Solid superacid catalysis: kinetics of butane isomerization catalyzed by a sulfated oxide containing iron, manganese, and zirconium

A.S. Zarkalis [a], C.-Y. Hsu [b] and B.C. Gates [a,1]

[a] *Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA*
[b] *Sun Company, PO Box 1135, Marcus Hook, PA 19061, USA*

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Kinetics of the isomerization of *n*-butane and of isobutane catalyzed by sulfated zirconium oxide containing 1.5 wt% Fe, 0.5 wt% Mn, and 4.0 wt% sulfate at 60°C are well represented by a Langmuir–Hinshelwood equation accounting for the reaction equilibrium and for adsorption of both butanes. The adsorption equilibrium constants estimated from the kinetics data are nearly the same for the two butanes. The form of the rate equation and the observation that disproportionation accompanies isomerization suggest that the reaction proceeds via a C_8 intermediate.

Keywords: superacid; butane; *n*-butane; isobutane; isomerization; sulfated zirconia

1. Introduction

Sulfated zirconium oxide containing Fe and Mn, a solid superacid, is one of the most active known catalyst for *n*-butane isomerization and is potentially valuable for industrial applications [1,2]. There are almost no quantitative data characterizing the performance of any solid superacid catalysts [3–5], which undergo rapid deactivation. Here we report kinetics of the isomerization of *n*-butane and of isobutane determining the performance of the undeactivated sulfated zirconium oxide catalyst containing Fe and Mn.

2. Experimental

The catalyst, sulfated zirconium oxide containing 1.5 wt% Fe, 0.5 wt% Mn, and 4.0 wt% sulfate [1], was investigated in a once-through flow reactor with analy-

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[1] To whom correspondence should be addressed, at: Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA.

sis of the products by gas chromatography. Rate equations were determined for both the forward and reverse *n*-butane isomerization reactions. The ranges of conditions were as follows: temperature, 60°C; pressure, 2.02 atm; mass of catalyst, 1.17–7.00 g; feed flow rate, $(0.42-2.50) \times 10^{-5}$ mol of butane/s; inverse space velocity, $(2.80-8.41) \times 10^{5}$ (g of catalyst s)/mol of butane fed; *n*-butane partial pressure, 0.37–1.10 atm; isobutane partial pressure, 0.58–1.10 atm; N_2 partial pressure, 1.02–1.65 atm; run length, 1–17 h.

3. Results

The principal product of the reaction of *n*-butane was isobutane and vice versa. Each of the isomerization reactions was accompanied by disproportionation; the principal disproportionation products formed from *n*-butane and from isobutane were propane and isopentane; *n*-pentane was also observed, but in lower yields than the other disproportionation products. The disproportionation reactions were at least an order of magnitude slower than the isomerization reactions.

Measurements of low (differential) conversions (and hence rates of reaction) as a function of time on stream showed an initial period of increasing conversion (typically, 5–10 min) followed by deactivation, with the catalyst typically losing 50% of its maximum activity within 30 min on stream, followed by slower deactivation. Rates characteristic of the undeactivated catalyst were taken as the maximum rates in each experiment, as these gave a more consistent set of data than the rates extrapolated to zero time on stream by including only the data taken after the maximum rate was attained.

The butane isomerization equilibrium at 60°C was confirmed by approaching the equilibrium composition from both sides. The measured equilibrium constant, $(C_{\mathrm{isobutane}}/C_{n\text{-butane}})_{\mathrm{equil}}$, 3.78, agrees well with the accepted value, 3.88 [6].

Consistent with the concentration dependence of the reaction rates (table 1), the data are well represented by Langmuir–Hinshelwood rate equations of the following forms:

$$r = \frac{kK_{\mathrm{n}}(P_{n\text{-butane}} - K_{\mathrm{i}}P_{\mathrm{isobutane}}/K_{\mathrm{n}}K_{\mathrm{eq}})}{(1 + K_{\mathrm{n}}P_{n\text{-butane}} + K_{\mathrm{i}}P_{\mathrm{isobutane}})}\,, \tag{1}$$

$$r = \frac{kK_{\mathrm{n}}^{2}(P_{n\text{-butane}}^{2} - K_{\mathrm{i}}^{2}P_{\mathrm{isobutane}}^{2})}{(1 + K_{\mathrm{n}}P_{n\text{-butane}} + K_{\mathrm{i}}P_{\mathrm{isobutane}})^{2}}\,. \tag{2}$$

These equations have been used to fit all the rate data measured at 60°C, including data for *n*-butane isomerization and the reverse reaction (table 1). Here, according to the Langmuir–Hinshelwood formalism, P is partial pressure, k is the surface reaction rate constant, in mol of butane produced/(g of catalyst s atm^{-1}); K_{n} is the adsorption equilibrium constant of *n*-butane and K_{i} is that of isobutane, in atm^{-1}; and K_{eq} is the reaction equilibrium constant defined above. K_{eq} was set equal to

Table 1
Comparison of observed and predicted rates of butane isomerization at 60°C

P_n (atm)	P_i (atm)	P_{N_2} (atm)	Observed rate[a] $\times 10^7$	Predicted rate[a,b] $\times 10^7$	Predicted rate[a,c] $\times 10^7$
0.58	0.00	1.44	18.2	16.3	16.1
0.00	0.58	1.44	−2.12	−4.49	−3.19
0.37	0.00	1.65	9.73	13.5	12.5
0.90	0.00	1.12	20.1	18.8	19.2
1.02	0.00	1.10	20.6	19.4	19.9
1.10	0.00	1.02	20.7	19.7	20.4
0.00	0.58	1.44	−2.13	−4.49	−3.19
0.00	0.90	1.12	−2.41	−5.11	−4.12
0.00	1.10	1.02	−2.61	−5.36	−4.52
0.89	0.22	0.91	13.6	14.5	15.0
0.61	0.28	1.13	9.28	10.8	10.9
0.46	0.43	1.13	5.03	6.76	6.55
0.25	0.85	0.92	0.47	0.00	−0.27
0.22	0.88	0.92	−0.12	−0.65	−0.88
0.20	0.90	0.92	−0.36	−1.09	−1.27
0.17	0.93	0.92	−1.50	−1.73	−1.84
0.13	0.97	0.92	−1.73	−2.67	−2.57
0.23	0.87	0.92	0.19	−0.44	−0.68

[a] Units of rate: mol of butane/(g of catalyst s); a positive rate indicates formation of isobutane and a negative rate indicates formation of *n*-butane.
[b] Eq. (1).
[c] Eq. (2).

3.78 on the basis of the results of the equilibrium experiments. Values of the kinetics parameters were determined by regression with a Simplex routine [7].

Eq. (1) corresponds to the Langmuir–Hinshelwood formalism of a reversible first-order surface reaction, with the reaction of the adsorbed species being rate determining. Eq. (2) corresponds to the formalism of a reversible second-order surface reaction, with the reaction between two adsorbed species being rate determining.

The best values of the kinetics parameters determined for eq. (1) are the following:

$$k = (2.58 \pm 0.54) \times 10^{-6} \text{mol of } n\text{-butane converted/(g of catalyst s atm}^{-1}),$$

$$K_n = 3.00 \pm 0.72\,\text{atm}^{-1},$$

$$K_i = 3.36 \pm 0.80\,\text{atm}^{-1}.$$

A positive value of the rate corresponds to the conversion of *n*-butane to isobutane, and a negative value corresponds to the reverse.

The best values of the kinetics parameters determined for eq. (2) are the following:

$$k = (2.77 \pm 0.47) \times 10^{-6} \text{mol of } n\text{-butane converted}/(\text{g of catalyst s atm}^{-1}) ,$$

$$K_n = 5.54 \pm 1.00 \, \text{atm}^{-1} ,$$

$$K_i = 3.40 \pm 0.62 \, \text{atm}^{-1} .$$

The data are well represented by both equations, as shown by the comparison of observed and predicted values in table 1. The sum of the squares of the deviations between the observed and calculated rates is 3.7×10^{-12} [mol of *n*-butane converted/(g of catalyst s)]^2 for eq. (1) and 2.3×10^{-12} [mol of *n*-butane converted/(g of catalyst s)]^2 for eq. (2). Thus eq. (2) fits the data better than eq. (1) and is the recommended equation. A more detailed discussion and a comparison of the data with other, less successful, forms of rate equation are given in a thesis [8]. We stress that the rate equations are empirical and the data are not sufficient to rule out other, similar equations, such as one corresponding to an Eley–Rideal mechanism.

4. Discussion

The values of adsorption equilibrium constants are of the order of magnitude of 1 atm^{-1}, which implies that the paraffins are relatively strongly adsorbed on the catalytic sites. The adsorption equilibrium constants are approximately the same for both *n*-butane and isobutane, which implies that the two isomers have nearly the same strength of adsorption on the catalytic sites. The form of the rate equation giving the best fit suggests a bimolecular rate-determining step, which would be consistent with the formation of a C_8 intermediate, in agreement with the occurrence of disproportionation. Results of tracer experiments for paraffin isomerization catalyzed by H-mordenite at 350°C indicate such a mechanism [9,10].

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References

[1] C.-Y. Hsu, C.R. Heimbuch, C.T. Armes and B.C. Gates, J. Chem. Soc. Chem. Commun. (1992) 1645.
[2] A. Jatia, C. Chang, J.D. MacLeod, T. Okubo and M.E. Davis, Catal. Lett. 25 (1994) 21.
[3] K. Tanabe, H. Hattori and T. Yamaguchi, Crit. Rev. Surf. Chem. 1 (1990) 1.

[4] T. Yamaguchi, Appl. Catal. 61 (1990) 1.
[5] K. Arata, Adv. Catal. 37 (1990) 165.
[6] F.D. Rossini, K.S. Pitzer, R.L. Arnett, R.M. Braun and G.C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie Press, Pittsburgh, 1953).
[7] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical Recipes* (Cambridge Univ. Press, Cambridge, 1986) ch. 10.
[8] A.S. Zarkalis, MChE Thesis, University of Delaware, USA (1993).
[9] M. Guisnet, F. Avendano, C. Bearez and F. Chevalier, J. Chem. Soc. Chem. Commun. (1985) 336.
[10] C. Bearez, F. Avendano and M. Guisnet, Bull. Soc. Chim. France 3 (1985) 346.