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NAS (novel aluminosilicates) as catalysts for the aromatisation of propane
Studies of zinc and gallium modified zeolite-based systems having various extents of XRD crystallinity

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Abstract

A review of existing literature on the behaviour of H-, Zn- and Ga-ZSM-5 systems in the aromatisation of propane suggest that no clear picture emerges regarding: (i) the relative merits of zinc and gallium with respect to activity and aromatics selectivity; (ii) the effects of the extent of crystallinity of the zeolitic material on catalysis. The work now reported involves a direct comparative study of H-NAS, Zn-NAS and Ga-NAS catalysts (NAS = novel aluminosilicates, comprising ZSM-5-based structures having XRD crystallinities ranging from the substantially amorphous to the partially crystalline and their highly crystalline ZSM-5 analogues. Zinc or gallium has been introduced into the parent zeolitic structure by means of solid-state ion-exchange. Zinc appears to enhance both activity and BTX (benzene, toluene and xylenes) selectivity, relative to the zeolitic parent solid, in contrast to gallium, which affects only BTX selectivity. In addition, optimum activity plus BTX selectivity under the conditions used are found for XRD crystallinities in the range 50–85%. The maximum BTX yields (single pass basis) are lowest for the H-NAS samples, markedly higher for the Zn-NAS catalysts, and at an intermediate level for the Ga-NAS samples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Novel aluminosilicates; XRD crystallinity; ZSM-5 system; Propane aromatisation

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1. Introduction

Light alkanes are found in natural gas or may be obtained by those versions of the Fischer–Tropsch synthesis, such as the Sasol Synthol Process, that favour the formation of comparatively light hydrocarbon products [1]. The conversion of light alkanes into aromatics offers a useful route into high octane fuels and chemical feedstocks [2,3]. A steady effort has been made to investigate zeolite catalysts for this type of reaction with emphasis on materials of the ZSM-5-type [4]. The enhancement of selectivity to benzene, toluene and xylenes (BTX), in particular, by incorporation of zinc [2,4–7] or gallium [6,8–22] has attracted much attention. The action of indium [21,22], or platinum in combination with gallium [23,24] has also been reported.

Recently, a new series of novel aluminosilicates (NAS), consisting of materials that are either substantially amorphous or only partially crystalline zeolite-based materials has been disclosed [25]. The crystalline ranges for the different types of zeolite-based materials can be defined, for the purposes of

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this publication, and for our continuing research in this area of zeolite synthesis and catalysis, to be as follows: substantially amorphous materials have XRD crystallinities lower than 30%, partially crystalline samples are those possessing 30–70% crystallinity and highly crystalline materials are those with >70% XRD crystallinity. We have selected these specific ranges based on the catalytic performances of the materials obtained using catalytic test reactions, such as *n*-hexane cracking [26]. The substantially amorphous materials and the partially crystalline materials are together designated as NAS, whereas the highly crystalline materials are effectively ZSM-5 as commonly used. In some cases, for convenience, the NAS materials and the ZSM-5 materials are collectively referred to as ZSM-5-based materials—this appellation then covers solids having any XRD crystallinity.

It was previously discovered that the catalytic behaviour of these solids for various acid catalysed reactions depended markedly on the degree of crystallinity as reflected in the intensities of their X-ray diffraction (XRD) peaks. For example, catalysts of the H-ZSM-5-type exhibited a maximum yield for the skeletal isomerisation of *n*-butenes at an XRD crystallinity of about 2% [25]. Higher crystallinities (>30%) were, however, required for the cracking of alkanes such as *n*-hexane [26]. It was, therefore, of interest to examine these NAS catalysts and their ZSM-5 analogues for the aromatisation of light alkanes, such as propane, to assess the dependence of catalytic behaviour on the %XRD crystallinity and to investigate the behaviour of zinc- or gallium-containing samples. Elsewhere, we have reported that the ZSM-5-based samples exhibit a pronounced maximum in both activity and BTX selectivity as a function of %XRD crystallinity [27]. A similar maximum is found with Zn-ZSM-5-based samples with respect to conversion, but BTX selectivity, in contrast, is largely independent of %XRD crystallinity for crystallinity values above about 30%.

In reviewing the various reports on the catalytic performances of H-, Zn- and Ga-ZSM-5 systems in the aromatisation of light alkanes, it is apparent that no immediately clear picture emerges as to whether zinc or gallium is the more beneficial "additive". In fact, this paper shows that in reviewing the literature, it is seen that many gallium-loaded samples are less active and less selective than some H-ZSM-5 samples, and, in addition, gallium-containing samples appear to be more active and selective than zinc-containing samples in some cases, whereas the reverse is true for other data. A notable omission in work reported to date is the almost complete lack of comparative data obtained for zinc- and gallium-containing samples derived from the identical parent H-ZSM-5. Only two reports on this aspect appear to be available. Scurrell [2] showed that for ZSM-5 samples (Si/Al atomic ratio = 19) impregnated with aqueous solutions of zinc or gallium nitrate (zinc and gallium contents up to ca. 1.0 mass%), the zinc samples exhibited a somewhat higher BTX selectivity (%C basis) than the gallium samples (e.g. 46% compared with 40%) for propane conversion. Elsewhere, Shibata et al. [6] found that Ga-ZSM-5 samples (Si/Al atomic ratio = 23.5), subjected to wet ion-exchange procedures for the introduction of the gallium into the zeolite, were associated with significantly higher BTX selectivities (72%) than the zinc-containing samples (50%), with the gallium content of 1.2 mass% being significantly lower than that of the zinc (1.8 mass%).

2. Experimental

Highly crystalline batches of ZSM-5 were prepared according to our previously described methods, with or without stirring of the reactant mixture [25]. Products with different crystallinity levels, and with the same nominal Si/Al atomic ratio of 35, based on the molar amounts of reagents used in the synthesis of the zeolite precursor gels, were obtained by varying the hydrothermal synthesis temperature employed in each of these preparations [25]. The method used to determine the %XRD crystallinity of individual samples has also been fully described [25]. The sum of the intensities of the three prominent XRD peaks between 22 and 25° 2θ of the sample was divided by the sum of these three peaks obtained with a highly crystalline sample [25,26].

After hydrothermal synthesis, the samples were calcined at 630 °C for 3.5 h and were then ion-exchanged with 1 M NH_4Cl solution three times at room temperature and subsequently washed with deionised water to remove the chloride and other non-desirable ions. The H^+-NAS or H^+-ZSM-5-forms were obtained by calcination of the corresponding $NH_4{}^+$-forms at

550 °C for 3 h. The Zn^{2+}-forms were obtained using a solid-state ion-exchange (SSIE) procedure, involving a homogeneous physical mixture of zinc nitrate and the ZSM-5-based material. This mixture was heated at 500 °C for 3 h in a quartz reactor under nitrogen. A zinc loading of 2.8 mass% was used; this loading corresponds to a Zn/Al atomic ratio in the solid of approximately 1.0. For the gallium samples, gallium nitrate was substituted for the zinc nitrate and an otherwise identical SSIE procedure was followed. A gallium loading of 2.8 mass% was also used.

The conversion of propane was studied using a stainless steel tubular reactor under the following conditions: propane was flowed through the reactor at a rate of $20\,cm^3\,min^{-1}$ (with a flow of nitrogen also at $20\,cm^3\,min^{-1}$ in the case of the zinc- and gallium-loaded materials), using a reaction temperature of 530 °C. The reactor bed comprised 0.5 g catalyst diluted with 2.0 g silica gel (Grace type 432). Analysis of the exit stream was carried out using on-line gas chromatography (Porapak Q column, detection by FID). The BTX selectivities are reported on a %C basis.

3. Results

The behaviour of the three series of catalysts, H-ZSM-5-based, Zn-ZSM-5-based and Ga-ZSM-5-based samples with respect to conversion and BTX selectivity are depicted in Figs. 1–3. It is clear that the gallium-exchanged samples exhibit a dependence of conversion on %XRD crystallinity that is essentially identical to that displayed by the parent H-ZSM-5-based materials and, in addition, the activities of both series of catalysts are very close. The BTX selectivity dependence on %XRD crystallinity of the gallium-exchanged catalysts is, however, intermediate between that of the zinc-exchanged series and the parent series.

In attempting to summarise the previously reported work on ZSM-5 catalysts, the BTX selectivity/conversion relationship is a useful one (see Fig. 4). The data presented is as reported for the aromatisation of propane, and in some cases, *n*-butane. Although it is recognised that not all work has been conducted under precisely identical experimental conditions (and that the composition of the catalysts and the methods of preparation are not identical in all cases), the actual spread of temperatures, partial pressure of alkane and reactant feed-rate is sufficiently small that the comparison is considered valid in broad terms. Clearly, all zinc-containing samples exhibit higher

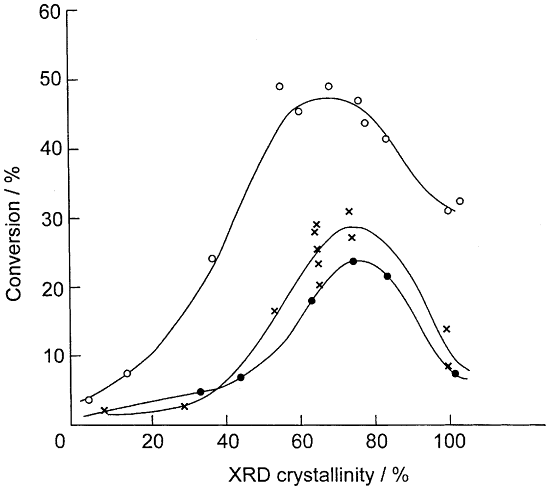

Fig. 1. Propane conversion as a function of XRD crystallinity: (○) Zn-ZSM-5-based catalysts; (×) Ga-ZSM-5-based catalysts; (●) H-ZSM-5-based catalysts (for the experimental conditions used see text).

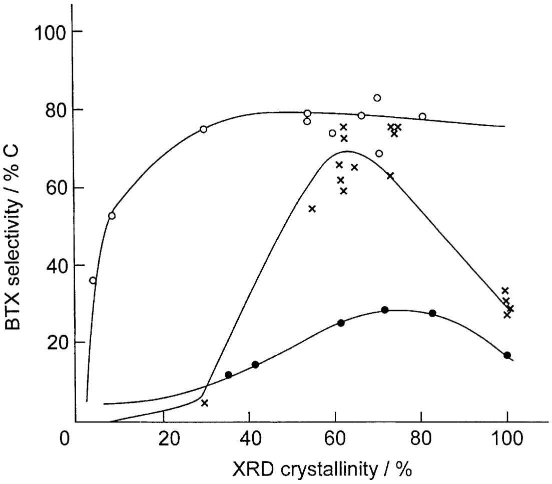

Fig. 2. BTX selectivity as a function of XRD crystallinity: (○) Zn-ZSM-5-based catalysts; (×) Ga-ZSM-5-based catalysts; (●) H-ZSM-5-based catalysts (for the experimental conditions used see text).

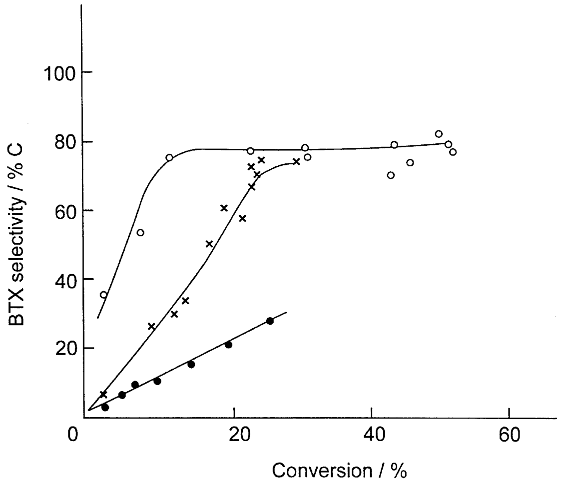

Fig. 3. BTX selectivity as a function of conversion derived from the data depicted in Figs. 1 and 2: (○) Zn-ZSM-5-based catalysts; (×) Ga-ZSM-5-based catalysts; (●) H-ZSM-5-based catalysts.

BTX selectivities than H-ZSM-5 at comparable conversion levels, and some exhibit higher selectivities than gallium-containing samples. There is particularly a large spread in the data reported for both Ga- and H-ZSM-5 catalysts, with some gallium-containing systems exhibiting lower BTX selectivities than some of the H-ZSM-5 samples at comparable conversion levels. All PtGa-ZSM-5 samples lie at the bottom of the selectivity/conversion spread compared with platinum-free Ga-ZSM-5 samples. What comparatively few data are available for In-ZSM-5 samples suggest a behaviour comparable with those displayed by some zinc- and gallium-containing samples.

From the viewpoint of catalytic performance, the upper boundary of the selectivity/conversion region covered by each catalyst type is of particular interest and the situation is summarised in Fig. 5 for the five catalyst types together with data now reported for the H-NAS, Zn-NAS and Ga-NAS samples. Data for the H-NAS samples (not actually shown in Fig. 5 for reasons of clarity) falls almost exactly on the H-ZSM-5 curve, whereas the BTX selectivity of the Zn-NAS samples exceeds those found for Zn-ZSM-5 samples (as reported in the literature) at comparable conversions for all conversion levels. The Ga-NAS samples exhibit lower BTX selectivities than Zn-NAS, and lower than for some Ga-ZSM-5 samples, for conversions up to about 20%, but above this level of conversion, the BTX selectivity of both Ga-NAS and Zn-NAS catalysts are very similar and relatively high at about 75–80%C basis. The highest BTX yields (single pass basis) observed under the conditions used in this work are 40 and 30% for the Zn-NAS and Ga-NAS samples,

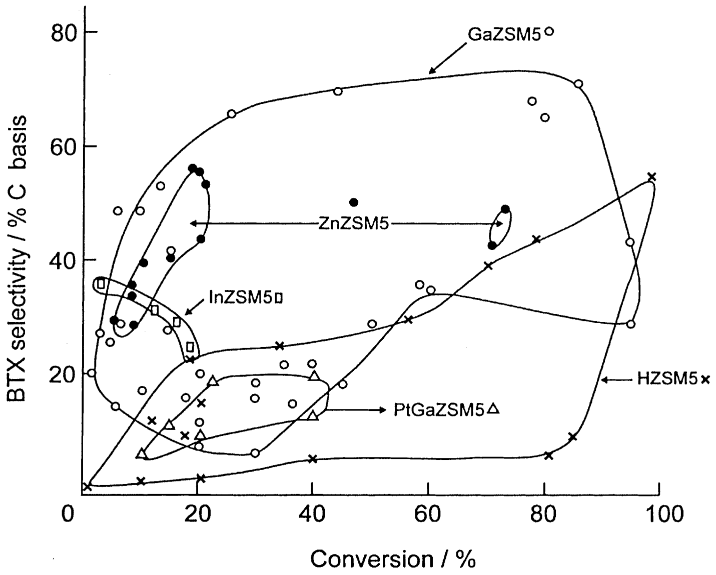

Fig. 4. Data reported for various ZSM-5-based catalysts for the aromatisation of propane and *n*-butane.

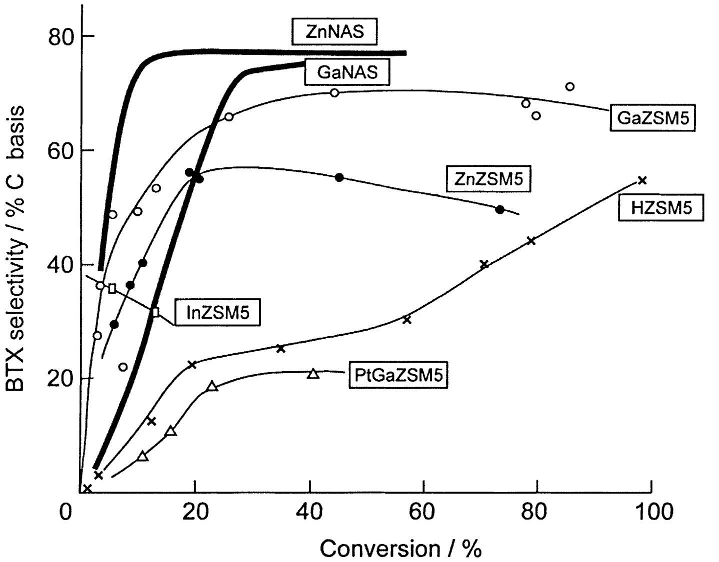

Fig. 5. Upper BTX selectivity conversion boundaries for the various catalyst systems depicted in Fig. 4 with superimposed experimental data obtained for Zn-NAS and Ga-NAS catalysts.

respectively, and 7% for the H-NAS catalysts. Overall, the Zn- or Ga-exchanged NAS samples exhibit some of the highest BTX selectivities so far reported for catalysts of this type.

4. Discussion

The activities of the Ga-ZSM-5-based samples are almost identical to those found for the parent H-ZSM-5-based catalysts at all %XRD crystallinities (Fig. 1). The maximum in activity observed for both series of catalysts as a function of %XRD crystallinity is ascribed to: (i) the need for a reasonably well-developed zeolitic domain to be present, in order for the acid-catalysed sequence of conversions required for conversion of propane, since activity levels rise only after an XRD crystallinity of about 30% has been reached; (ii) a fall in intrinsic activity per unit mass of catalyst as the XRD crystallinity approaches 100%, due, as discussed elsewhere [27], to the fact that in our work carried out to date, high crystallinity levels are inseparable from physical growth of the zeolite crystallites [28]. As Beschmann et al. [29] have revealed, in reactions involving aromatic entities such as those encountered in the present work, the operation of diffusion constraints results in a fall in activity as crystallite size increases in the range 0.045–4.5 μm for reaction rates in the range 0.5×10^{-6}–$19 \times 10^{-6}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$. The absolute rates of conversion observed in the present work on highly crystalline samples fall near $3.8 \times 10^{-6}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$, which is within the range encountered by Beschmann et al. The dimensions of the crystallites associated with the highly crystalline samples used in this study are about 6 μm or slightly higher [28].

The similarity in conversion levels seen with the H-ZSM-5-based and Ga-ZSM-5-based samples has a parallel with the work of Price et al. [16], who found a similar situation (conversion levels observed in the range 1–22%) for samples prepared by a reductive solid-state ion-exchange (RSSIE) method, in which it is claimed that Ga^+ ions are formed in the zeolite lattice during the reduction process (hydrogen at 575 °C). Additionally, Guisnet and Gnep [9] reported that conversion levels (in the range 5–90%) were virtually identical for Ga-ZSM-5 and H-ZSM-5 samples when the gallium was introduced via impregnation using gallium nitrate. A further example is provided by the work of Kwak and Sachtler [30] for samples prepared by the sublimation of $GaCl_3$ into H-ZSM-5 (conversion levels studied in the range 17–28%). In some other cases, it is apparent that conversion levels of Ga-ZSM-5 samples tend to be somewhat higher than those of the parent H-ZSM-5. Thus, Buckles and Hutchings [8] reported conversions of the gallium form that are about twice those found for the parent H-form (conversion levels in the range 6–42%), for samples prepared by wet ion-exchange. The relative conversions narrow slightly to about 1.3 if gallium is introduced by physically mixing gallium trioxide and the H-ZSM-5. For gallium samples prepared by wet ion-exchange, Nakamura and Fujimoto [10] report conversion levels for the Ga- and H-forms as 95.4 and 65.5%, respectively. Assuming that first-order kinetics apply, their data suggests that the gallium-containing samples are more active by a factor of some 2.8. It should be noted that in cases where the gallium is deliberately incorporated into the zeolite synthesis mixture so that the element is, at least initially, contained within the zeolite framework, then the activity relative to the aluminium analogue is much reduced [31].

It is concluded that, under our reaction conditions, gallium-exchanged ZSM-5-based samples display almost exactly the same activities for propane conversion as those exhibited by the parent H-samples. The BTX selectivity is, however, much higher in the case of the gallium-loaded samples. It appears, therefore, that the role of gallium is largely to influence the later stages of the overall reaction, particularly hydrogen transfer reactions associated with concomitant formation of aromatic molecules and light alkanes. The gallium centres seem not to promote the initial dehydrogenation of propane, if we make the assumption that this step is the quasi-rate determining step in the overall conversion.

In contrast, zinc-exchanged samples, even at very low crystallinity levels, exhibit both higher activity and higher BTX selectivity compared with those displayed by the parent H-samples. The role of XRD crystallinity and zeolite structure has not been assessed before. Clearly, the activity and BTX selectivity of all catalysts first increase with increasing XRD crystallinity. However, for zinc ion-exchanged samples the dramatic increase in conversion and BTX selectivity seen at relatively low XRD crystallinities suggests that structural demands, as far as the extent of development of the zeolitic domains in the partially crystalline samples is concerned, are much reduced if zinc ions are involved. Specifically, although the activity for propane activation and conversion normally (in the absence of zinc) seem to demand a threshold XRD crystallinity of about 30% (similar to the demands for *n*-hexane cracking on these H-NAS samples [26]), this requirement would appear to be relaxed to some extent if zinc ions are present. A further potential manifestation of this type of effect, and a further contrast between the Ga- and Zn-exchanged catalysts, is the sustained high BTX selectivity found with the Zn-NAS samples for XRD crystallinities in excess of about 70%. The high BTX selectivity is maintained despite the steady fall in conversion as the XRD crystallinity is increased. This is a most significant finding and reveals that zinc centres probably promote both the initial dehydrogenation of propane and influence the subsequent aromatisation/H-transfer reactions. The role of zinc ions in assisting formation of dihydrogen by what is essentially a reverse spillover phenomenon has been discussed in detail by others [4]. The precise origin of this difference in behaviour (zinc vs. gallium) is still unclear. It may be a reflection of the detailed kinetics operating on the zinc and gallium samples respectively, or it may reflect differences in the detailed manner in which zinc ions, as opposed to gallium ions, are located within the zeolite lattice. The accessibility of the Ga(+1) state, i.e. Ga^+ ions can be formed from the reduction of Ga^{3+} [16], or the formation of other singly charged ions such as $[Ga(O^{2-})]^+$ [23,30] may be of significance here in that it provides a basis for considering that one gallium centre may be associated with each framework aluminium. Such 1:1 stoichiometry is less easily accepted for high silica zeolites hosting a divalent cation interacting with spatially distant Al centres, though the formation of partially hydroxylated cations, such as $[Zn(OH)]^+$ [32] can provide one explanation for such stoichiometry. More characterisation work aimed at clarifying the oxidation state, chemical environment and the physical location of gallium and zinc entities in the NAS systems is in progress in an attempt to clarify some of these issues.

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References

[1] M.E. Dry, Catal. Today 6 (1990) 183.
[2] M.S. Scurrell, Appl. Catal. 41 (1988) 89.
[3] D. Seddon, Catal. Today 6 (1990) 351.
[4] J.A. Biscardi, E. Iglesia, J. Catal. 182 (1999) 117.
[5] T. Mole, J.R. Anderson, G. Greer, Appl. Catal. 17 (1985) 141.
[6] M. Shibata, H. Katagawa, Y. Senoda, Y. Ono, Stud. Surf. Sci. Catal. 28 (1986) 717.
[7] H. Berndt, G. Leitz, J. Volter, Appl. Catal. A 146 (1996) 365.
[8] G. Buckles, G.J. Hutchings, Catal. Today 31 (1996) 233.
[9] M. Guisnet, N.S. Gnep, Catal. Today 31 (1996) 275.
[10] I. Nakamura, K. Fujimoto, Catal. Today 31 (1996) 335.
[11] G.L. Price, V. Kanazirev, J. Catal. 126 (1990) 267.
[12] R. Le Van Mao, J. Yao, L.A. Dufresne, R. Carli, Catal. Today 31 (1996) 247.
[13] G. Buckles, G.J. Hutchings, Catal. Lett. 27 (1994) 361.
[14] O.P. Keipert, M. Baerns, Stud. Surf. Sci. Catal. 84 (1994) 1757.
[15] K.M. Dooley, G.L. Price, V.I. Kanazirev, V.I. Hart, Catal. Today 31 (1996) 305.
[16] G.L. Price, V. Kanazirev, K.M. Dooley, V.I. Hart, J. Catal. 173 (1998) 17.
[17] S.B. Abdul Hamid, E.G. Derouane, P. Meriaudeau, C. Naccache, M.A. Yarmo, Stud. Surf. Sci. Catal. 48 (1994) 2335.
[18] P. Meriaudeau, C. Naccache, Catal. Lett. 32 (1995) 235.
[19] G. Giannetto, G. Leon, J. Papa, R. Monque, R. Galiasso, Z. Gabelica, Catal. Lett. 22 (1993) 381.
[20] M. Barre, N.S. Gnep, P. Magnoux, S. Sansare, V.R. Choudhary, M. Guisnet, Catal. Lett. 21 (1993) 275.
[21] J. Halasz, Z. Konya, A. Fudala, A. Beres, I. Kiricsi, Catal. Today 31 (1996) 293.
[22] V.I. Hart, M.B. Bryant, L.G. Butler, X. Wu, K.M. Dooley, Catal. Lett. 53 (1998) 111.
[23] B.S. Kwak, W.M.H. Sachtler, J. Catal. 145 (1994) 456.
[24] B.S. Kwak, W.M.H. Sachtler, J. Catal. 149 (1994) 465.
[25] C.P. Nicolaides, Appl. Catal. 185 (1999) 211.
[26] C.P. Nicolaides, M.S. Scurrell, N.P. Sincadu, Unpublished results.
[27] C.P. Nicolaides, N.P. Sincadu, M.S. Scurrell, in: Proceedings of the Sixth Natural Gas Conversion Symposium, Alyeska, Alaska, June 2001, Stud. Surf. Sci. Catal. 136 (2001) 333.
[28] P.B. Ramatsetse, M.Sc. Dissertation, University of the North, 1998.
[29] K. Beschmann, L. Rieckert, U. Muller, J. Catal. 145 (1994) 243.
[30] B.S. Kwak, W.M.H. Sachtler, J. Catal. 141 (1993) 729.
[31] G. Giannetto, A. Montes, N.S. Gnep, A. Florentino, P. Cartraud, M. Guisnet, J. Catal. 145 (1993) 86.
[32] J.A. Biscardi, G.D. Meitzner, E. Iglesia, J. Catal. 179 (1998) 192.