React. Kinet. Catal. Lett., Vol. 26, Nos 1—2, 153—157 (1984)

C_4 OLEFIN CONVERSION ON REDUCED NICKEL Y FAUJASITE: EVIDENCE FOR C_5 OLEFIN FORMATION VIA C_4 OLEFIN DISPROPORTIONATION

Th. Bein[1], P. J. Plath and G. Schulz-Ekloff

Applied Catalysis, Department of Chemistry, University of Bremen,
D – 2800 Bremen 33, FRG
[1]Institut für Physikalische Chemie, Universität Hamburg,
Laufgraben 24, D – 2000 Hamburg 13

Received November 15, 1983
Accepted December 20, 1983

The reaction of isobutene as well as butene-2 on reduced NiNaY zeolite was studied by the microcatalytic pulse technique. The induction periods for the product propene and C_5 olefins were found to be always identical in the investigated temperature region (520–720 K), whereas deviating changes of yield with the number of pulses could be observed for all other products. The results favor a proton catalyzed disproportionation mechanism for C_5 olefin formation rather than a paring reaction.

Реакция изобутена, а также бутена-2 на восстановленном цеолите NiNaУ была исследована с помощью микрокаталитической импульсной техники. Индукционные периоды для пропеновых и C_5 олефиновых продуктов оказались всегда идентичными в исследованном интервале температур, в то время как для всех других продуктов наблюдались различные изменения выходов с числом импульсов. Результаты свидетельствуют скорее в пользу механизма диспропорционирования, катализированного протоном, в случае образования C_5 олефинов, чем в пользу механихма „лущильной изомеризации".

The conversion of C_4 olefins on acid catalysts has been investigated repeatedly [1–7]. The reactions are proton catalyzed and rapidly poisoned, but some mechanistic paths are still discussed controversially. So, the C_5 olefins are assumed to be formed via a disproportionation mechanism [2] or a paring reaction [6]. The study of induction periods can be helpful for the elucidation of reaction paths, but requires a low load of the catalyst. This can be achieved either by a continuous feed of the catalyst with very low educt cuncentrations in the carrier gas [6], or by application of the pulse technique. The latter has been used in the following study of C_4 olefin conversion on a reduced nickel faujasite.

EXPERIMENTAL

The faujasite NaY (Si/Al ratio = 3) was synthesized by standard procedures of hydrothermal crystallization [8, 9] and ion-exchanged in solution (0.025 M) of $Ni(CH_3COO)_2$ and $Ca(CH_3COO)_2$. The degree of exchange

$(Ni_{10.8}Ca_{2.6}Na_{21.1}Y)$ was determined by atomic absorption spectroscopy. Samples (20 mg) of the crystalline powders (crystal size ≈ 1 μm) were pressed (0.5 GPa), pelletized (grain size ≈ 0.2 mm), filled in a glass tube (diameter: 6 mm) and used as a fixed bed catalyst. The reduction was carried out with hydrogen (heating at 2 K min^{-1} up to 720 K; 8 h at 720 K). It is well known that nickel faujasites cannot be reduced totally. The transmission electron micrographs exhibited bidispersed nickel. Pulses (0.24 mg) of the educts (i-butene, trans-2-butene or propene; purity 99.5, Messer-Griesheim) were dosed into a dried and oxygen-free carrier gas of argon (2.4 l h^{-1}). The products were analyzed by capillary gas chromatography (squalan SCOT column). The separation of i-butene and 1-butene could not be achieved with the column used.

RESULTS

Product distributions obtained with 0.24 mg pulses of iso-butene, trans-2-butene and propene at 623 K are given in Table 1. The mass balance calculations refer to the total product pulse which was ejected into the gas chromatograph. The sum of the products in the gas phase was found to be

Table 1

Product distributions (wt.%) of the fourth pulse for olefin conversion on reduced NiCaY at 620 K

Product	i-Butene[a]	trans-Butene[a]	Propene[a]
methane	0.097	0.098	0.061
ethane	0.249	0.25	0.89
propene	9.2	8.0	93.5
i-butane	17.6	4.6	0.084
1-butene[b]	15.0	10.1	0.30
i-butene[b]	30.2	20.5	0.62
n-butane	0.1	0.38	–
trans-2-butene	8.0	25.9	0.52
cis-2-butene	5.8	20.1	0.356
3-methyl-1-butene	0.23	0.19	–
1-pentene	0.27	0.23	0.016
2-methyl-1-butene	1.5	1.2	0.092
trans-2-pentene	1.0	0.85	0.092
cis-2-pentene	0.47	0.4	0.039
2-methyl-2-butene	3.9	3.2	0.26
i-pentane	2.6	1.7	0.056
$C_{5}+$	3.9	2.3	1.0

[a] Educts, 0.24 mg per pulse; [b]The i-butene/1-butene ratio was calculated from the thermodynamic equilibrium of butenes

> 80 wt.% of the educt. The distributions of Table 1 are taken from the fourth pulse, which represents maxima, minima or attainment of plateaus with respect to most products. Irrespective of the nature of the educt, the main products are butene isomers, propene, pentenes and the monobranched C_4, C_5 alkanes. A comparable pattern is obtained with propene as educt, though the conversion is considerably lower.

The fractions of representative products with increasing load of the catalyst in i-butene conversion are given in Fig. 1. The highest yield of olefins is reached within the first four pulses, whereas the paraffin portions increase only gradually with the number of pulses above 620 K. The fraction of methane, which is a representative cracking product, strongly decreases during the first four pulses.

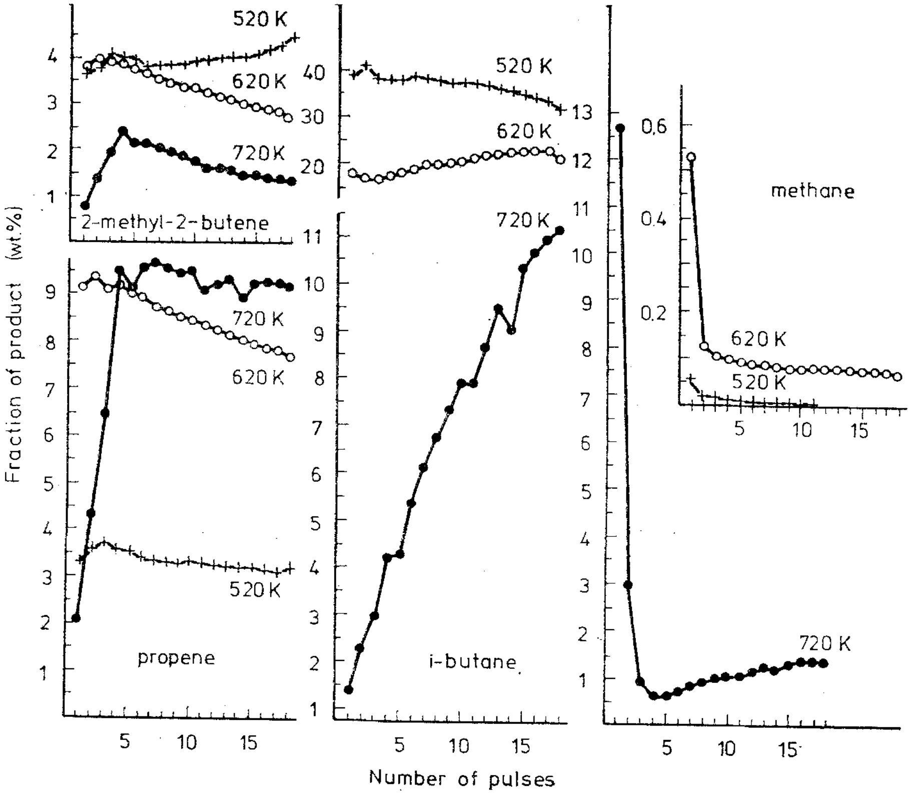

Fig. 1. Fractions of the representative products 2-methyl-2-butene, propene, i-butane and methane formed in i-butene conversion on a reduced nickel faujasite versus number of pulses

DISCUSSION

Reduced nickel faujasites are strongly acidic zeolite catalysts which are able to convert methanol to hydrocarbons [10, 11]. The product distributions (Table 1) are very similar to those obtained on a NaHY zeolite [6] and support the assumption that the conversions of the C_4 olefins are mainly proton catalyzed with negligible contribution by Ni^0 and Ni^{2+}. The following competitive reaction paths should be taken into account for olefin conversion on an acidic zeolite like the reduced nickel faujasite used here: (a) isomerization; (b) oligomerization; (c) disproportionation; (d) paraffin formation via hydride shifts; (e) cracking; (f) coke-formation; (g) paring reactions. All reactions, except (a) and (c), should contribute to deactivation of the faujasite catalyst by clogging of the zeolite pore system due to oligomerization, on the one hand, and due to the inhibition of the catalytically active sites via coke deposition, on the other hand.

A contribution of nickel ions to the isomerization process cannot be excluded, but it does not result in a selectivity for a cis-butene formation, as reported, e.g., for Cr^{3+} ions [12], since the trans-butene/cis-butene ratio is close to the thermodynamic equilibrium value. The capability of reduced nickel for catalyzing dehydrogenation/hydrogenation reactions should not be responsible for the paraffin fractions formed, which are even smaller than those found on transition metal-free faujasites [6]. The changes of the relative amounts of propene and of C_5 olefins are strictly correlated with respect to the temperature as well as to the number of pulses (Fig. 1), whereas distinct induction periods were found for all other products. This effect can be understood on the basis of a disproportionation mechanism [2] for C_5 olefin formation which was questioned because of experimental olefin ratios $C_3/C_5 \neq 1$ [6]. The ratios observed by us range from 0.5 at 520 K to 2.5 at 720 K and are in agreement with the experience that propene has higher polymerization probabilities at low temperatures and higher desorption probabilities at high temperatures as compared to C_5 olefins, which can form relatively stable carbenium ions. Consequently, olefin ratios $C_3/C_5 \neq 1$ do not rule out a disproportionation mechanism for C_4 olefin conversion to C_5 olefins.

The formation of paraffins can be explained by an intermolecular shift of hydride ions [13, 14], resulting in the reaction olefins $\rightarrow$ paraffins + aromatics, which is well known to proceed on zeolites with strong acid sites. Since only small amounts of propane and C_5 paraffins are obtained from the acid catalyzed reaction, the paring mechanism should not be the main reaction route. The results obtained by the micropulse technique show corresponding induction periods for the C_3 and C_5 olefins and predict olefin ratios $C_3/C_5 = 1$ under defined reaction conditions and, therefore, favor a disproportionation mechanism. Cyclic compounds from olefin oligomerization can be assumed as intermediates.

Acknowledgment. The authors are indebted to Prof. H. Lechert for his promotion and for helpful discussions.

REFERENCES

1. P. E. Eberly, Jr.: J. Phys. Chem., *17*, 1717 (1967).
2. A. L. Lapidus, Ya. I. Isakov, R. V. Avetisyan, A. K. Sendel, Kh. M. Minachev, Ya. T. Eidus: Izv. Akad. Nauk SSSR (English transl.), 53 (1970).
3. N. W. Cant, W. K. Hall: J. Catal., *25*, 161 (1972).
4. M. L. Poutsma, ACS Monograph *171*, 437 (1976); Zeolite Chemistry and Catalysis (ed.: J. A. Rabo), Washington 1976.
5. L. Kubelková, J. Novakova, P. Jiru: React. Kinet. Catal. Lett., *4*, 151 (1976).
6. B. E. Langner: J. Catal. *65*, 416 (1980)
7. J. Datka: in "Catalysis by Zeolites" (ed.: B. Imelik et al.), pp. 212–126. Elsevier, Amsterdam 1980.
8. D. W. Breck, E. M. Flanigen: in "Molecular Sieves" p. 47. (Society of Chemical Industry) London 1968.
9. H. Kocirek, H. Lechert: J. Phys. Chem., *79*, 1589 (1975).
10. N. Davidova, D. Shopov, N. Jaeger, G. Schulz-Ekloff: React. Kinet. Catal. Lett., *12*, 229 (1979).
11. N. Jaeger, A. Jahn, G. Schulz-Ekloff: React. Kinet. Catal. Lett., *19*, 79 (1982).
12. A. Barth, G. Geisler, J. Hoffmann, K. Scherzer, Z. phys. Chem. (Leipzig), *260*, 545 (1979).
13. R. F. Sullivan, C. J. Egan, G. E. Langlois, R. P. Sieg: J. Amer. Chem. Soc., *83*, 1156 (1961).
14. F. E. Shepard, J. J. Rooney, J. Kemball: J. Catal., *1*, 379 (1962).