rate constant is therefore higher than on the surface coverage. Higher adsorption energy for n-hexane leads to an increased n-hexane coverage of the catalyst (Table 3). A high concentration of adsorbed hexane leads to a high coverage of platinum sites and a high concentration of n-alkoxy species (protonated n-hexenes). This leads to a more active catalyst (relate Table 3 to Table 4). It may therefore be concluded that the hypothesis in paragraph 3.1 is true. When, however, the surface coverage of hexane becomes too high the reaction rate is inhibited. This is due to a slow rate of deprotonation of the product iso-alkenes from the acid sites to undergo hydrogenation on the platinum sites. Therefore it can be concluded that an optimum surface coverage exist, invoked by an optimum adsorption energy. At higher temperature a competition between a lower surface coverage, leading to lower

activities, and higher rate constants will eventually cause a decrease of the slope in the Arrhenius plot. This leads to lower apparent activation energies at higher temperatures.

Table 3

Simulated surface coverages at the end of the reactor as a function of temperature and zeolite

T [K]	Mordenite			ZSM-5		
	Adsorbed n-hexane	n-alkoxy species	Atomic H on platinum (empty)	Adsorbed n-hexane	n-alkoxy species	Atomic H on platinum (empty)
493	0.34	0.94	0.91 (0.077)	0.86	0.98	0.82 (0.069)
513	0.18	0.85	0.86 (0.13)	0.72	0.90	0.79 (0.12)
533	0.09	0.62	0.78 (0.21)	0.53	0.72	0.74 (0.20)

Table 4

Simulated TOF at the end of the reactor as a function of temperature and zeolite

T [K]	Mordenite [h ⁻¹]	ZSM-5 [h ⁻¹]
493	1.39	7.45
513	4.62	23.83
533	11.94	57.13

Although the absolute values from Table 4 and Table 1 are not equal, both experiment and simulation show a factor of 5 higher activity for ZSM-5 relative to Mordenite.

At lower temperatures (< 240 °C) and conversions (< 15 %) straight plots of the simulated conversions as a function of axial position (z) were observed. In this temperature and conversion range one can use simple equations to numerically evaluate experiments. Above these conversions (e.g. in case of reaction on Mordenite at 260 °C), a curved rather than a straight line is obtained. In this case the TOF and surface coverages decrease linearly with position z.

3.3 Positron Emission Profiling

The influence of the amount of non-labelled n-hexane in the gas-phase on the retention time of the labelled pulse was measured. Labelled material was pulsed into a pure hydrogen stream or into one which also contained n-hexane. These measurements show strong interference between the pulse of labelled material and coadsorbed n-hexane in the micropores of the zeolite. This is due to reduced zeolite accessibility for the labelled material caused by high non-labelled surface coverages. The apparent n-hexane steady state surface coverage measured at reaction temperature (230 °C) and hexane gas phase concentration, calculated from these

measurements, is found to be high: 80 %. Details of the calculation method will be published elsewhere [16] The apparent hexane coverage must be considered as an upper limit to the true coverage. Nevertheless, these PEP data support the high surface coverages found by the computer simulations (Table 3).

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