JOURNAL OF CATALYSIS **145**, 54–57 (1994)

A Test Method for Quantitative Characterization of Zeolite Hydrogen Transfer Activity

D. B. Lukyanov[1]

Karpov Institute of Physical Chemistry, Ulitsa Obukha 10, Moscow 103064, Russia

Received January 11, 1993; revised April 29, 1993

A simple method for quantitative characterization of hydrogen transfer activity of ZSM-5 and Y zeolites is proposed, based on the determination of the rate of isobutane formation during the *n*-hexane cracking reaction at 400°C. Good agreement is found between quantitative estimations of HZSM-5 hydrogen transfer activity obtained on the basis of this method and on the basis of complex kinetic models. © 1994 Academic Press, Inc.

INTRODUCTION

Hydrogen transfer plays a key role in many reactions catalyzed by zeolites, such as paraffin cracking (Y zeolites), paraffin and olefin aromatization (HZSM-5), and methanol to hydrocarbon conversion (HZSM-5) (1). Because of the importance of these reactions, it is of interest to have a test method which can characterize quantitatively the hydrogen transfer activity of zeolite catalysts. Such a method could be used as a tool for elucidation of the relation between various paramaters in catalyst preparation, on the one hand, and catalyst activity in hydrogen transfer reactions, on the other hand. In principle, quantitative data on zeolite hydrogen transfer activity can be obtained on the basis of complex kinetic models. However, our own experience has shown (2, 3) that the procedure of determination of kinetic parameters is very complex and labour-intensive.

In this paper we propose a test method for the quantitative determination of zeolite activity in hydrogen transfer reactions, and report data on HZSM-5 and HY activity obtained by this method. The idea of the method is based on the results of a recent investigation (4) that has demonstrated that an increase in *n*-hexane conversion is followed by an increase in the rate of *n*-hexane transformation. The autocatalytic effect, particularly pronounced at 400°C, was described quantitatively by the kinetic model (4) developed on the basis of two mechanisms of paraffin cracking (5, 6).

Mechanism A. Protolytic cracking of C–H and C–C bonds in the *n*-hexane molecule via a nonclassical pentacoordinated carbonium ion ($C_6H_{15}^+$):

$$C_6H_{14} + H^+ \rightarrow C_6H_{15}^+ \rightarrow \text{reaction products.}$$

Mechanism B. Hydride transfer from *n*-hexane to smaller carbenium ions ($C_nH_{2n+1}^+$, $n < 6$) followed by beta-scission of the carbenium ion ($C_6H_{13}^+$):

$$C_6H_{14} + C_nH_{2n+1}^+ \rightarrow C_6H_{13}^+ + C_nH_{2n+2}$$
$$C_6H_{13}^+ \rightarrow \text{reaction products.}$$

It is evident that the increase in *n*-hexane cracking rate, which is due to *n*-hexane transformation via mechanism B, should be followed by an increase in the rates of formation of propane, *n*-butane, and isobutane, which are the major paraffinic products of the hydrogen transfer steps of this mechanism (5). It is demonstrated later in the paper that the determination of the rate of formation of isobutane in the *n*-hexane cracking reaction at 400°C (*n*-hexane conversions below 4%) yields quantitative data on the hydrogen transfer activity of HZSM-5 and HY zeolites.

EXPERIMENTAL

Two HZSM-5 zeolites with a SiO_2/Al_2O_3 ratio of 34 and 240, respectively, (samples defined as Z-34 and Z-240, respectively) and two HY zeolites (samples HY-1 and HY-2, SiO_2/Al_2O_3 = 4.4 and 4.8, respectively) were used in this study. Another sample, defined as Z-34ST, was obtained by steaming the ammonium form of ZSM-5 (SiO_2/Al_2O_3 = 34) with pure water vapour at 400°C for 2 h. Details of the catalyst preparation have been reported elsewhere (7). The *n*-hexane cracking reaction was carried out in a quartz microflow reactor at 400°C. The feed consisted of nitrogen and *n*–hexane in a molar ratio 3 : 2.

---

[1] Present address: Catalyse en Chimie Organique (Chimie 7), URA CNRS 350, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France.

0021-9517/94 $5.00

The GC analysis of the reaction products was carried out on line at a catalyst time-on-stream of 7 min. Analyses taken at different catalyst time-on-stream values (1, 3, and 7 min) demonstrated no change in activity and selectivity of the catalysts used in this study. It should also be noted that under the chosen conditions *n*-hexane cracking was the only reaction observed. The alpha-test was performed on all samples at 538°C according to the procedure described by Olson *et al.* (8).

RESULTS AND DISCUSSION

In accordance with the mechanism of *n*-hexane cracking (5), the formation of isobutane follows hydride transfer from *n*-hexane to a *tert*-butyl carbenium ion. This ion is a product of the rapid isomerization of the secondary butyl carbenium ion which, in its turn, is the primary product of *n*-hexane cracking via a hexyl carbonium ion, i.e.,

$$n\text{-}C_6H_{14} + H^+ \rightarrow n\text{-}C_6H_{15}^+ \qquad [1]$$

$$n\text{-}C_6H_{15}^+ \rightarrow C_2H_6 + n\text{-}C_4H_9^+ \qquad [2]$$

$$n-C_4H_9^+ \rightleftharpoons i\text{-}C_4H_9^+ \qquad [3]$$

$$n\text{-}C_4H_8 + H^+ \rightleftharpoons n\text{-}C_4H_9^+ \qquad [4]$$

$$i-C_4H_8 + H^+ \rightleftharpoons i\text{-}C_4H_9^+ \qquad [5]$$

$$n\text{-}C_6H_{14} + i\text{-}C_4H_9^+ \rightarrow i\text{-}C_4H_{10} + n\text{-}C_6H_{13}^+. \qquad [6]$$

The reaction scheme shown above results in the following equation for the rate of isobutane formation:

$$R(iC_4) = k_{HT}[C_6][iC_4^=Z]. \qquad [7]$$

Here k_{HT} is the rate constant of the hydride transfer step between $n-$hexane and a *tert*-butyl carbenium ion, $[C_6]$ is the concentration of *n*-hexane in the reaction mixture, $[iC_4^=Z]$ is the surface concentration of *tert*-butyl carbenium ion. Assuming a rapid equilibrium between carbenium ions and olefins, one can write

$$[iC_4^=Z] = \frac{K_a[iC_4^=]}{1 + K_a[iC_4^=] + \Sigma K_{an}[C_n^=]}, \qquad [8]$$

where K_a and K_{an} are the adsorption constants for isobutene and $C_n^=$ olefin, respectively; $[iC_4^=]$ and $[C_n^=]$ are the concentrations of isobutene and $C_n^=$ olefin in the reaction mixture. At low *n*-hexane conversion the olefin concentration is low, and $(K_a[iC_4^=] + \Sigma K_{an}[C_n^=]) \ll 1$. Therefore, Eq. [7] can be simplified,

$$R(iC_4) = k_{HT}^*[C_6][iC_4^=], \qquad [9]$$

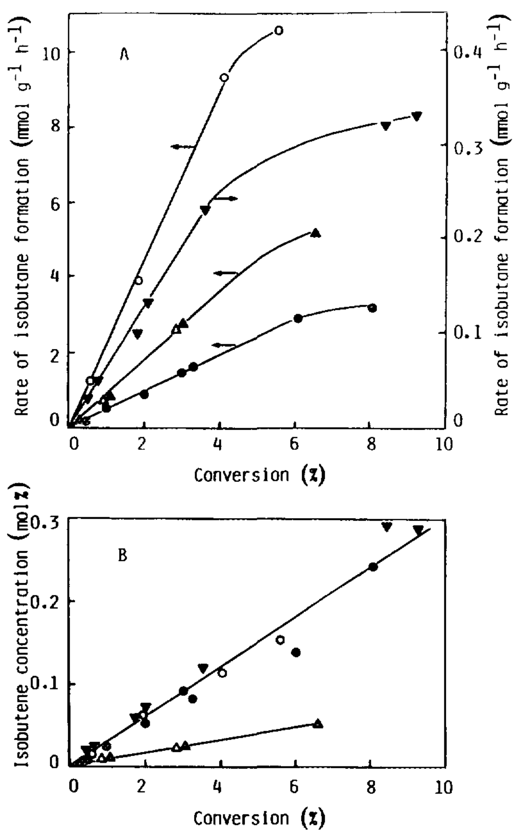

FIG. 1. Effect of *n*-hexane conversion on the rate of isobutane formation (A) and on the isobutene concentration (B). Catalysts: Z-34 (●), Z-34ST (○), Z-240 (▼), HY-1 (△), HY-2 (▲).

where $k_{HT}^* = k_{HT}K_a$. The rate constant k_{HT}^* can be used for quantitative description of the hydrogen transfer activity of zeolite catalysts.

It follows from Eq. [9] that the ratio between the rate of isobutane formation and isobutene concentration should be constant at low hexane conversion (under these conditions the hexane concentration is approximately constant). Experimental data of this work confirm this conclusion. Figure 1 shows that both isobutane formation rate and isobutene concentration are strictly proportional to the conversion of *n*-hexane (at conversions below 4%). Hence, the ratio between them is constant. Figure 1 demonstrates that the isobutene concentration is the same for all three HZSM-5 samples used in this study. This finding allows one to obtain quantitative estimations of the hydrogen transfer activity of these zeolites directly on the basis of the rates of isobutane formation, determined at the same conversion level (at conversions below 4%).

Table 1 compares quantitative estimations of HZSM-5 activity obtained in this work with the estimations obtained previously on the basis of the kinetic models for the olefin aromatization reaction (3) and for the methanol to hydrocarbon reaction (9, 10) (in these two cases estima-

TABLE 1

Quantitative Estimations of Hydrogen Transfer Activity of Different HZSM-5 Zeolites

Method of determination	Relative activity[a]		
	Z-240	Z-34	Z-34ST
Method proposed in this work	0.130	1	4.5
Kinetic model for olefin aromatization reaction (Ref. *(3)*)	0.154	1	6.0
Kinetic model for methanol to hydrocarbon reaction (Refs. *(9, 10)*)	0.147	1	5–6

[a] The relative activity is equal to the ratio between the rate constant for a given zeolite and the rate constant for the reference zeolite Z-34.

tions were obtained for zeolite activity in hydrogen transfer between olefins and naphthenes). The data presented demonstrate that all estimations, obtained by different means and on a different experimental basis, are in good agreement. It should also be noted that the data on the hydrogen transfer activity of Z-34 and Z-34ST zeolites confirm the previously made conclusion (7) concerning the remarkably high hydrogen transfer activity of the new catalytic sites which are generated in HZSM-5 under mild steaming conditions.

Recently it has been shown (4) that the well-known alpha-activity test (8, 11, 12) measures zeolite activity in hexane protolytic cracking steps (mechanism A of hexane cracking). Since the method proposed in this paper measures zeolite activity in the hydrogen transfer steps (mechanism B), the use of the term "beta-test" for designation of this method seems to be reasonable.

Experimental data shown in Fig. 1 demonstrate that the proposed beta-test can be applied not only for HZSM-5 zeolites, but also for HY zeolites which are widely used in preparation of FCC catalysts. In order to compare quantitatively the hydrogen transfer activity of HY and HZSM-5 zeolites, we have used the ratio $R(iC_4)/[iC_4^=]$ that is proportional to k^*_{HT}. Table 2 shows that both samples of large-pore Y zeolite are of the same activity, which is 6.1 times higher than the activity of the medium-pore HZSM-5 zeolite. This result is in agreement with the generally observed reduced ability of HZSM-5 to catalyze hydrogen transfer reactions proceeding via a sterically large bimolecular transition state (13). On the other hand, Table 2 demonstrates that the protolytic cracking activity (alpha-activity) is higher for HZSM-5 than for HY zeolites. In consequence of this, mechanism A of *n*-hexane cracking should predominate on HZSM-5, whereas with HY zeolites mechanism B should be more important. This conclusion coincides completely with the conclusion made previously (5, 14) on the basis of the product selectivity data on the *n*-hexane cracking reaction. It should also be noted that the contribution of mechanism B in *n*-hexane cracking over parent and mildly steamed HZSM-5 is practically the same, since mild steaming increases the activity of HZSM-5 both in the steps of hydrogen transfer (4.5 times) and in the *n*-hexane protolytic cracking steps (4.1 times).

Recently Wielers *et al.* (14) have proposed to use the "cracking mechanism ratio" (CMR) as a qualitative characteristic for the relative contributions of the two mechanism A and B to the *n*-hexane cracking reaction. The CMR has been defined as the ratio $\{(C_1 + C_2 + C_2^=)/\text{i-}C_4\}$, where C_1, C_2, $C_2^=$, and $\text{i-}C_4$ denote the molar selectivities of methane, ethane, ethene, and isobutane, respectively. In view of the results obtained in the present work it was of interest to compare the CMR values for HZSM-5 and HY zeolites. Such a comparison has shown that under the reaction conditions used in this study the CMR is equal to 6.5 and 0.53 for Z-34 and HY-2 zeolites, respectively (at an *n*-hexane conversion of 3%). From these data one can conclude that the decrease of the k_{alpha}/k^*_{HT} ratio by a factor of 14.5 (see Table 2) leads to a decrease of the "cracking mechanism ratio" by a factor of 12.

CONCLUSIONS

A test method for quantitative characterization of zeolite hydrogen transfer activity is proposed, based on the determination of the isobutane formation rate and isobutene concentration during the *n*-hexane cracking reaction at 400°C. Good agreement was found between quantitative estimations of HZSM-5 hydrogen transfer activity obtained on the basis of this method and on the basis of complex kinetic models. Hydrogen transfer activities of HZSM-5 and HY zeolites were compared: HY zeolite was found to be 6.1 times more active than HZSM-5.

TABLE 2

Hydrogen Transfer Activity and Alpha-Activity of HZSM-5 and HY Zeolites

Type of activity	Relative activity[a]		
	Z-34	HY-1	HY-2
Hydrogen transfer activity	1	6.1	6.1
Alpha-activity	1	0.36	0.42

[a] The relative activity is equal to the ratio between the rate constant for a given zeolite and the rate constant for the reference zeolite Z-34.

ACKNOWLEDGMENTS

The author thanks N. N. Rostanin, VNII NP (Moscow), and V. G. Stepanov, Institute of Catalysis (Novosibirsk), for providing the samples of HY zeolite.

REFERENCES

1. Chen, N. Y., and Haag, W. O., *in* "Hydrogen Effects in Catalysis. Fundamentals and Practical Applications" (Z. Paál and P. G. Menon, Eds.), p. 695. Dekker, New York, 1988.
2. Luk'yanov, D. B. *Kinet. Catal.* **30,** 216 (1989).
3. Luk'yanov, D. B., and Shtral, V. I., *in* "Preprints of ACS Symposium on Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts," Vol. 36, No. 4, p. 693. ACS Division of Petroleum Chemistry, New York, 1991.
4. Luk'yanov, D. B., Shtral, V. I., and Khadzhiev, S. N., *in* "Extended Abstracts and Program of the 9th Intern. Zeolite Conference" (J. B. Higgins, R. von Ballmoos, and M. M. J. Treacy, Eds.), RP36. Butterworth–Heinemann, Stoneham, 1992.
5. Haag, W. O., and Dessau, R. M., *in* "Proceedings of the 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 305. Dechema, Frankfurt am Main, 1984.
6. Corma, A., Planelles, J., Sanchez-Marin, J., and Tomas, F. *J. Catal.* **93,** 30 (1985).
7. Luk'yanov, D. B., *Zeolites* **11,** 325 (1991).
8. Olson, D. H., Haag, W. O., and Lago, R. M., *J. Catal.* **61,** 390 (1980).
9. Luk'yanov, D. B., *Appl. Catal.* **68,** L9 (1991).
10. Luk'yanov, D. B., *Zeolites* **12,** 287 (1992).
11. Weisz, P. B., and Miale, J. N., *J. Catal.* **4,** 527 (1965).
12. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966).
13. Haag, W. O., Lago, R. M., and Weisz, P. B., *Faraday Discuss. Chem. Soc.*, **72,** 317 (1982).
14. Wielers, A. F. H., Vaarkamp, M., and Post, M. F. M., *J. Catal.* **127,** 51 (1991).