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Catalytic activity of a mechanically mixed Ga_2O_e/H-MFI catalyst under distance preservative conditions

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Abstract

The distance between active centers is the key factor in studying the activity of a gallium promoted zeolite catalyst. Special conditions, preserving the long distance between gallium and zeolite acid center (i.e. distance preservative conditions), were found in mechanically mixed catalysts. Catalyst samples were tested with the *n*-butane aromatization reaction under these conditions. The observed catalytic cooperation between active centers was ascribed to a bifunctional catalyst and/or a remote control mechanism.

Keywords: Mechanically mixed Ga_2O_e/H-MFI; Ga_2O_e/H-MFI; Distance preservative conditions

1. Introduction

Aromatization of light paraffins, using gallium promoted HZSM-5 zeolite catalyst, which has been implemented in the Cyclar process, was recently developed by BP and UOP [1]. Extensive industrial research has been done to scale up this process to the commercial 1000 bpd plant at the BP oil refinery in Grangemouth (UK) [2,3]. This large financial and technological effort has now started to show great benefits in the planning of a 46000 bpd unit for SABIC, Yarbu (AE) [4].

Much scientific research on gallium modified zeolite catalysts has followed since the introduction of the Cyclar process as evidenced by the number of recent reviews published on this topic [5–8].

In spite of this extensive investigation the specific role of the catalyst components and their cooperation in the catalytic activity is still not completely understood (in the following we use expressions catalytic cooperation and synergistic effect as analogous, overlooking the actual differences between cooperation and synergy).

The main aim of the present work is to propose a heuristic criterion for synthetic and clear analysis of a large set of published experimental data. Moreover we focus our research work on defining special conditions allowing us to study the catalytic activity of some gallium oxide zeolite mechanically mixed catalysts, preserving the long distance between the active centers of these catalytic systems.

1.1. Distance between the active centers

It has been found that the promoting effect of gallium is quite independent of the technique

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used in the catalyst preparation. Thus, catalyst prepared by various methods, such as impregnation [9] or ion exchange [10] and more recently by CVD of $GaCl_3$ [11,12], performs as well as a steamed gallosilicate [13,14] or a mechanical mixture of gallium oxide and zeolite, usually of MFI structure [15–17].

Trying to schematize the concepts involved with these experimental results, it is suggested to consider, firstly, that the various catalyst preparation methods produce a difference in the distance between gallium and zeolite acid center, d[Ga–HZ], as shown in Fig. 1. Taking into account these observations, we could remark that the synergistic effect between gallium and the zeolite acid center seems to overcome any distance between the active sites.

Because of this singular feature the catalytic cooperation between gallium oxide and the zeolite could be explained in terms of one of the following: (i) a bifunctional catalyst, (ii) a remote control mechanism. Both these mechanisms suggest that gallium enhances the paraffin dehydrogenation reaction. In the first case, gallium directly provides an additional dehydrogenation function [18–23], whereas in the second case, gallium provides a recombinative desorption function for hydrogen adatoms, formed as a result of C–H bond cleavage on the zeolite acid centers [15,16,24–27]. Therefore, the difference between the two viewpoints arises from the site at which paraffin activation occurs: in the first case on both the gallium and the zeolite acid center or as in the second case just the acid center [12].

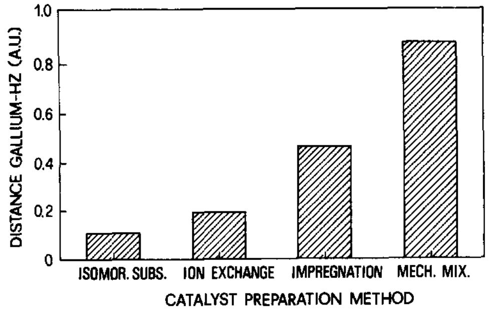

Fig. 1. Distance between active centers in gallium promoted zeolite catalysts prepared by different methods.

In the following we refer to these mechanisms as LDMs (the acronym stands for long distance mechanisms).

1.2. Interaction between the active centers

In some recent work it has been shown that Ga_2O_3/H-MFI mechanically mixed catalyst (long d[Ga–HZ]) [28–30] and also gallium impregnated or ion exchanged MFI zeolite [31], when treated with hydrogen (pretreatment procedure) or light paraffins (aromatization reaction) at 700–900 K, undergoes a great transformation. In fact gallium oxide interacts directly with the zeolite acid center by means of a solid state reaction, composed of the following steps: (i) reduction of Ga_2O_3 to Ga_2O; (ii) migration of Ga_2O species into the zeolite phase; (iii) reaction of spread Ga_2O with the zeolite acid centers [29].

This reaction has been recently named reductive solid state ion exchange, RSSIE [32]. Similar phenomena have been reported for some others metals/H-MFI zeolite systems such as In [32], Cu [33,34], Zn [35], Mo and Cr [36].

Consistently with the former observation, the parameter d[Ga–HZ] seems to be pointless, because of the following conceptual equation:

$$\text{Long}\,d[\text{Ga-HZ}] \overset{\text{RSSIE}}{\rightarrow} \text{Short}\,d[\text{Ga-HZ}] \qquad (1)$$

Moreover, from the point of view of the paraffin activation mechanism, Eq. (1) introduces the possibility that metal species directly participate in the paraffin activation, sharing the heterolytic dissociation of the paraffin into H and the corresponding carbocation [37].

In the following we refer to this mechanism as SDM (short distance mechanism). It should be stressed that the solid state reaction between gallium and the zeolite acid center [38] or at least their proximity [39,40], is an essential requirement for direct participation of metal in paraffin activation/dissociation but it does not exclude, in principle, any of the LDMs, discussed in the former paragraph. Light paraffins transformation requires both gallium and the zeolite acid center. Indeed, catalysts without any residual acid function, prepared by completing the replacement of H^+ with gallium using the CVD technique, resulted in a catalyst with no activity for paraffin aromatization [41].

1.3. RSSIE limit temperatures

In our previous work [42] we focused our attention on verifying the actual occurrence of RSSIE in a mechanically mixed Ga_2O3/H-MFI catalyst. By means of XPS measurements we have shown that in situ hydrogen treatment over a wide range of temperatures (400–800 K) produces a detectable reduction of Ga^{III} to a lower oxidation-state species, recognized to be Ga^I [43]. As far as the migration of such reduced species is concerned, we have pointed out that no significant transfer phenomena occur between gallium oxide and MFI zeolite phases below 673 K. Only at higher temperature (773 K), clear evidence of gallium spreading onto the MFI zeolite phase has been found. This corresponds to a remarkable decrease of the Ga/Si signal ratio [42] as reported also by other authors [44–46].

These important experimental observations allow us to define two limits of temperature for RSSIE: (i) HNRT = 673 K (highest no RSSIE temperature) the highest temperature at which RSSIE does not occur; (ii) LRT = 773 K (lowest RSSIE temperature) the lowest temperature at which RSSIE does occur.

Accordingly, Eq. (1) should be modified as follows:

$$\text{Long d[Ga-HZ]} \underset{T>\text{LRT}}{\overset{\text{RSSIE}}{\rightarrow}} \text{Short d[Ga-HZ]} \qquad (2)$$

For a hydrogen pretreatment temperature T_a < HNRT we expect that the RSSIE is not activated. Furthermore, while for T_a > LRT the RSSIE is definitely activated, for HNRT < T_a < LRT we assume that RSSIE might or might not be activated, depending on the specific morphological characteristics of the catalysts (ion exchanged, impregnated, etc.). Indeed, well dispersed gallium oxide particles have been found to be less liable to reduction than larger gallium oxide particles [47].

1.4. Reaction map

With the aim of analyzing the correlations between hydrogen pretreatment, reaction temperature and the catalytic activity of a Ga_2O_3/HMFI mechanically mixed catalyst, we summarize in a synoptical scheme the observations discussed in the former paragraph.

Thus, a graph assigning the pretreatment temperature values to the abscissae and the reaction temperature values to the ordinates is drawn. Reporting HNRT and LRT both on the X and Y axes, we obtain the patchwise reaction map, reported in Fig. 2.

For a description of the zones composing this reaction map, it is important to keep track of the fact that RSSIE leads to the process described in Eq. (2), thus, giving the basis for the SDM hypothesis on the paraffin activation mechanism. On the contrary, absence of RSSIE accounts for a complete exclusion of SDM, supporting LDMs hypotheses.

1.4.1. Zone 'A'

The catalyst has been pretreated in hydrogen at a temperature T_a > LRT, thus, RSSIE has been activated. The catalytic activity at any temperature could be ascribed to the synergistic effect due to the short distance between gallium and zeolite acid center, i.e. SDM.

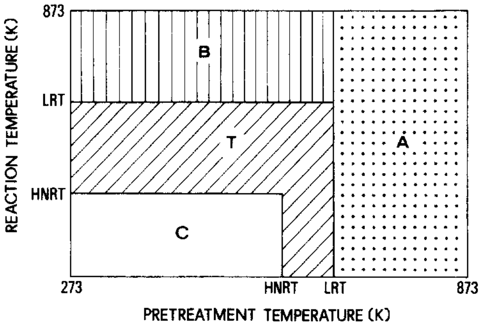

Fig. 2. Reaction map. See text for description of the zones composing the reaction map.

1.4.2. Zone 'B'

The catalyst has been pretreated in hydrogen at a temperature $T_a <$ HNRT, thus, RSSIE has not been activated. Since the reaction is carried out at a temperature $T_r >$ LRT, the activity increases during the reaction, leading to an induction period for aromatics production. This phenomenon is due to auto-activation of the catalyst [28–31]. In this case, changes in the catalytic activity could be ascribed to the activation of RSSIE during the reaction. This results in a gradual enhancement of the synergistic effect by reduction in the distance between gallium and the zeolite acid center or a solid state reaction between them.

1.4.3. Zone 'T'

The catalyst has been activated at temperature HNRT $< T_a <$ LRT, thus, RSSIE has been partially activated. The catalytic activity could show an intermediate behavior between zones A and B.

1.4.4. Zone 'C'

The catalyst has been pretreated in hydrogen at temperature $T_a <$ HNRT, thus, RSSIE has not been activated. The reaction is carried out at a temperature $T_r <$ HNRT: no activation of RSSIE is expected. Catalytic activity, if observed, maybe due to a mechanism consistent with the long distance of the active sites, as expected for a Ga_2O_3/H-MFI mechanically mixed catalyst.

2. Experimental

Comments stated in the former paragraph give a new perspective to the discussion on the mechanism governing the activity of mechanically mixed catalysts.

It has been pointed out that cooperation between gallium and zeolite acid center in zone C of the reaction map, if found, may account for a complete exclusion of SDM, strongly supporting the LDMs hypotheses. Therefore, studies on the catalytic activity of mechanically mixed catalysts in these distance preservative conditions are of great importance.

To our knowledge, very few authors have reported experimental data on the activity of gallium promoted zeolite catalysts for light paraffins aromatization at low temperature ($T_r <$ HRNT) [40,48]. Unfortunately, the catalysts samples, used by these authors, did not clearly match the characteristics of long d[Ga–HZ], which is the essential parameter in order to ascribe their activities to zone C behavior. For these reasons, in the following work, zone C catalytic activities of some Ga_2O_3/H-MFI mechanically mixed catalysts, are thoroughly investigated.

2.1. Catalyst preparation

MFI zeolite (Si/Al = 32.0) was synthesized according to the well-known method of Argauer and Landolt [49]. XRD analysis showed the high crystallinity of our sample. The acid form of the zeolite, HZ (HZ standing for the zeolite in its acidic form), was prepared by multiple ion-exchange treatments with a 0.1 M NH_4Cl solution followed by drying and activation at 823 K. The final sodium content was 0.2 wt%.

The catalysts were prepared by mechanical admixing of the zeolite and the following co-catalysts:

α-Quartz (Fisher Scientific), was crushed, acid washed and sieved. The sample was named HZ-QZ.

Ga_2O_3, produced by thermal decomposition of $Ga(NO_3)_3$ (Strem Chemicals). The sample prepared was defined as HZ-GAOX.

Ga_2O_3/SiL, gallium oxide supported on Silica Ludox (AS 40, Dupont) obtained by co-evaporation of a gallium nitrate–Silica Ludox solution followed by activation at 800 K as described in [16]. This sample was defined as HZ-CO46, CO standing for co-catalyst of composition 4:6 (this composition referred to the weight ratio $Ga(NO_3)_3$/SiL in the starting solution).

For all our samples, the relative composition was kept constant: zeolite 80.0% wt, co-catalyst 16.0% wt. The final form of each catalyst was prepared by extrusion with bentonite (Aldrich) as binder (4.0% wt), followed by thermal activation at 813 K. So the total amount of gallium in HZ-QZ, HZ-CO46 and HZ-GAOX was respectively 0.0% wt, 2.0% wt and 16.0% wt.

2.2. Catalysts testing

Catalysts were tested for the *n*-butane aromatization reaction. The catalytic testing procedure was as follow: 4 g of fresh catalyst was charged into a quartz reactor heated to the operating temperature under a flow of nitrogen (10 ml/min). As soon as the temperature was stable, in order to start the catalytic test, the reactor was fed with flowing *n*-butane (14 ml/min, WHSV = 0.5). The average time employed to perform a single run was approximately 3 h. All products, being in the gas phase, were identified by using a Hewlett-Packard GC (model 5790, FID detector) equipped with a 3-m column packed with Chromosorb P coated with 20% wt of Squalene. Some of the products were identified by using a Hewlett-Packard GC-MS (model 5890, quadrupole). Then, the collected data were elaborated to obtain the *n*-butane conversion and hydrocarbon selectivities. Moreover, the calculated final material balance was satisfactory for all runs.

In order to measure the amount of hydrogen produced, GC analysis was also performed in an independent way with a Hewlett-Packard GC (model 5890, TCD detector) equipped with a HayeSep A packed column, from Chromatographic Specialties.

Several catalytic tests were done at different temperatures chosen in the range of 573–650 K.

3. Results and discussion

3.1. Catalytic activity in zone C

The first results showed that all catalyst samples show comparable activities at the lowest testing temperature, 573 K. In particular, the cracking, the isomerization and the oligomerization activities have corresponding values. Indeed selectivities to cracking products (C_2–C_3 hydrocarbons), to isomerization products (isobutane and butenes) and oligomerization products (C_{5+}) are quite similar. Only traces of aromatics are produced at this temperature. Further, as shown in Table 1, these data are consistent with other data reported for *n*-butane aromatization on HZSM-5 zeolite catalyst carried out under similar conditions [50].

Table 1
Comparison between experimental results of the present work and published data

Samples	HZ-QZ	HZSM-5 [a]
Reaction temp. (°C)	300	300
Butane conversion (C atom%)	28.2	23.2
Cracking products (C atom%)	62.9	59.0
Isomeriz. products (C atom%)	15.9	24.0
C_{5+} (C atom)	21.2	16.0
Aromatics (C atom%)	0.0	0.0

[a] Data from [50].

Differences depending on the catalyst gallium content were seen when the reaction temperature was adjusted to a value higher or equal to 598 K, see Tables 2–4. Selectivity to aromatic hydrocarbons improved by increasing the amount of gallium introduced into the co-catalyst formulation, in the following order:

$$\text{HZ-QZ} < \text{HZ-CO46} < \text{HZ-GAOX} \quad (3)$$

The above outcome is consistent with the hydrogen production data which become significant at temperatures higher than 623 K, show-

Table 2
Catalytic activity of sample HZ-QZ

Reaction temp. (°C)	300	325	350	375
Butane Conversion (C atom%)	28.2	31.2	39.4	48.0
Cracking products (C atom%)	62.9	65.9	68.9	71.6
Isomeriz. products (C atom%)	15.9	14.8	13.4	11.9
C_{5+} (C atom%)	21.2	16.3	14.0	11.8
Aromatics (C atom%)	0.0	3.0	3.7	4.7
Hydrogen (% gas vol.)	0.0	0.28	0.38.	0.83

Table 3
Catalytic activity of sample HZ-CO46

Reaction temp. (°C)	300	325	350	375
Butane conversion (C atom%)	26.4	31.2	39.4	48.2
Cracking products (C atom%)	62.1	65.9	68.9	72.6
Isomeriz. products (C atom%)	15.8	14.4	13.2	11.8
C_{5+} (C atom%)	22.1	15.9	13.7	10.3
Aromatics (C atom%)	0.0	3.8	4.2	5.3
Hydrogen (% gas vol.)	0.0	0.35	0.82	1.9

ing a relevant difference between gallium containing samples and HZ-QZ, see Table 2, Tables 3 and 4.

By reaching the highest testing temperature, 648 K, we can induce further changes in the behavior of our catalysts as evidenced for the similar results obtained for both hydrogen and aromatics production by gallium containing samples. At this temperature the aromatization activity is beginning to not simply depend on the amount of gallium content but also is strongly correlated to its dispersion [40,51], i.e. to the reduction properties of the co-catalyst as already pointed out for these catalytic systems at 813 K [16,52].

These interesting results imply that the synergy between the catalyst components (zeolite acidic center, gallium site) has a large effect on both the hydrogen and aromatics production, even in zone C of the reaction map. Such experimental results need to be thoroughly examined, since the question arises on the specific role of gallium in light paraffin aromatization activity.

Table 4
Catalytic activity of sample HZ-GAOX

Reaction temp. (°C)	300	325	350	375
Butane conversion (C atom%)	27.0	33.0	40.9	49.1
Cracking products (C atom%)	62.2	65.7	69.0	73.3
Isomeriz. products (C atom%)	15.9	14.2	12.9	11.7
C_{5+} C atom%)	21.9	15.5	13.1	9.3
Aromatics (C atom%)	0.0	4.6	5.0	5.7
Hydrogen (% gas vol.)	0.0	0.86	1.49	2.18

3.2. *Paraffin activation in zone C*

As pointed out in a previous paragraph, absence of RSSIE in a mechanically mixed catalyst, strongly supports LDMs hypothesis for paraffin activation at low temperature ($T <$ LNRT). Therefore, it seems worthwhile to analyze the experimental data in order to check for the consistency of our findings with the aforementioned mechanisms.

The data in Table 2, Tables 3 and 4 suggest that: (i) catalyst samples at any reaction temperature show similar cracking and isomerization product selectivities; (ii) dehydrogenation activity, as depicted from the hydrogen production data, is higher in gallium containing samples than in HZ-QZ. The first remark emphasizes that, for these temperatures, no changes are produced in the activation path of *n*-butane, by increasing the gallium content of the catalyst composition. Actually, no significant differences in $C_4/C_4^=$ have been found, probably for the following reasons: (i) the data correspond to relatively high conversion activities; (ii) gallium oxide is known to be only active at high temperature for the dehydrogenation of small alkanes [8,53,54].

These experimental results seem to suggest that *n*-butane activation in this temperature range occurs on the zeolite acid center. On the other hand, the second observation suggests a contribution of gallium oxide towards dehydrogenation activity. All these aspects of the nature of gallium and zeolite acid center cooperation in zone C of the reaction map are consistent with LDMs hypotheses.

3.3. *Role of gallium*

Despite the fact that our experimental results seem to fit the LDMs hypotheses satisfactorily, the actual role of gallium in zone C catalytic activity deserves discussion.

In order to propose a suitable explanation for the nature of the observed zone C gallium promoting effect, we should first consider that the aromatic and C_{5+} product selectivities appear strongly interdependent: when aromatic production increases, C_{5+} production decreases, see the data in Table 2, Tables 3 and 4. It is well-known that the last step of aromatics synthesis from light paraffins consists of the oligomers dehydrocyclization reaction.

Thus, it seems reasonable to assume that gallium oxide participate in this reaction step, directly enhancing the dehydrogenation of C_{5+} oligomers [54–56] to triene intermediates undergoing thermal cyclization [24]. This fact could be due to a specific activity of gallium oxide in the dehydrogenation of C_{5+} paraffins. However, it is also important to consider the relevant hydrogen ads/desorption functions of gallium oxide zeolite mechanically mixed catalyst. As we demonstrated in a previous work [57], our samples show two hydrogen ads/desorption sites identified by means of H_2-TPD measurements. These analyses revealed the presence of two signals with peak maxima centered, respectively, at 663 and 758 K. Analogous results have been published by other authors [15,41,57–60]. It has to be stressed that the site, showing a peak maximum centered at the lower temperature, could provide a recombinative desorption function for hydrogen adatoms.

4. Conclusions

Our experiments demonstrate that, gallium oxide (pure or silica supported) seems to play a key role in promoting the aromatization activities of H-MFI in mechanically mixed catalysts, even at temperatures which are quite different than the usual operating temperatures. In particular, before reductive solid state ion exchange becomes effective (reaction temperature, $T_r <$ 673 K), gallium oxide composing the co-catalyst phase, can improve the aromatic selectivity and hydrogen production of our catalyst samples. It has been pointed out that gallium present in our catalyst samples seems to provide a dual function: (i) alternative path for dehydrogenation of oligomers; (ii) hydrogen ads/desorption sites.

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References

[1] J.R. Mowry, R.F. Anderson and J.A. Johnson, Oil Gas J., December (1985) 128.

[2] P.C. Doolan and P.R. Pujado, Hydrocarbon Process., September (1989) 72.

[3] C.D. Gosling, F.P. Wilcher, L. Sullivan and R.A. Mountford, Hydrocarbon Process., December (1991) 69.

[4] Hydrocarbon Process., March (1995) 100.

[5] D. Seddon, Catal. Today, 6 (1990) 351.

[6] M. Guisnet, N.S. Gnep and F. Alario, Appl. Catal., 89 (1992) 1.

[7] Y. Ono, Catal. Rev. Sci. Eng., 34 (1992) 179.

[8] G. Giannetto, R. Monque and R. Galiasso, Catal. Rev. Sci. Eng., 36 (1994) 271.

[9] C.R. BAyense and J.H.C. van Hooff, Appl. Catal. A: General, 79 (1991) 127.

[10] T. Mole, J.R. Anderson and G. Creer, Appl. Catal., 17 (1985) 141.

[11] B.S. Kwak and W.M.H. Sachtler, J. Catal., 141 (1993) 729.

[12] B.S. Kwak and W.M.H. Sachtler and W.O. Haag, J. Catal., 149 (1994) 465.

[13] J. Kanai and N. Kawata, Appl. Catal., 55 (1989) 115.

[14] D.K. Simmons, R. Szostak, P.K. Agrawal and T.L. Thomas, J. Catal., 106 (1987) 287.

[15] K. Fujimoto, I. Nakamura, K. Yokota and K. Aimoto, Bull. Chem. Soc. Jpn., 64 (1991) 2275.

[16] R. LeVanMao and J. Yao, Appl. Catal. A: General, 79 (1991) 77.

[17] G. Buckles and G.J. Hutchings, Catal. Lett., 27 (1994) 361.

[18] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, Appl. Catal., 35 (1987) 93.

[19] P. Meriaudeau, P. Sapaly and C. Naccache, in P.A. Jacobs and R.A. van Santen (Editors), Zeolite: Facts, Figures, Future, Elsevier, Amsterdam, 1989, p. 1423.

[20] N.S. Gnep, J.Y. Doyemet, and M. Guisnet, J. Mol. Catal., 45 (1988) 281.

[21] V.B. Kazanky, L.M. Kustov and A. Yu Khodakov, in P.A. Jacobs and R.A. van Santen (Editors), Zeolite: Facts, Figures, Future, Elsevier, Amsterdam, 1989, p. 1173.
[22] G. Giannetto, A. Montes, N.S. Gnep, A. Florentino, P. Cartraud and M. Guisnet, J. Catal., 145 (1993) 86.
[23] H. Kitagawa, Y. Sendoda and Y. Ono, J. Catal., 101 (1986) 12.
[24] E. Iglesia, J.E. Baumgartner and G.L. Price, J. Catal., 134 (1992) 549.
[25] E. Iglesia and J.E. Baumgartner, Catal. Lett., 21 (1993) 55.
[26] G.D. Meitzner, E. Iglesia, J.E. Baumgartner and E.S. Huang, J. Catal., 140 (1993) 2099.
[27] T. Inui, in T. Inui (Editor), Successful Design of Catalysts, Elsevier, Amsterdam, 1989, p. 189.
[28] V. Kanazirev, G.L. Price and K.M. Dooley, J. Chem. Soc., Chem. Commun., (1990) 712.
[29] G.L. Price and V. Kanazirev, J. Catal., 126 (1990) 267.
[30] G.L. Price and V. Kanazirev, J. Mol. Catal., 66 (1991) 115.
[31] K.M. Dooley, C. Chang and G.L. Price, Appl. Catal. A: General, 84 (1992) 17.
[32] V. Kanazirev and G.L. Price, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Holderich (Editors), Zeolites and Related Microporous Materials: State of the Art 1994, Elsevier, Amsterdam, 1994, p. 1935.
[33] V. Kanazirev, G.L. Price, J. Mol. Catal. A: Chem., 96 (1995) 145.
[34] G.L. Price, V. Kanazirev and D.F. Church, J. Phys. Chem., 99 (1995) 864.
[35] K. Osako, K. Nakashiro and Y. Ono, Bull. Chem. Soc. Jpn., 66 (1993) 755.
[36] Z. Fu, D. Yin, Y. Yang, X. Guo, Appl. Catal. A: General, 124 (1995) 59.
[37] P. Meriaudeau, P. Sapaly and C. Naccache, J. Mol. Catal., 81 (1993) 293.
[38] P. Meriaudeau and C. Naccache, J. Mol. Catal., 50 (1989) L7.
[39] P. Meriaudeau and C. Naccache, in L. Guczi, F. Solymosi and P. Tétényi (Editors), Proc. 10th Int. Congr. Catalysis, Elsevier, Amsterdam, 1993, p. 2341.
[40] E.G. Derouane, S.B. Abdul Amid, I. Ivanova, N. Blom and P.-E. Hojlund-Nielsen, J. Mol. Catal., 86 (1994) 371.
[41] B.S. Kwak and W.M.H. Sachtler, J. Catal., 145 (1994) 456.
[42] R. Carli, C.L. Bianchi, R. Giannantonio and V. Ragaini, J. Mol. Catal., 83 (1993) 379.
[43] R. Carli and C.L. Bianchi, Appl. Surf. Sci., 74 (1994) 99.
[44] P. Meriaudeau and C. Naccache in C.H. Bartholomew and J.B. Butt (Editors), Catalyst Deactivation 1991, Elsevier, Amsterdam, 1991, p. 767.
[45] E.S. Shpiro, D.P. Shevchenko, M.S. Kharson, A.A. Dergachev, Kh.M. Minachev, Zeolites, 12 (1992) 670.
[46] V. Kanazirev, G.L. Price, G. Tyuliev, Zeolites, 12 (1992) 846.
[47] R. Carli, R. LeVanMao, C.L. Bianchi, V. Ragaini, Catal. Lett., 21 (1993) 265.
[48] M. Barre, N.S. Gnep, P. Magnoux, S. Sansare, V.R. Choudhary and M. Guisnet, Catal. Lett., 21 (1993) 275.
[49] R.L. Argauer and G.R. Landolt, US Pat., 3 702 886 (1972).
[50] R. Shigeishi, A. Garforth, I. Harris and J. Dwyer, J. Catal., 130 (1991) 423.
[51] S.B. Abdul Hamid, E.G. Derouane, G. Demortier, J. Riga, M.A. Yarmo, Appl. Catal. A: General, 108 (1994) 85.
[52] R. LeVanMao, J. Yao and R. Carli, Appl. Catal., 86 (1992) 127.
[53] N.S. Gnep, J.Y. Doyemet anf M. Guisnet, in H.G. Karge and J. Weitkamp (Editors), Zeolites as Catalysts, Sorbents and Detergent Builders, Elsevier, Amsterdam, 1989, p. 153.
[54] P. Meriaudeau and C. Naccache, J. Mol. Catal., 50 (1987) L7.
[55] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, Appl. Catal., 43 (1988) 155.
[56] Y. Ono and K. Kanae, J. Chem. Soc., Faraday Trans., 87 (1991) 669.
[57] R. Carli, C.L. Bianchi and V. Ragaini, Vuoto, 23 (1994) 87.
[58] L. Petit, J.P. Bournonville and F. Raatz, in P.A. Jacobs and R.A. van Santen (Editors), Zeolite: Facts, Figures, Future, Elsevier, Amsterdam, 1989, p. 1163.
[59] J.F. Joly, H. Ajot, E. Merlen, F. Raatz and F. Alario, Appl. Catal. A: General, 79 (1991) 249.
[60] S. Jia, S. Wu and Z. Meng, Appl. Catal. A: General, 103 (1993) 259.