

ISOMERIZATION AND HYDROCRACKING OF ALKANES ON Pt/CeY, Pt/LaY AND Pd/LaY ZEOLITES - BIFUNCTIONAL OR METALLIC CATALYSIS?

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ABSTRACT

MeNaY zeolites (Me = Ce³⁺ or La³⁺, degree of exchange = 72 equiv.-%) were loaded with 0.03 to 0.50 wt.-% of Pt or Pd. The resulting Pt/ and Pd/MeY-72 catalysts were tested in isomerization and hydrocracking of *n*-undecane at P_{H₂} = 2 MPa. Neither the rate nor the selectivity of isomerization depend on the content of noble metal, the selectivity being, moreover, independent of its nature. Hydrocracking typically starts at conversions around 40 %, then leading to large amounts of *i*-alkanes. Much lower rates of reaction and very different selectivities are encountered on non-acidic 0.50 Pt/NaY and 0.27 Pd/NaY. The detailed discussion of all results strongly suggests that, on Pt/ and Pd/MeY-72, bifunctional isomerization and hydrocracking predominate. However, on the Pt/MeY-72 zeolites, the bifunctional pathways tend to be accompanied by some hydrogenolysis at the noble metal, especially at high Pt loadings.

INTRODUCTION

Catalysts consisting of a large-pore zeolite in a Brønsted acid form and small amounts of a noble metal are used in isomerization of light alkanes and in hydrocracking of heavy petroleum distillates [1]. Since these catalysts possess different kinds of active sites, there is an inherent ambiguity as to mechanisms of reaction [2,3]. In particular, both isomerization and hydrocracking may proceed *via a bifunctional mechanism* or *on the noble metal alone*. In the bifunctional mechanism [3-5], skeletal rearrangement and carbon-carbon bond rupture occur at the level of carbocations chemisorbed at *the acidic sites*, while the main role of the noble metal is to open a fast route for interconversion of alkanes and carbocations via alkenes. In the metal-

lic mechanism [6-8], on the other hand, rearrangement and cleavage take place during chemisorption of the hydrocarbon *at a metal cluster*. On platinum, two different mechanisms of isomerization have been identified [6-8] which are usually referred to as the *bond shift* and the *cyclic* mechanism, respectively. Hydrocracking on metals is often called *hydrogenolysis*.

According to Weisz [3], the bifunctional mechanisms predominate over typical catalysts consisting of platinum on an acidic carrier, provided that the carbon number of the feed is sufficiently high. Indeed, a pronounced shift from bifunctional hydrocracking to hydrogenolysis was observed [9] with a Pt/CaY zeolite catalyst, when the chain length of the feed was lowered from n-octane to n-hexane. Some more recent papers tend to emphasize the importance and to generalize the validity of the metallic mechanisms. Christoffel and Paál even went so far to claim that, with bifunctional catalysts made from platinum on an acidic carrier, *mainly platinum catalyzed reactions contribute to the measured product distributions at temperatures below 350 °C* [10]. Unfortunately, these authors used an ill-defined zeolite catalyst (beside Pt/Al₂O₃ and Pt black) referred to as 0.5 wt.-% Pt/Y, the acidic nature of which was not disclosed.

In the present study, an attempt was undertaken to resolve these contradictions. Series of catalysts were prepared based on zeolite Y. The nature of the noble metal, its content, and the acidity were varied. The catalysts were comparatively tested in the hydroconversion of n-undecane which possesses enough carbon atoms to avoid non-typical side reactions.

EXPERIMENTAL

NaY zeolite with a unit cell composition Na₅₄Al₅₄Si₁₃₈O₃₈₄ was the starting material for all catalysts. Cerium or lanthanum were introduced by repeated ion exchange at 80 °C using aqueous solutions (0.03 mol-%) of the respective nitrates. After excessive exchange cycles, chemical analyses gave the formulas Me₁₃Na₁₅Al₅₄Si₁₃₈O₃₈₄ (Me = Ce or La), i.e., the final degrees of Ce and La exchange were 72 equiv.-% (MeY-72). The washed zeolites were dried at 110 °C and then stored at room temperature over the saturated aqueous solution of NH₄Cl. After equilibration, the water content was determined by TGA.

NaY, CeY-72, and LaY-72 were loaded with a noble metal by ion exchange with [Pt(NH₃)₄]Cl₂ or [Pd(NH₃)₄]Cl₂. A slurry of the zeolite was vigorously stirred at room temperature while the ammine complex,

dissolved in several hundred times its weight of water, was added dropwise over a period of two hours. Afterwards, stirring was continued for 48 h. It was ascertained that under these conditions, the complexes were taken up quantitatively by the zeolites. After drying at 110 °C the zeolite powder was pressed without a binder, the tablets were ground, and the particle size 0.2-0.3 mm was further used.

The ammine complex was decomposed in a purge of O₂ (0.1 MPa, 10 l/h, T_{max.} = 300 °C; for Pt/CeY-72 T_{max.} = 350 °C). The zeolite was then transferred to the fixed bed reactor and dried in flowing N₂ (0.1 MPa, 5 l/h, T_{max.} = 350 °C). Finally, the metal was reduced in a purge of H₂ (0.1 MPa, 5 l/h, T_{max.} = 300 °C, for Pt/CeY-72 T_{max.} = 400 °C). In the catalyst notation used hereinafter the content of noble metal is given in wt.-% on a dry basis. A total of 12 catalysts were prepared, viz. 0.05, 0.10, 0.25, and 0.50 Pt/CeY-72; 0.05, 0.20, and 0.50 Pt/LaY-72; 0.027, 0.055, and 0.27 Pd/LaY-72; 0.50 Pt/NaY; 0.27 Pd/NaY.

The flow-type apparatus with a high-pressure saturator for the feed hydrocarbon has been described earlier [11]. The purities of n-undecane and hydrogen were at least 99.8 wt.-% and 99.99 vol.-%, respectively. The products were analyzed by high-resolution capillary GLC [12] with on-line sampling. Platinum dispersions were determined by conventional H₂ chemisorption techniques.

RESULTS AND DISCUSSION

Activities, isomerization vs. hydrocracking. Fig. 1 shows the conversion of n-undecane along with the yields of isomerized and cracked products for two Pt/CeY-72 catalysts which differ in their content of noble metal. The results are typical for all Pt/ and Pd/MeY-72 zeolites employed in this study and resemble those obtained earlier on 0.5 Pt/CaY [12] or 0.5 Pt/ultrastable Y [13]: Under mild conditions, isomerization predominates. With increasing severity, the yield of isomers passes through a maximum indicating that the i-undecanes formed are consumed by consecutive hydrocracking. The height of this maximum was between 50 and 60 % for all Pt/ and Pd/MeY-72 catalysts.

A closer look at Fig. 1 reveals that, on 0.05 Pt/CeY-72, there is virtually no hydrocracking up to ca. 40 % conversion, whereas on 0.50 Pt/CeY-72 some hydrocracking does occur even at much lower conversions. It will be shown later that this hydrocracking at low conversions (as opposed to hydrocracking starting at X_{n-Un} ≈ 40 %) is probably due to hydrogenolysis on platinum. In agreement with this interpretation, 0.10 Pt/CeY-72 and 0.25 Pt/CeY-72 gave intermediate extents of

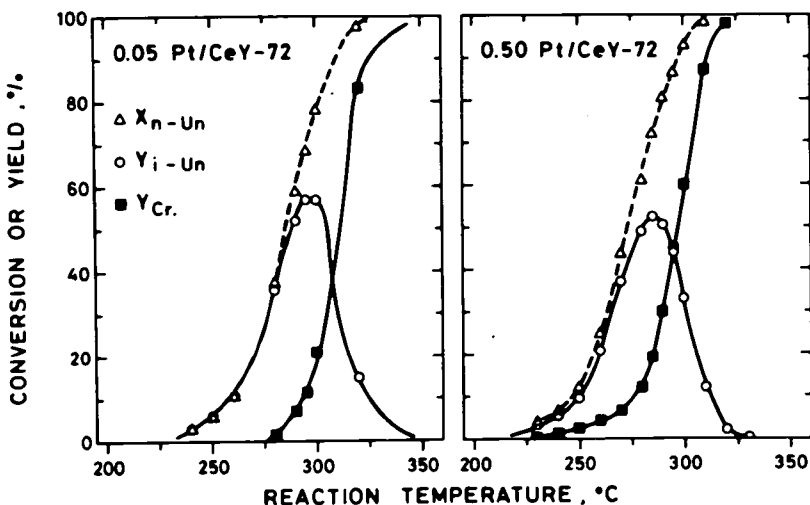


Fig. 1. Conversion of n-undecane, yield of i-undecanes, and yield of cracked products in dependence of reaction temperature ($P_{n-Un} = 20$ kPa, $P_{H_2} = 2.0$ MPa, $W/F_{n-Un} = 150$ g·h/mol).

hydrocracking at low conversions. Moreover, the same qualitative behavior was observed on the Pt/LaY-72 series, even though, at comparable conversions below 40 %, the extent of hydrogenolysis over 0.50 Pt/LaY-72 was somewhat lower than on 0.50 Pt/CeY-72. On the Pd/LaY-72 series, there was no hydrocracking at all at $X_{n-Un} \lesssim 40$ %, even not on the catalyst with the highest Pd loading, i.e., 0.27 Pd/LaY-72. It seems that, in an acidic faujasite, Pd has a lower activity for hydrogenolysis than Pt.

At this point already, it appears unlikely that, over the Pt/ or Pd/MeY-72 catalyst, *isomerization* occurs on the metals. If it did, the one would expect (based on the results of numerous investigations on the conversion of light alkanes over noble metal catalysts, e.g., [6-8]) that (i) isomerization is *always* accompanied by some hydrogenolysis and (ii) there is only little, if any, isomerization on *palladium*. The same conclusion can be drawn from Fig. 2 in which the rates of isomerization (as determined in the differential reactor regime at $X_{n-Un} \lesssim 20$ %) are plotted versus the metal content of the acidic catalysts. With one exception (0.05 Pt/LaY-72), the rate is practically independent of the metal content. Hence, it is unlikely that isomerization takes place on the metal clusters to any significant extent. One might argue that an increasing metal content could have been counterbalanced by a decreasing dispersion. This, however, was not the case, at least not for the Pt/CeY-72 and Pt/LaY-72 series (Pt dispersions around 40 and 55 %, respectively). The reasons for the relatively low activity

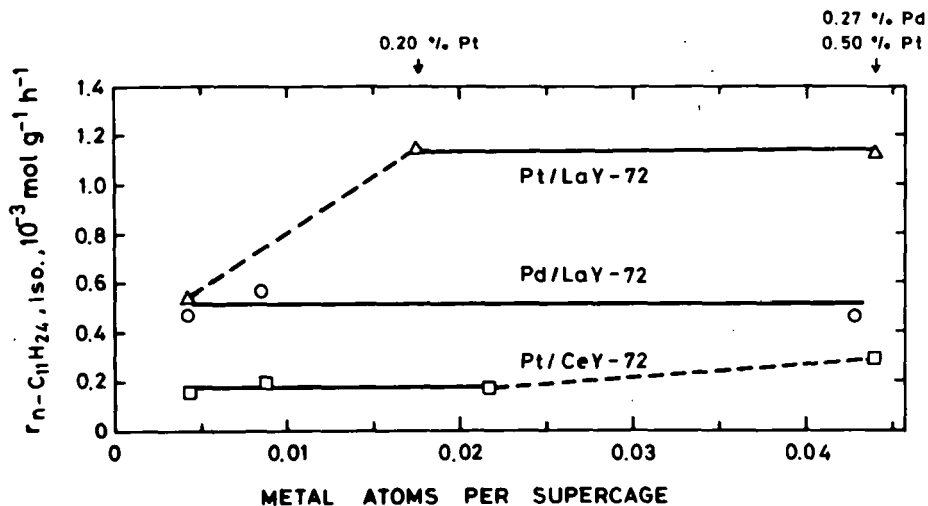


Fig. 2. Influence of the content of noble metal on the rate of n-undecane isomerization ($T = 240\text{ }^{\circ}\text{C}$, $P_{n\text{-Un}} = 20\text{ kPa}$, $P_{\text{H}_2} = 2.0\text{ MPa}$).

of 0.05 Pt/LaY-72 are not clear, at present. Nor can we explain the different activity levels of the Pt/LaY-72 and Pd/LaY-72 series. Perhaps, the nature of the noble metal influences the acidity somewhat. The relatively low activity level of the Pt/CeY-72 catalysts might be due, at least in part, to the higher pretreatment temperatures (loss of Brönsted acid sites by dehydroxylation).

It must be concluded that, on the Pt/ and Pd/MeY-72 zeolites, isomerization occurs via a bifunctional mechanism. One would then expect that the acidity of the zeolite (number and/or strength of Brönsted sites) has a pronounced influence on its activity. This is, indeed, the case as demonstrated in Table 1: With 0.27 Pd/NaY and 0.50 Pt/NaY (Pt dispersion $\approx 50\%$) which are practically non-acidic (except for some few OH groups formed during reduction of the noble metal), there is hardly any conversion even at $300\text{ }^{\circ}\text{C}$. At this temperature, most or all of the undecane is converted on the acidic zeolites (cf. also Fig. 1).

To arrive at a somewhat higher conversion on 0.50 Pt/NaY, the hydrogen partial pressure was lowered to 0.48 MPa at $P_{n\text{-Un}} = 20\text{ kPa}$, $T = 300\text{ }^{\circ}\text{C}$, and $W/F_{n\text{-Un}} = 150\text{ g}\cdot\text{h}/\text{mol}$. The resulting conversion and yields were $X_{n\text{-Un}} = 4.5\%$, $Y_{i\text{-Un}} = 0.6\%$, and $Y_{\text{Cr.}} = 2.8\%$ (in addition, there were some unidentified hydrocarbons, presumably C_{11} -naphthenes, with a total yield of 1.1%).

Selectivities of isomerization. In Table 2, the selectivities of isomerization are compared for 0.5 Pt/NaY and several selected Pt/ and

Table 1

Influence of acidity on conversion and yields ($P_{n-Un} = 20$ kPa, $P_{H_2} = 2.0$ MPa, $W/F_{n-Un} = 150$ g·h/mol).

Catalyst T, °C	non-acidic				acidic			
	0.50 Pt/NaY 260	0.27 Pd/NaY 300	0.27 Pd/NaY 260	0.1 Pd/NaY 300	0.50 Pt/LaY-72 260	0.27 Pd/LaY-72 300	0.27 Pd/LaY-72 260	0.1 Pd/LaY-72 300
X_{n-Un} , %	0	0.5	0	0.1	58	100	27	95
Y_{i-Un} , %	0	0	0	0	48	0	27	32
Y_{Cr} , %	0	0.5	0	0.1	10	100	0	63

Pd/MeY-72 catalysts at low conversions. All the acidic zeolites give practically identical distributions of i-undecanes, irrespective of the nature and the content of noble metal. This is again strong evidence for a common mechanism of skeletal rearrangement at the acidic sites, i.e., for a bifunctional mechanism. It has been shown [14,15] that ionic rearrangements in which a branching is created are best interpreted in terms of a pathway via protonated cyclopropanes. It has, moreover, been deduced [12] that such a mechanism of branching is expected to result in low rates of formation of 2-methyldecane amounting to about one half of the rates of formation of 3-, 4-, and 5-methyldecane. Table 2 reveals that this is approximately fulfilled on the Pt/ and Pd/MeY-72 catalysts. On 0.50 Pt/NaY, on the other hand, a substantially different isomer distribution is encountered. Its salient feature is the preponderance of 4-methyldecane which has also been found during isomerization of n-undecane over platinum on non-acidic Al_2O_3 [16]. It can be shown [16] that the so-called cyclic mechanism [7,8] indeed predicts 4-methyldecane as a major product. We conclude that isomerization on 0.50 Pt/NaY occurs mainly or totally on the noble metal.

Selectivities of hydrocracking. It is relatively easy to discriminate between bifunctional hydrocracking and hydrogenolysis on metals: Hydrogenolysis inevitably gives a certain amount of methane and ethane [6-8], whereas in β -scission of classical alkylcarbenium ions which is involved in bifunctional hydrocracking [4], C_1 - and C_2 -moieties are forbidden (besides, an ionic mechanism of bond rupture via non-classical alkylcarbonium ions has been claimed [17] which, however, is unlikely to play an important role under our conditions). Furthermore, starting from a normal alkane, the primary products of hydrogenolysis are again n-alkanes, whereas i-alkanes prevail in bifunctional hydro-

Table 2

Selectivities of n-undecane isomerization (moles of i-undecane formed/100 moles of n-undecane isomerized; $P_{n-Un} = 20$ kPa, $W/F_{n-Un} = 150$ g.h/mol).

Catalyst	0.50 Pt/ NaY	0.50 Pt/ CeY-72	0.05 Pt/ LaY-72	0.20 Pt/ LaY-72	0.50 Pt/ LaY-72	0.27 Pd/ LaY-72
T, °C	300	240	220	220	220	220
P_{H_2} , MPa	0.48	2.0	2.0	2.0	2.0	2.0
X_{n-Un} , %	4.5	5.5	2.6	5.5	5.4	2.5
Y_{i-Un} , %	0.6	4.3	2.6	5.5	5.1	2.5
2-M-De	13	12	12	12	12	11
3-M-De	16	23	23	23	23	23
4-M-De	36	25	25	25	25	25
5-M-De	14	28	29	28	27	30
3-E-No	4	3	3	3	3	3
4-E-No	5	5	5	5	5	5
5-E-No	0	2	2	2	3	2
4-P-Oc	4	2	1	2	2	1
others	8	0	0	0	0	0

cracking because ionic β -scission is preceded by rapid skeletal rearrangements.

Typical selectivities of hydrocracking observed in this study are depicted in Fig. 3. On 0.27 Pd/LaY-72 both the carbon number distribution and the content of i-alkanes are representative for a pure primary cracking via a bifunctional mechanism [4,9,11]. With this catalyst, the selectivity of hydrocracking was found to be virtually independent of Y_{Cr} . Moreover, the results shown for 0.27 Pd/LaY-72 are representative for the whole Pd/LaY-72 series and for the Pt/MeY-72 zeolites with low metal loadings.

An entirely different selectivity is encountered on 0.50 Pt/NaY. C_1 and C_2 as well as C_{10} and C_9 now do occur and there are no branched alkanes at all in the cracked products. Without any doubt, they are formed on the noble metal.

On 0.50 Pt/LaY-72, the selectivity of hydrocracking is seen to depend markedly on the yield of cracked products. The cracking reactions which take place at low values of Y_{Cr} and, hence, at low con-

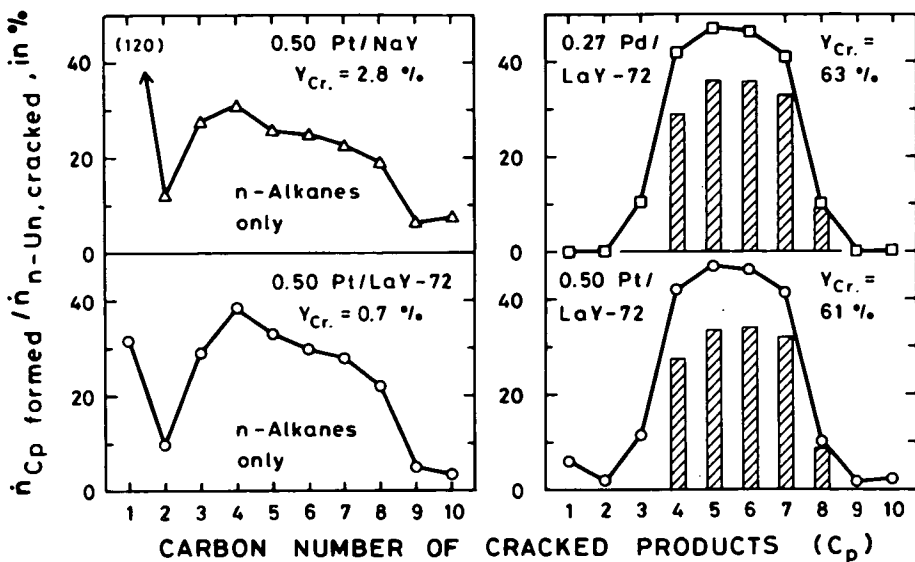


Fig. 3. Selectivities of n-undecane hydrocracking ($T = 240$ to 300 °C, partial pressures see Table 2, $W/F_{n-Un} = 150$ g·h/mol). The full curves comprise all products with a given carbon number, the bars are valid for branched alkanes.

versions (cf. also data for 0.50 Pt/CeY-72 in Fig. 1) are best interpreted in terms of a hydrogenolysis which is superimposed to ionic isomerization. This is concluded from a comparison of the selectivities with those found on 0.50 Pt/NaY. At elevated yields of cracked products the selectivities are much more representative for a bifunctional mechanism, i.e., ionic cleavage is much more accelerated than the superimposed hydrogenolysis.

CONCLUSIONS

Several independent results of this study suggest that, on catalysts encompassing a noble metal and a typical Brönsted acid (e.g., Pt/ or Pd/MeY-72), both isomerization and hydrocracking proceed mainly or exclusively via bifunctional mechanisms. This is at least true for (i) elevated conversions, (ii) elevated hydrogen partial pressures, and (iii) a sufficiently high carbon number of the feed, which are all relevant to industrial catalysis. Contrary statements as made in [10] should be considered with great caution.

Of course, the metallic mechanisms always compete with the bifunctional ones and their contributions to the overall hydrocarbon conversion are simply a matter of relative rates. If desired, the

importance of metallic catalysis can be enhanced by several factors, above all by lowering the acidity of the catalyst. On 0.50 Pt/NaY, n-undecane isomerization and hydrocracking probably occur at the noble metal, at least under the conditions applied in this investigation. But even on Pt/MeY-72 zeolites, some hydrogenolysis may be superimposed to the bifunctional pathways. Expectedly, the extent of hydrogenolysis increases as the Pt content is raised. The metal loading of zeolites should, therefore, be carefully optimized for every catalytic application. It can, furthermore, be concluded from this study that Pd is a better catalyst component than Pt, if pure bifunctional reactions of alkanes are aimed at.

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SYMBOLS AND ABBREVIATIONS

F_i	feed rate		mol h^{-1}		
n	molar flux		mol h^{-1}		
p	carbon number of cracked products				
P_i	partial pressure		Pa		
r_i	rate of disappearance		mol (g.h)^{-1}		
W	mass of dry catalyst		g		
X_i	conversion				
Y_i	yield				
M	methyl	Oc	octane	Iso.	isomerization
E	ethyl	No	nonane	Cr.	hydrocracking
P	propyl	De	decane	Me	cerium or lanthanum
		Un	undecane		

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