ELSEVIER

Catalysis Today 49 (1999) 193–199

CATALYSIS TODAY

Isobutane/butene alkylation on solid catalysts. Where do we stand?

J. Weitkamp*, Y. Traa

Institute of Chemical Technology I, University of Stuttgart, D-70550 Stuttgart, Germany

Abstract

Liquid-phase processes with concentrated sulfuric acid or hydrogen fluoride as catalysts are currently being used in petroleum refining for the manufacture of alkylation gasoline from isobutane and butenes. While the product, i.e., alkylate, is a most valuable gasoline component, the existing processes for its manufacture are less satisfactory. Replacement of the liquid catalysts by a solid acid is an important target of modern research. In the past two decades, a large number of solid acids have been scrutinized, and at least four developments were driven till the pilot plant stage. In this paper, an attempt is made to rationalize, on a mechanistic basis, the selectivity loss almost always encountered with solid acids after relatively short times-on-stream. Suggestions are made concerning a more target-oriented research on isobutane/alkene alkylation in the future.

Keywords: Isobutane/butene alkylation; Reformulated gasoline; Solid acids; Petroleum refining

1. The role of alkylation in modern petroleum refining

Alkylation is a refinery process in which the C_4 by-products of a catalytic cracking unit are converted into high-quality gasoline. More specifically, isobutane reacts with the mixture of the isomeric butenes. In many instances, an etherification plant is placed upstream of the alkylation unit. In this case, isobutene is transformed selectively with methanol into methyl-tertiary-butyl ether (MTBE). The remaining C_4 stream consists of *n*-butane, isobutane and the three isomeric *n*-butenes. A large excess of isobutane over the butenes ($\dot{n}_{\text{isobutane}} : \dot{n}_{\text{butenes}} \approx 10$) is sent into the alkylation unit. *n*-Butane is entirely unreactive under alkylation conditions, whereas the butenes are, as a rule, quantitatively converted. The product is alkylation gasoline or, synonymously, alkylate, and the excess isobutane is recycled to the reactor entrance.

Alkylation cannot be described adequately by a simple stoichiometry. Rather, alkylate is a complex mixture of isoalkanes. The major constituents of alkylation gasoline are the tribranched isooctanes, i.e., 2,2,3-, 2,2,4-, 2,3,3- and 2,3,4-trimethylpentane. These are the most desired products, due to their high octane numbers in the vicinity of 100. Besides, alkylate is inevitably composed of other isoalkanes, especially of dibranched isooctanes (dimethylhexanes and 3-ethyl-2-methylpentane). Even small amounts of monobranched isooctanes (methylheptanes and 3-ethylhexane) occur. Most interestingly, isoalkanes with carbon numbers which are not multiples of 4 are formed as well. Of these, isopentane, the isohexanes and the isoheptanes are usually referred to as the "light ends", whereas the isononanes, isodecanes,

---

*Corresponding author. Tel.: +49-711-685-4060; fax: +49-711-685-4065; e-mail: jens.weitkamp@po.uni-stuttgart.de

0920-5861/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(98)00424-6

etc., are grouped together as the "heavy ends". Generally speaking, all possible isoalkanes with 5 to ca. 10 carbon atoms are formed which possess at least one tertiary carbon atom. Detailed distributions of the products in alkylation gasoline from commercial units have been published elsewhere [1].

Commercial alkylate shows excellent combustion properties in Otto engines. Its research octane number is around 95, and its motor octane number only slightly lower, viz., around 93. It has the highest hydrogen content ($n_H/n_C \approx 2$, ideally $n_H/n_C = 2.25$ for C_8H_{18}) of all gasoline blending streams, a low Reid vapor pressure and it is free from both aromatics and alkenes. With all these properties, alkylate is the prime blending stock for reformulated gasoline.

In the commercial practice, two liquid acids are employed as catalysts for isobutane/butene alkylation, viz., concentrated sulfuric acid and hydrofluoric acid. By 1 January 1998, the worldwide production capacity for alkylation gasoline amounted to 29.3×10^6 t/a and 38.5×10^6 t/a for the H_2SO_4- and HF-catalyzed processes, respectively, which gives a total of 67.8×10^6 t/a [2]. In addition, new alkylation units with a total alkylate capacity of 1.6×10^6 t/a were under construction [3]. These figures clearly reflect the desirability of alkylate as a blending stock for modern motor gasoline. Fig. 1 shows that, by regions, North America is the domain of isobutane/butene alkylation, but the process exists in refineries all over the world. There are two industrially important H_2SO_4 processes, viz., the so-called effluent refrigeration and cascade autorefrigeration processes (the reaction temperature in the H_2SO_4 processes is sub-ambient), and the two commercially relevant HF processes are licensed by UOP and Phillips Petroleum. For a more detailed description of these liquid-phase processes, the reader is referred to [4].

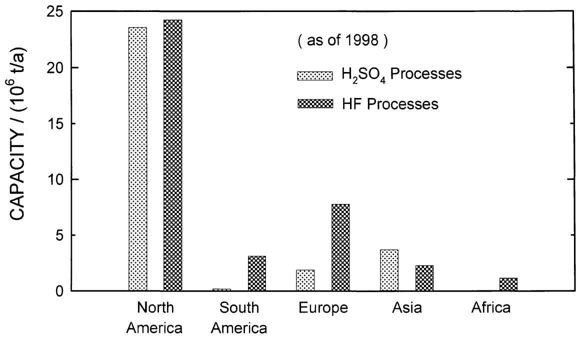

Fig. 1. Geographical distribution of the existing liquid-phase processes for the manufacture of alkylation gasoline, as of 1 January 1998 (North America includes Mexico, and Asia includes Indonesia and Australia). The data were taken from [3].

While the existing liquid-phase technology produces a high-quality, environmentally benign gasoline component, it suffers from a number of disadvantages and shortcomings. More specifically, the catalyst consumption in the H_2SO_4 processes is usually high and $\dot{m}_{\text{catalyst, consumed}}/\dot{m}_{\text{alkylate, produced}}$ may reach 70–100 kg/t. The spent sulfuric acid contains tarry hydrocarbons and water and has to be worked up externally which adds to the cost of the alkylate produced. Moreover, the quality of alkylate from H_2SO_4 processes is usually somewhat lower than the one of HF alkylate. The problem with the HF processes is different: there has recently been much concern about the toxicity of HF, in particular in view of its corrosiveness and volatility. In many industrialized countries, new HF alkylation processes are therefore no longer given approval by the authorities.

It is obvious that, in such a climate, there is a high incentive for the development of a completely new alkylation technology which makes use of a non-toxic, non-corrosive, environmentally friendly and easily regenerable solid catalyst. Since a large number of solid acids are known in heterogeneous catalysis, it was a logical and straightforward step that the potential of these materials in isobutane/butene alkylation was scrutinized worldwide.

2. The search for solid alkylation catalysts

In the late 1960s, Mobil researchers reported on isobutane alkylation with ethylene and propylene on rare-earth(RE)-exchanged zeolite X [5]. Starting approximately at the same time, Kirsch, Potts and Barmby from Sun Oil began to publish their in-depth studies on isobutane/butene alkylation using mainly REHY zeolite as catalyst [6–8]. As early as 1974, Yang from Union Carbide discovered that spent zeolitic alkylation catalysts can be regenerated under relatively mild conditions in a hydrogen atmosphere, if small amounts of a noble metal, e.g., 0.01–0.1 wt% platinum are incorporated into the zeolite [9,10]. Nonzeolitic solids such as HF-SbF_5 on fluorided alumina

[11] or BF_3-modified Amberlyst-15 [12] were found to catalyze isobutane/butene alkylation as well. A detailed account on the search for solid alkylation catalysts has been published recently [1].

3. Salient features of isobutane alkylation on solid acids

In the late 1970s, Weitkamp developed special laboratory techniques tailored for a time-resolved investigation of isobutane/alkene alkylation on solid catalysts. The main features of these techniques were product sampling in short intervals (“instantaneous” or “differential” sampling) combined with high-resolution analysis of the complex product mixtures by capillary gas chromatography. Typical results obtained on an acid form of zeolite Y are depicted in Fig. 2.

As shown in the left-hand part of Fig. 2, the alkene is completely converted at the beginning of the experiment, i.e., as long as the catalyst is fresh. After a certain time-on-stream (in the example chosen in Fig. 2 after ca. 30 min), the butene conversion begins to drop and finally stabilizes at a low level (in the example chosen at ca. 30%). It should be noted that the butene conversion into hydrocarbons with five or more carbon atoms was considered only in Fig. 2, i.e., the double-bond isomerization of 1-butene into *cis*- and *trans*-2-butene is not included.

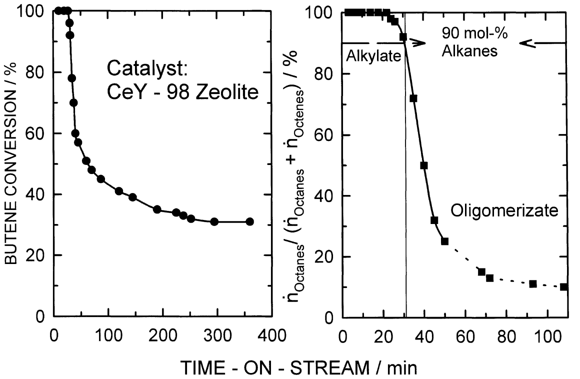

Fig. 2. Conversion of a liquid isobutane/1-butene mixture on a CeY-98 zeolite in a fixed-bed reactor (T=80°C, p=31 bar, liquid feed rate=7.5 cm^3/h, mass of catalyst=1.4 g, $\dot{n}_{isobutane}/\dot{n}_{1-butene} = 11:1$), after [13–15].

Probably much more serious than the loss of catalyst activity shown in the left-hand part of Fig. 2 is the loss of selectivity, as depicted for the same experiment in the right-hand part of the same figure: it can be easily seen that, initially, the C_8 product fraction consists of alkanes exclusively. This is the region where an alkylate is formed on the zeolite. Approximately at the time, when the butene conversion begins to drop, the product quality deteriorates dramatically, and as shown for the C_8 product fraction in Fig. 2, more and more alkenes are formed. Late in the experiment, no alkylation takes place any more, instead the zeolite catalyzes nothing else than the oligomerization of the butene.

Qualitatively, the unsatisfactory time-on-stream behavior shown in Fig. 2 is typical for all solid acids scrutinized as catalysts for isobutane alkylation, and this has so far prevented solid catalysts from being employed in commercial isobutane/butene alkylation processes. There has, however, been some progress in analyzing the reasons for the poor time-on-stream behavior of solid alkylation catalysts. A limited number of process developments have even been driven till the pilot plant stage.

4. Process developments at the pilot plant stage

Listed in Table 1 are the process developments which rely on solid catalysts for the manufacture of alkylation gasoline. The most detailed information has been released in the literature on the Haldor Topsøe process which makes use of trifluoromethanesulfonic acid (triflic acid, F_3CSO_3H) on a porous support in a fixed-bed reactor. One feature of this process is that the liquid acid or a reaction intermediate (perhaps an ester of triflic acid) is soluble to some extent in the hydrocarbon phase and migrates slowly along the fixed-bed. To some extent, the acid deactivates while acting as an alkylation catalyst, on account of oils dissolving in the acid. The deactivated acid leaving the alkylation reactor is sent to a second reactor where the spent acid is regenerated or recovered according to proprietary technique.

It is interesting to notice that a slurry reactor is employed in at least one of the process developments listed in Table 1. A slurry reactor probably helps to slow down the deactivation and “deselectivation” of

Table 1
Isobutane/alkene alkylation on solid catalysts. Current process developments at the pilot plant stage

No.	Developer/licenser	Catalyst	Reactor type	Alkylate capacity (kg/d)	References
1	Haldor Topsøe A/S	Trifluoromethanesulfonic acid on a porous support	Fixed bed, acid moves along bed, proprietary process for acid regeneration	55	[16,17]
2	Catalytica, Neste Oy, Conoco	Proprietary	Unknown, with recycle and catalyst regeneration	780	[18,19]
3	Chemical Research & Licensing, Chevron	Antimonypentafluoride on acid-washed silica	Slurry reactor	1110	[18,19]
4	UOP	Proprietary, resembles traditional hydrocarbon conversion catalysts	Unknown, with continuous catalyst regeneration using hydrogen	Unknown	[18,19]

the solid catalyst, due to the low olefin concentration everywhere in this reactor.

It is very difficult and probably too early to forecast if (and when) the process developments in Table 1 will be implemented on a commercial scale.

5. Reasons for the deactivation and selectivity loss of solid alkylation catalysts

The simplest mechanism one can invoke for the acid-catalyzed (e.g., zeolite-catalyzed) alkylation of isobutane with 2-butene is depicted in Fig. 3. The double bond of the alkene adds to the positively charged carbon atom of the tertiary-butyl cation chemisorbed on an acid site (this olefin addition, i.e., step II in Fig. 3, is sometimes referred to as the alkylation step in the narrower sense). It can easily be seen that a highly branched, secondary octyl cation with the skeleton of 2,2,3-trimethylpentane emerges from this olefin addition. Next, an *intra*molecular hydride transfer (step III) can be envisaged which gives the tertiary cation with the same carbon skeleton. Such tertiary carbenium ions can undergo acid-catalyzed *inter*molecular hydride transfer (step V in Fig. 3), e.g., from an isobutane molecule, which liberates the product molecule 2,2,3-trimethylpentane, and at the same time, closes the catalytic cycle.

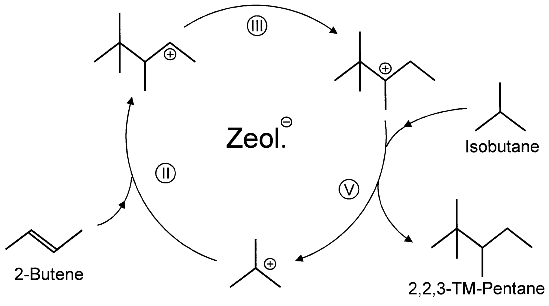

Fig. 3. Simplest catalytic cycle for the alkylation of isobutane with 2-butene.

It is beyond the scope of this account to discuss, in full depth, the validity of this mechanism for isobutane/2-butene alkylation on solid acids. It is obvious, however, that it suffers from at least two severe shortcomings: (i) it fails to explain the formation of the other trimethylpentanes, i.e., 2,2,4-, 2,3,3- and 2,3,4-trimethylpentane, of the dibranched and monobranched isooctanes, and of the isoalkanes with less and more than eight carbon atoms (light and heavy ends). To account for the formation of the other trimethylpentanes, acid-catalyzed rearrangements of the carbon skeleton at the level of the chemisorbed isooctyl cations are usually invoked (even if this is accepted, it remains open why so little 2,2,3-trimethylpentane is formed in isobutane/2-butene alkylation). There is no way, however, to interpret the

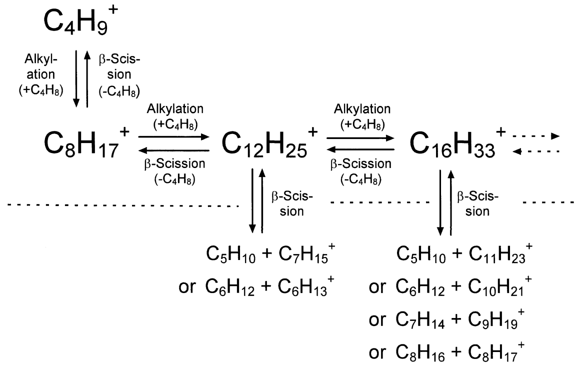

Fig. 4. Simplest pathway for the formation of the light and heavy ends in the alkylation of isobutane with butenes.

ubiquitous formation of light and heavy ends on the basis of the simple mechanism shown in Fig. 3.

As shown in Fig. 4, the occurrence of light and heavy ends can only be rationalized, if one envisages the intermediate formation of heavier carbenium ions. The addition of another butene molecule to the $C_8H_{17}^+$ cation results in a dodecyl cation and another butene addition gives a hexadecyl cation (the ongoing butene addition gives even higher carbenium ions). The only reasonable way to explain the occurrence of i-C_5H_{12} to i-C_7H_{16} and i-C_9H_{20} to ca. i-$C_{10}H_{22}$ products is to claim the formation of some $C_{12}H_{25}^+$ and $C_{16}H_{33}^+$ followed by acid-catalyzed skeletal rearrangements and β-scissions. Much detailed information on these carbocation reactions has recently been gained in model studies on isomerization and hydrocracking of long-chain alkanes over certain bifunctional catalysts, such as Pt/CaY zeolite [20,21]. One important conclusion from these studies is that, at the very mild reaction conditions employed in isobutane/alkene alkylation, only the most facile β-scissions can occur which are referred to in the pertinent literature as type-A β-scissions [22].

A crucial step in the mechanism of isobutane/alkene alkylation is the intermolecular hydride transfer (step V in Fig. 3). If the catalyst is, for whatever reason, unable to promote this step efficiently, and/or if the local alkene concentration is too high, addition of the alkene is favored over intermolecular hydride transfer, and high-molecular weight carbenium ions are steadily building up.

While it is generally accepted that the selectivity loss of solid alkylation catalysts (cf. Fig. 2) has to do with a decreasing ability to promote the intermolecular hydride transfer, it is mostly unknown *why* exactly almost all solid acids loose their hydride transfer activity so soon while on stream. Systematic and innovative research into the precise mechanism of intermolecular hydride transfer on solid acids is mandatory for the rational search for improved solid catalysts for isobutane/butene alkylation.

6. Kinetic measurements

A catalytic system with a time-on-stream behavior as shown in Fig. 2 is inappropriate for kinetic measurements. Recently, however, Simpson et al. [23,24] were able to demonstrate that finite (<100%) and reproducible butene conversions can be achieved at extremely high dilution of the butene, i.e., at extremely high $n_{\mathrm{isobutene}}/n_{\mathrm{2\text{-}butene}}$ ratios in the order of 500–3500. Of course, such reaction conditions are far away from those which are industrially attractive.

Using an ultrastable Y-type zeolite at 100°C under the above-mentioned conditions, Simpson et al. encountered a reasonably slow catalyst deactivation, hence an accurate enough extrapolation of the reaction rate to zero time-on-stream became feasible. Experiments with catalyst particles of different size (90–230 μm) suggested that the liquid-phase alkylation of isobutane even in the large-pore zeolite Y is severely diffusion-limited. Moreover, modelling of the kinetics suggested that, on the same catalyst, intermolecular hydride transfer is slow relative to the addition of an alkene to the carbenium ions. A rapid build-up of higher carbenium ions ($C_{12}H_{25}^+, C_{16}H_{33}^+$, etc.) is, hence, unavoidable.

All this corroborates that for a true step forward in the search for solid alkylation catalysts, novel solutions for the hydride transfer problem have to be found, and innovative approaches into this direction should be encouraged.

7. The Shell concept

Innovative solutions of the hydride transfer problem should be embedded into a general strategy for isobutane/butene alkylation. In this respect, the work published recently by de Jong et al. [25] deserves particular attention and consideration. Key features of Shell's published research strategy include [25,26]:

1. Halogen-containing solid acids may offer advantages from the viewpoint of their acidic properties, especially with respect to acid strength; it is, however, doubtful whether this class of acids represents the ultimate choice, due to the inherent disadvantages associated with an industrial use of such materials, such as their corrosiveness, toxicity, problems during regeneration and disposal problems.
2. Instead, a "true solid acid", such as a zeolite or a zeolite-like microporous or mesoporous material seems to be advantageous.
3. The existing data suggest that zeolite Beta seems to be a reasonable candidate since, according to the knowledge available, a high density of Brønsted acid sites seems to be favorable both for the quality of the alkylate produced and for the catalyst lifetime, every attempt should be undertaken to extend the n_{Si}/n_{Al} ratio of zeolite Beta to lower values. Novel approaches for the synthesis of such materials should be pursued.
4. High local concentrations of alkenes and alkylate in the reactor should be avoided. To fulfill this very important requirement, each set-up for studying isobutane/alkene alkylation on solid catalysts should be equipped with a reactor with an efficient back-mixing characteristic, a good choice being a slurry reactor. Conversely, plug-flow fixed-bed reactors should be avoided.
5. A feasible and economically reasonable method for catalyst regeneration probably remains mandatory. The coke formed in isobutane alkylation mostly consists of high molecular weight isoalkanes which are relatively easy to remove by hydrocracking under relatively mild conditions. Such regeneration procedures are superior, from the point of view of the overall economics, to oxidative burning of the coke.

8. Conclusions

Since ca. 1980, a huge number of solid acids have been scrutinized for their potential as catalysts in isobutane/butene alkylation [1]. It is probably time to abandon this trial-and-error approach. There is, however, much room for innovative and knowledgeable work with the aim to proceed in the identification of the precise reasons for the much too rapid selectivity loss of solid catalysts. Some ways to tackle the problem have been outlined in the preceding paragraphs.

In particular, the following items should be addressed and considered:

- Investigate in full detail the crucial step, i.e., intermolecular hydride transfer. Consider a cooperative project encompassing the leading groups worldwide.
- Encourage researchers to look for truly innovative solutions for the hydride transfer problem.
- Develop and tailor new materials on a rational basis. For example, starting from existing zeolites, e.g., zeolite Beta, develop materials with the same high surface area, the same high (or even higher) density of Brønsted acid sites and the same high (or even higher) strength of Brønsted acid sites. Somewhat larger pores could also be helpful to overcome diffusional limitations in the pores.
- Test such new materials in an appropriate catalytic equipment (liquid phase, slurry reactor, appropriate procedures for product sampling, adequate analysis of the complex product mixtures, and reliable material balances).
- Investigate in detail the available, and perhaps, novel techniques for removing carbonaceous deposits.

Acknowledgements

Financial support by the German Science Foundation (Deutsche Forschungsgemeinschaft), Fonds der Chemischen Industrie and Max-Buchner-Forschungsstiftung is gratefully acknowledged.

References

[1] J. Weitkamp, Y. Traa, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, VCH Verlagsgesellschaft mbH, Weinheim, 1997, p. 2039.
[2] M. Radler, Oil Gas J. 95(51) (1997) 41.
[3] M. Radler, Oil Gas J. 95(41) (1997) 57.

[4] A. Corma, A. Martínez, Catal. Rev.-Sci. Eng. 35 (1993) 483.
[5] W.E. Garwood, P.B. Venuto, J. Catal. 11 (1968) 175.
[6] F.W. Kirsch, J.D. Potts, D.S. Barmby, Preprints, Div. Petr. Chem., Am. Chem. Soc. 13(1) (1968) 153.
[7] F.W. Kirsch, J.D. Potts, D.S. Barmby, Oil Gas J. 66(29) (1968) 120.
[8] F.W. Kirsch, J.D. Potts, D.S. Barmby, J. Catal. 27 (1972) 142.
[9] C.-L. Yang, US Patent 3 893 942, assigned to Union Carbide Corp., 8 July 1975.
[10] C.-L. Yang, German Patent 2 445 881, assigned to Union Carbide Corp., 26 May 1976.
[11] J.D. Kemp, US Patent 3 852 371, assigned to Chevron Research Co., 3 December 1974.
[12] T.J. Huang, S. Yurchak, US Patent 3 855 342, assigned to Mobil Oil Corp., 17 December 1974.
[13] J. Weitkamp, Compendium 80/81, Erdöl, Kohle Erdgas Petrochem., Supplementary Volume, Industrieverlag von Hernhaussen, Leinfelden-Echterdingen, 1980, p. 71.
[14] J. Weitkamp, in: L.V.C. Rees (Ed.), Proceedings of the Fifth International Zeolite Conference, Heyden, London, 1980, p. 858.
[15] J. Weitkamp, S. Ernst, in: Proceedings of the 13th World Petroleum Congress, vol. 3, Wiley, New York, 1992, p. 315.
[16] B. Sarup, S.I. Hommeltoft, M. Sylvest-Johansen, P. Søgaard-Andersen, in: J. Weitkamp, B. Lücke (Eds.), Proceedings of the DGMK Conference on Catalysis on Solid Acids and Bases, Berlin, 14–15 March 1996, ISBN 3-931850-00-5, DGMK German Society for Petroleum and Coal Science and Technology, Hamburg, 1996, p. 175.
[17] Anonymous, Oil Gas J. 94 (14) (1996) 69.
[18] A.K. Rhodes, Oil Gas J. 92(34) (1994) 49.
[19] P. Rao, S.R. Vatcha, Oil Gas J. 94(37) (1996) 56.
[20] J. Weitkamp, S. Ernst, in: J.W. Ward (Ed.), Catalysis 1987, Studies in Surface Science and Catalysis, vol. 38, Elsevier, Amsterdam, 1988, p. 367.
[21] J. Weitkamp, S. Ernst, in: D. Barthomeuf, E.G. Derouane, W. Hölderich (Eds.), Guidelines for Mastering the Properties of Molecular Sieves, NATO Advanced Science Institutes Series B, vol. 221, Plenum Press, New York, 1990, p. 343.
[22] J. Weitkamp, P.A. Jacobs, J.A. Martens, Appl. Catal. 8 (1983) 123.
[23] M. Simpson, J. Wei, S. Sundaresan, in: P.T. Anastas, T.C. Williamson (Eds.), Green Chemistry – Designing Chemistry for the Environment, American Chemical Society Symposium Series, vol. 626, American Chemical Society, Washington, DC, 1996, p. 105.
[24] M. Simpson, J. Wei, S. Sundaresan, Ind. Eng. Chem. Res. 35 (1996) 3861.
[25] K.P. de Jong, C.M.A.M. Mesters, D.G.R. Peferoen, P.T.M. van Brugge, C. de Groot, Chem. Eng. Sci. 51 (1996) 2053.
[26] C.M.A.M. Mesters, D.G.R. Peferoen, J.P. Gilson, C. de Groot, P.T.M. van Brugge, K.P. de Jong, in: J. Weitkamp, B. Lücke (Eds.), Proceedings of the DGMK Conference on Catalysis on Solid Acids and Bases, Berlin, 14–15 March 1996, ISBN 3-931850-00-5, DGMK German Society for Petroleum and Coal Science and Technology, Hamburg, 1996, p. 57.