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Indium and gallium containing ZSM-5 zeolites: acidity and catalytic activity in propane transformation

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Abstract

Surface acidity and propane transformation on In- and Ga-containing ZSM-5 type zeolites were investigated to find relation between the acidic character of catalysts prepared by conventional or solid state ion-exchange and the catalytic activity in alkane aromatization. On the basis of the concentration of Brönsted and Lewis acid sites measured by IR spectroscopy the In and Ga containing samples may be ordered into three main groups. The presence of Brönsted acid sites results in cracking of the hydrocarbon molecules, whereas the aromatization activity is attributed to Lewis acidity associated with the intimate contact of the oxide/zeolite assemblies.

1. Introduction

The direct conversion of light paraffins (primarily propane and butane) to aromatic compounds is of expanding importance for production of gasoline additives. The UOP/BP Cyclar process using a Ga/H-ZSM-5 catalyst has been scaled up for industrial operation [1]. As no metallic component is present in Ga/H-ZSM-5 zeolite the oxide component and the acid sites should operate as catalytically active sites [2]. The chemical state, the concentration and the dispersion of gallium oxide and the Brönsted or Lewis acid sites have frequently been the subjects of research papers [3–5].

Beside gallium, indium and, less, thallium containing zeolites were also investigated. The general aim was to improve the activity and BTX selectivity of the catalysts in light alkane reactions [6,7].

Three different procedures have usually been applied for preparation of metal containing catalysts of MFI structure.

(i) Synthesis of isomorphously substituted metal silicates with an appropriate metal content in the framework [8,9]. It has been demonstrated that the concentration of the M^{3+} ions incorporated into the framework decreases with increasing ion radius. As a result, preparation of silicates with identical and high M^{3+} (Al, In or Tl) concentration was generally unsuccessful [10]. However, Giannetto et al. confirmed relatively high Ga incorporation due to the presence of stable monomer gallate ions in the alkaline synthesis media [11–13].

(ii) In connection with the conventional (liquid phase) ion-exchange it is necessary to mention that the solutions of Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+} ions are stable in acidic media. This

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fact limits the applicability of the conventional ion-exchange procedure apart from the use of siliceous zeolites such as H-ZSM-5 resistant under acidic circumstances [14].

(iii) The solid state ion-exchange method is the most promising procedure for introducing metal ions into zeolites [15]. In general, an intimate mixture of the respective metal oxide and H-ZSM-5 zeolite is prepared and heat treated by a certain temperature program in oxidative or reductive atmosphere [16].

Metal halides are very rarely used for the preparation of gallium or indium containing catalysts [17] although H-ZSM-5 zeolite is resistant to HCl generated [14]. The most probable explanation is the difficult preparation and low stability of these halides.

The acidic character of these catalysts and the effect of acidity on their activity and/or selectivity have been the topic of quite a large number of papers ([3,18–22], and the references therein). Although this property is of crucial importance in the LPG (low paraffins to gasoline) process, clear-cut correlations have not been found yet.

The aim of the present communication is to disclose data for establishing a relation between the acidic character of Ga and In containing zeolites prepared by various methods and their catalytic activity in the dehydrocyclooligomerization of propane.

2. Experimental

Na-ZSM-5 zeolite was synthesized in our laboratory according to the recipe in [23] using tetrapropyl ammonium bromide as template. The Si/Al ratio in the reacting gel was 40. After burning the template off, the ammonium form of the zeolite was prepared by conventional ion exchange in 0.1 molar ammonium chloride solution. Deammonization of this sample yielded the required H-form.

For the conventional ion-exchange, 0.1 molar $Ga(NO_3)_3$ or $In(NO_3)_3$ solutions were applied. The liquid phase ion-exchange was performed at 353 K with the exchange suspension stirred overnight followed by centrifugation. The procedure was repeated three times using the wet cake and fresh solutions. The solid material was subsequently washed nitrate free with double distilled water and dried in a desiccator at ambient temperature. The samples produced by this method are denoted as Ga(l)-ZSM-5 and In(l)-ZSM-5. The degree of (liquid phase) ion-exchange of In was determined by UV-VIS spectroscopic analysis of the solutions measuring the absorbance of the complex of In^{3+} with 8-hydroxyquinoline at 396 nm.

For the solid state ion-exchange Ga_2O_3, In_2O_3 or $InCl_3$ was carefully mixed with H-ZSM-5 zeolite in an agate ball-mill. These mechanical mixtures were heated to 800 K in a nitrogen atmosphere and baked at this temperature for 12 h. After cooling to room temperature the samples were rehydrated in an adhumator. The samples prepared are denoted as Ga_2O_3/ZSM-5, In_2O_3/ZSM-5 and In(s)-ZSM-5.

For checking the crystallinity of the prepared catalyst precursors X-ray diffraction and IR spectroscopy in the framework vibration region were used. XRD patterns were collected from well-powdered samples applying a DRON3 diffractometer. For IR analysis KBr pellets with 0.25% zeolite content were pressed and analyzed by a Mattson Genesis FTIR spectrometer.

BET measurements were used for monitoring the effect of ion-exchange and pretreatments. Adsorption isotherms of nitrogen were measured in a wide equilibrium pressure range at 77 K. The BET surface area was selected as a measure of the adsorption capacity of the catalyst precursors. Preceding the measurements the samples were pretreated at 723 K for 3 h in vacuum.

Acidity of the samples was determined by pyridine adsorption monitored by IR spectroscopy. For this purpose self-supported wafers with a thickness of 10 mg/cm^2 were pressed and placed into the sample holder of the IR cell.

The wafers were degassed at 723 K for 3 h in vacuum (the final vacuum was less than 10^{-4} Pa). After cooling to room temperature the background spectrum was registered followed by adsorption of 10 Torr (1333 Pa) of pyridine. Samples were treated in the presence of pyridine vapour for 1 h at 473 K followed by evacuation at the same temperature. Spectra of adsorbed pyridine were registered at room temperature.

The conversion of propane as test reaction was studied in a fixed-bed flow reactor in the presence or absence of oxygen. Catalyst samples (0.5 g) in a quartz tubular reactor were pretreated in nitrogen flow at 773 K for 2 h to standardize the catalyst surface. In some cases reductive pretreatment with a flow of 1:1 = N_2:H_2 was utilized under identical conditions.

In the catalytic measurements the total gas flow rate in the reactor was 120 cm^3 s^{-1}, ensuring a contact time was of 0.5 s. The inlet gas composition were 20% C_3H_8 + 80% N_2 or 20% C_3H_8 + 20% O_2 + 60% N_2 at atmospheric pressure.

Product analysis was performed by an on-line GC (CHROM-5 equipment) using a Porapack-Q column for the analysis of gaseous products, and a Shimadzu GC-16A chromatograph with a 30 m long SPB-1 capillary column for the analysis of the liquid phase products collected during the 2 h runs. The normalized amounts of products were calculated on carbon basis, with carbon mass balances being accurate within 5–8%. This deficiency may be attributed to coke formation.

3. Results

3.1. Catalyst characterization

The composition of the samples used in this study is summarized in Table 1. The UV-VIS method used to determine the level of conventional ion-exchange indicated that In^{3+} occupied 40% of ion-exchange positions of the parent zeolites.

Table 1
Physical properties of the catalyst

Sample	M_2O_3 content (mass %)	BET area (m^2/g)	I_{550}/I_{450} ratio
Ga_2O_3	100	65	
In_2O_3	100	69	
H-ZSM-5		336	0.89
Ga(l)-ZSM-5	1.1	302	0.90
Ga_2O_3/ZSM-5	5.0	313	0.93
In(l)-ZSM-5	1.5	338	0.89
In_2O_3/ZSM-5	5.0	323	0.86
In(s)-ZSM-5	4.8	299	0.85

The BET data listed in the third column of Table 1 show that no significant change in the zeolite structure occurred upon treatments used to prepare catalyst precursors (the small decrease for the In(s)-ZSM-5 sample is insignificant). In contrast with the finding of Parvulescu et al. [24] no change in the shape of nitrogen isotherms was observed. This shows that ion-exchange did not result in the formation of secondary pore systems.

Powder X-ray diffraction measurements revealed no structural change, i.e. no loss of crystallinity was observed.

In the fourth column the ratio of the integrated areas of the absorption bands at 550 and 450 cm^{-1} are to be seen. These bands are regarded as structure sensitive vibrations. Their ratio, consequently, can be used for the characterization of the ZSM-5 structure [25,26]. The data presented show only small deviations around the average figure that is 0.89.

In Fig. 1 the spectra of Ga and In modified ZSM-5 zeolites exhibiting some remarkable features are shown. The first is the absence of the respective oxide phases in the solid state exchanged materials; it might be due to the very little size of the oxide phases. This finding is in accordance with the X-ray results. Second, the band generally appearing around 920–970 cm^{-1} assumed to be the indication of successful isomorphous substitution [27] is present only in the Ga_2O_3/ZSM-5 sample. It should be stressed already here, however, that according to a different assignment, the band at around 930 cm^{-1} is due to framework vacancies [28].

Fig. 2 shows the spectra in the range of OH vibrations of catalysts pretreated at 723 K in vacuum for 3 h. In Fig. 2A spectra of materials prepared by conventional ion-exchange are depicted. It is clearly seen that considerable changes took place for both the In^{3+} and Ga^{3+} forms upon ion-exchange since very intense bands appeared at 3608 cm^{-1} characteristic of Si–(OH)–Al bridged OH groups [29]. The intensity of this band is much stronger for these samples than for the parent H-ZSM-5 zeolite (spectrum c). A small shift from 3745 to 3730 cm^{-1} in the position of the Si–OH band due to terminal silanol groups can also be observed. In addition, new intense absorption developed at 3666 cm^{-1} for Ga(l)-ZSM-5. Bands in this spectral region are assigned to vibrations of OH groups linked to extraframework species.

The sample prepared by solid state ion-exchange gives very similar spectra taken after treatment in oxygen at 723 K for 3 h (Fig. 2B). Here, the band due to the Si–(OH)–Al bridged OH groups is very intense for H-ZSM-5, less intense for In_2O_3/ZSM-5, even smaller for In(s)-ZSM-5 and the weakest for the Ga_2O_3/ZSM-5 sample. For each zeolite, an indication is seen for the presence of OH groups attached to extraframework species. The Si–OH band is centered at 3745 cm^{-1} for H-ZSM-5 whereas it appears at 3730 cm^{-1} for In_2O_3/ZSM-5. Spectra registered after hydrogen treatment (723 K, 3 h) show fundamental dissimilarities (Fig. 2C). The spectra of H-ZSM-5 and Ga_2O_3/ZSM-5 taken after treatment either in reductive or oxidative atmosphere are quite similar. However, this is not the case for the indium containing materials. For In_2O_3/ZSM-5, after reductive treatment both the bridged OH band at 3608 cm^{-1} and the OH absorption due to extraframework species are intense. It is also obvious that two Si–OH bands can be distinguished in the spectrum at 3745 and 3730 cm^{-1}. The spectrum of the In(s)-ZSM-5 sample does not show the absorption of bridged OH groups and only a small band appears at the position of OH groups attributed to extraframework species. On the basis of spectral features of the OH groups substantial differences should be expected for the acidity of the samples prepared and pretreated in different ways.

It is well-known that the bands centered at 1450 and 1540 cm^{-1} can be used to calculate Brönsted and Lewis acidity. Figs. 3 and 4 show

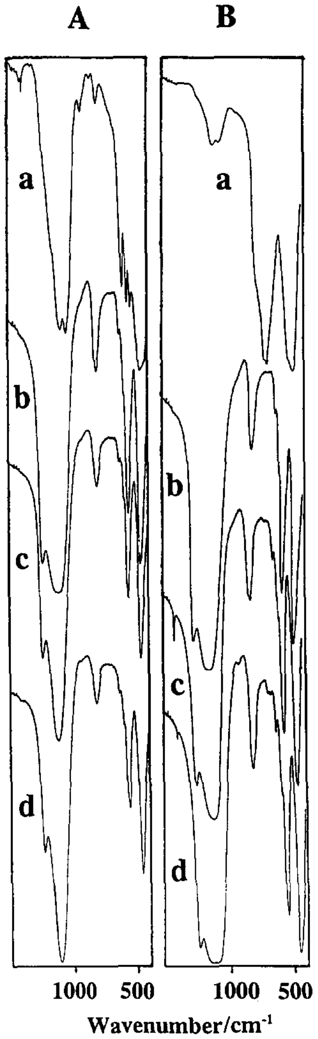

Fig. 1. IR spectra of modified zeolites in the framework vibration range. Indium containing samples (A): a, In_2O_3; b, In(l)-ZSM-5; c, In(s)-ZSM-5; d, In_2O_3-ZSM-5. Gallium containing samples (B): a, Ga_2O_3; b, H-ZSM-5; c, Ga(l)-ZSM-5; d, Ga_2O_3-ZSM-5.

the spectra of pyridine adsorbed on gallium and indium containing samples pretreated in oxygen or hydrogen. For comparison the spectrum of pyridine adsorbed on the parent H-ZSM-5 is also inserted. Conspicuous, the high concentration of Lewis acid sites of Ga_2O_3/ZSM-5 pretreated in hydrogen (Fig. 3, spectrum a). For the Ga(l)-ZSM-5 sample, the ratio of the two different acidities is roughly equivalent while on H-ZSM-5 more Lewis than Brönsted acid sites are present as can be concluded from the areas of the bands centered at 1450 and 1540 cm^{-1}.

The spectra of indium containing zeolites taken after treatment in oxygen (at 723 K for 3 h) are displayed in Fig. 4. An interesting trend, the increase in Lewis acidity is seen going from the conventionally ion-exchanged In(l)-ZSM-5, to the solid phase ion-exchanged In_2O_3/ZSM-5 and In(s)-ZSM-5 specimens shown by the integrated peak areas at 1450 cm^{-1}.

Acidity data calculated from the integral absorption of pyridine spectrum taken after either oxidative or reductive pretreatment of the zeolite samples are collected in Table 2. For these calculations, absorption coefficients for pyridine bonded to Brönsted and Lewis sites were taken from the work of Take et al. [30]. The data show that both preparation and pretreatment conditions have fundamental influence on the acidic character of the modified zeolites. The concentration of Brönsted acid sites proved to be the highest for In(l)-ZSM-5 and the lowest for Ga_2O_3/ZSM-5 both pretreated in hydrogen. As Lewis acidity is concerned, the highest value was found for Ga_2O_3/ZSM-5 pretreated in hydrogen, while the lowest concentration was exhibited by Ga(l)-ZSM-5 pretreated in oxygen.

3.2. Propane transformation

The conversion and selectivity data of the propane transformation in the presence of dioxygen in 2 h runs can be seen in Figs. 5 and 6.

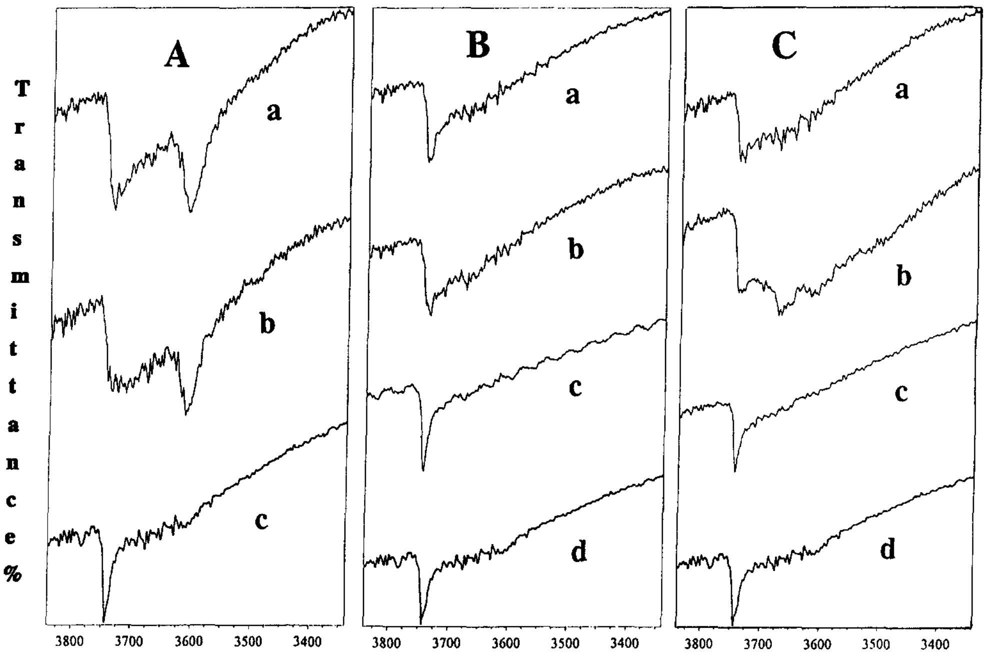

Fig. 2. IR spectra of modified zeolites in the OH vibration region. Conventional ion-exchange samples (A): a, In(l)-ZSM-5; b, Ga(l)-ZSM-5; and c, the parent H-ZSM-5. Solid state ion-exchanged samples after oxidative (B) and reductive (C) treatments: a, In_2O_3/ZSM-5; b, In(s)-ZSM-5; c, Ga_2O_3/ZSM-5; d, the parent H-ZSM-5.

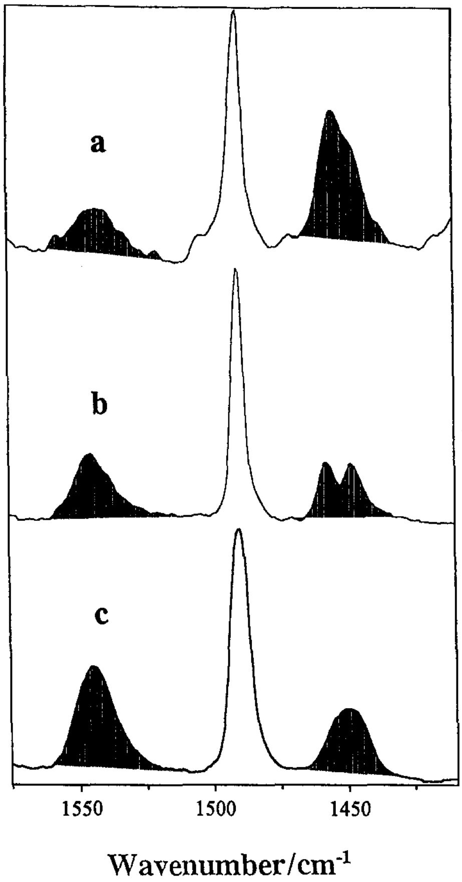

Fig. 3. IR spectra of pyridine absorbed on gallium containing samples prepared by reductive treatment: a, Ga_2O_3/ZSM-5; b, Ga(l)-ZSM-5; and c, H-ZSM-5.

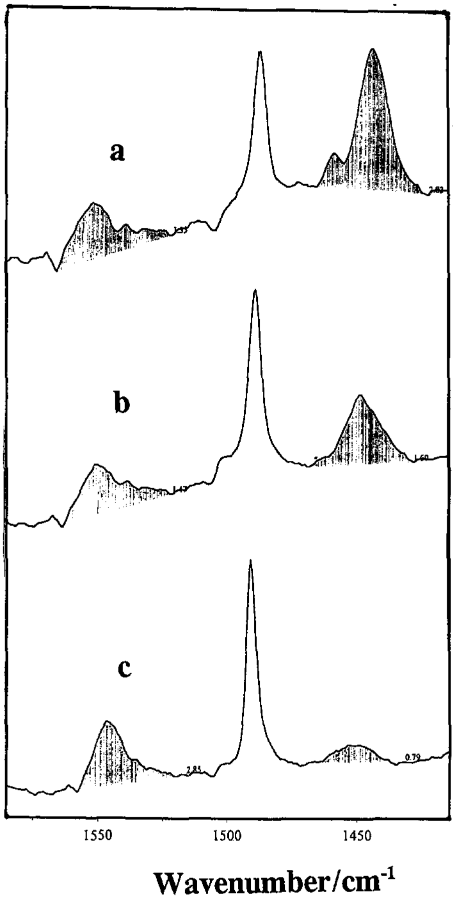

Fig. 4. IR spectra of pyridine adsorbed on indium containing samples prepared by oxidative treatment: a, In(s)-ZSM-5; b, In_2O_3/ZSM-5; c, In(l)-ZSM-5.

Below 673 K the conversion of propane cannot be detected at all. In contrast, comparable rates could be determined at 773 K on all the catalysts tested. In the absence of O_2, propane conversion was lower in each case than in the presence of oxygen, and relatively fast catalyst deactivation was observed. In contrast, the presence of O_2 results in a considerably increase in catalyst lifetime. This is due to the removal of the surface coke layer in the form oxygen containing compounds (mainly carbon oxides).

Table 2
Summary of acidity data

Sample	Brönsted (mmol/g)		Lewis (mmol/g)		Brönsted/Lewis acidity ratio	
	oxid	red	oxid	red	oxid	red
H-ZSM-5	0.071	0.071	0.081	0.081	0.87	0.87
Ga(l)-ZSM-5	0.121	0.131	0.042	0.085	2.88	1.54
Ga_2O_3/ZSM-5	0.079	0.045	0.131	0.987	0.60	0.05
In(l)-ZSM-5	0.219	0.237	0.053	0.078	4.13	3.04
In_2O_3/ZSM-5	0.113	0.147	0.113	0.102	1.00	1.44
In(s)-ZSM-5	0.102	0.085	0.189	0.143	0.54	0.59

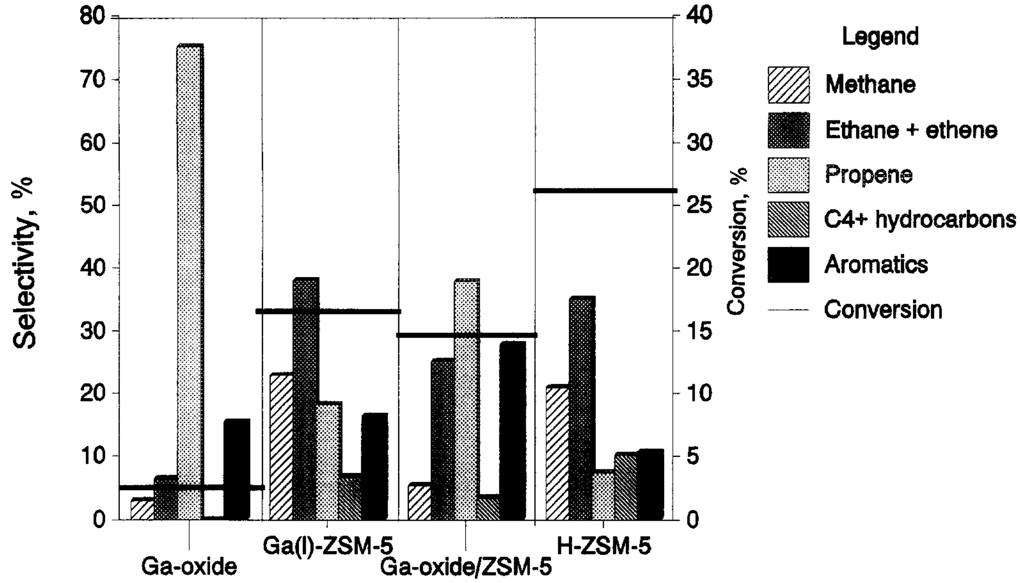

Fig. 5. Product distribution of propane transformation over Ga-containing zeolites at 773 K reaction temperature.

The activity of pure oxides (Ga_2O_3 and In_2O_3) is very low, even in the presence of oxygen, and the main reactions are propane dehydrogenation and benzene formation.

Over H-ZSM-5 the main products are methane, ethane and ethene, and aromatization takes place only to a relatively small extent. An almost uniform aromatic distribution in the C_6–C_9 range is detected. The deficiency of the mass balance can be explained by strong coke formation.

In accordance to the literature results [31,32] (Fig. 5) increasing dehydrogenation and aromatization selectivity could be realised by addition

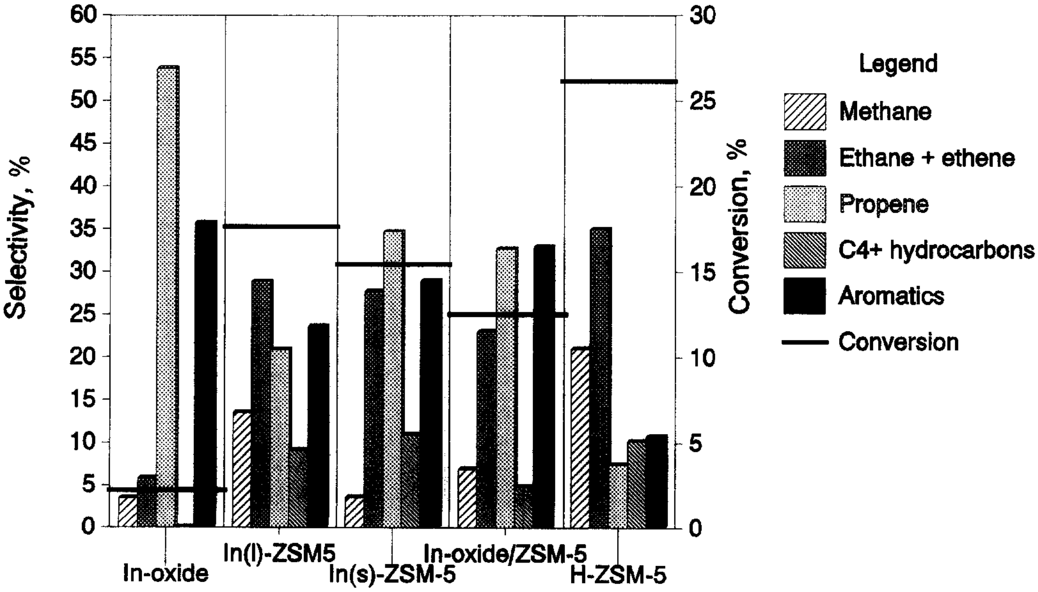

Fig. 6. Product distribution of propane transformation over In-containing zeolites at 773 K reaction temperature.

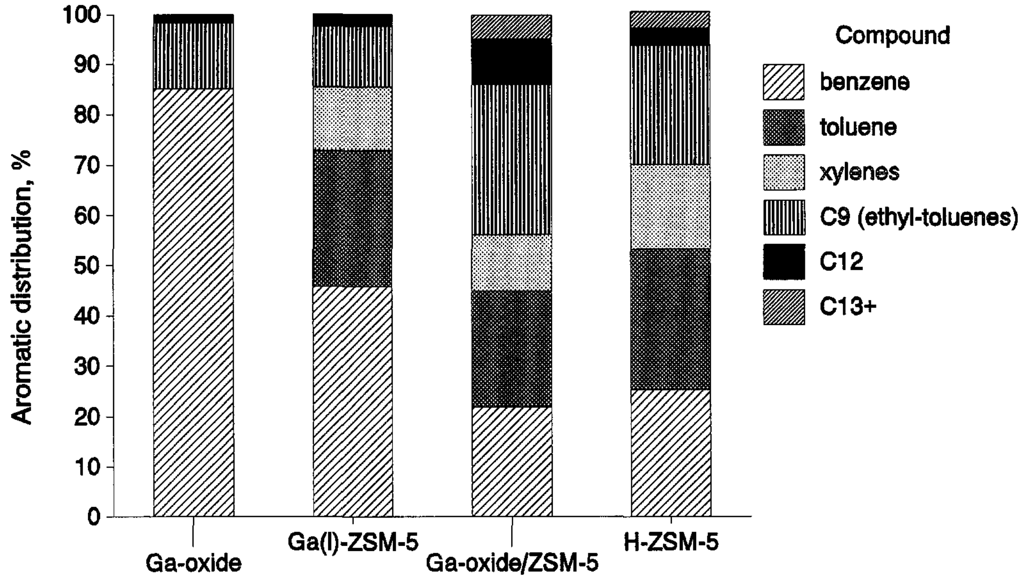

Fig. 7. Aromatic distribution in the propane reactions over Ga-containing catalysts.

of gallium to H-ZSM-5. This effect is the most characteristic of the Ga_2O_3/ZSM-5 sample, where the aromatic selectivity is close to 30% with considerable C_9 formation. The product distribution over Ga(I)-ZSM-5 is similar to that observed over the original H-ZSM-5 with approximately the same conversion.

Our earlier investigations revealed [33,34], the activity of indium containing samples is nearly the same as that of the gallium containing ones prepared in the same way.

The highest aromatic selectivity could be observed over In_2O_3/ZSM-5. The high propene yield on this catalyst proves that In^{3+} ions

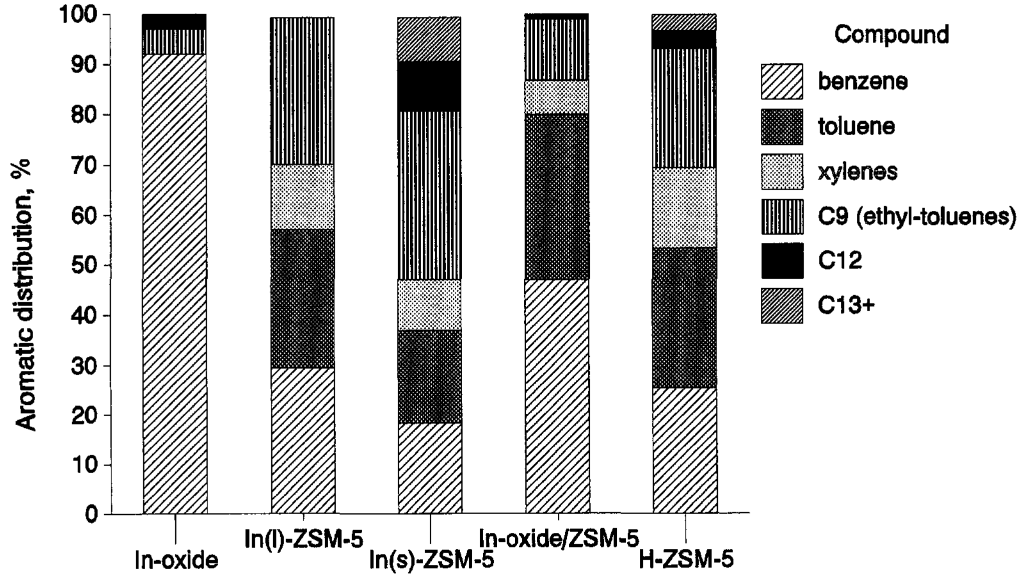

Fig. 8. Aromatic distribution in the propane reactions over In-containing catalysts.

enhance the dehydrogenation activity of the catalyst.

The distribution of aromatic products are shown in Figs. 7 and 8. Over the pure oxides benzene forms almost exclusively, while the zeolite catalysts promote the formation of alkylbenzenes up to C_{15}. Approximately 50% C_{9+} selectivity (within the aromatic fraction) is characteristic of Ga_2O_3/ZSM-5 and In(s)-ZSM-5 samples. High BTX selectivity can be observed over the catalysts prepared by conventional ion-exchange and on In_2O_3/ZSM-5.

The reductive pretreatment did not change the properties of the Ga(l)- and In(l)-ZSM-5 catalysts at all. In contrast, higher activity and higher aromatic selectivity could be found in the initial period of the runs (first 10 to 20 min) over catalysts prepared by the solid state ion-exchange methods. However, after this initial difference, the behaviour of the In-containing catalysts were the same as the ones pretreated by the usual method due to the oxidative reaction conditions. The effect of this pretreatment during the entire reaction is characteristic only of the Ga_2O_3/ZSM-5 sample.

4. Discussion

The catalytic aromatization of light paraffins over zeolites is usually related to the acidic properties and the shape selectivity effects of the catalysts. The acidic properties of ZSM-5 zeolite has been extensively studied. However, the effect of acidity modification on catalytic activity is still not clear. Consequently, any attempt to find correlations should be an important contribution in this field.

For interpretation of the IR spectra the first step is to account for the origin of the band at 963 cm^{-1}, which is not an easy task. This band is clearly visible in the spectrum of Ga_2O_3/ZSM-5, but only some indications are to be seen in the spectra of the other zeolites.

The appearance and the intensity of the band at 930–960 cm^{-1} are regarded, respectively, as the indication and extent of modification of structural units in zeolites. This band is generally appears in metal silicates irrespective to whether they are prepared by direct synthesis or postsynthesis treatment. Several authors recently assigned the band at 930–960 cm^{-1} as an indication of the successful isomorphous substitution of framework aluminum occurring upon solid state ion-exchange [9,35–37]. More than a decade ago, the band at 960 cm^{-1} was attributed to framework vacancies generated upon dealumination of mordenite type zeolites. It was also demonstrated that the intensity of this band increases with the concentration of aluminum removed from the framework. Oxihalides, non-metal and even metal chlorides were utilized as dealuminating reactants [28,38]. Recently, Namba et al. reported the ''atom-planting procedure'' in which metal chloride vapours were passed through a zeolite bed at elevated temperature [39], resulting in isomorphous incorporation. It is remarkable that others used the same procedure for dealumination of zeolites leading to the removal of the aluminum from the framework of zeolites [28]. Karge in his plenary lecture in Leipzig did not mention the appearance of a band in this region as a consequence of solid state ion-exchange performed for numerous metal ions [15]. These results clearly reveal that the precise assignment of the band at 930–960 cm^{-1} is ambiguous as concluded Vedrine [40]. It is also our opinion that a single band cannot be used as a rigorous experimental proof to indicate isomorphous substitution nor measure its extent.

The problem of band intensity at 550 cm^{-1} or the ratio of the optical density of bands at 600–550 and 480–450 cm^{-1} should also be discussed. A method to compare the intensity of bands at 550 and 450 cm^{-1} in the spectra of ZSM-5 zeolites was first suggested by Coudurier et al., in order to obtain a measure for the crystallinity of zeolites [25]. They suggested to use 0.72 as a limiting ratio. Samples characterized by higher value are regarded as well-crystallized, whereas lower values are considered to characterise poor crystallinity. In our practice this fast and simple qualification of zeolites proved to be successful. Our experience shows, however, that this intensity ratio cannot be directly used for indication or measure for isomorphous substitution or effective incorporation of various elements in the framework position of zeolites as suggested by several authors [41,42]. In our opinion, the high values of this ratio are characteristic of the completely or well-crystallized zeolites, which also requires the realization of perfect incorporation of the entering atoms.

Corresponding to literature the data of Table 2 clearly prove that Ga and In differ extensively in their response to reductive treatment. Kanazirev et al. [41] showed that Ga_2O_3 reduction required at least 450°C, and the product was Ga^+ which was able to migrate into the zeolite and replaced the proton. In_2O_3, however, requires only 300°C or so for onset of reduction [43]. If reduction temperature of 450°C (or above) is applied, In^0 may form which cannot replace protons as Ga^+ does (see Brönsted/Lewis acidity ratio of Table 2).

Both spectroscopic methods give useful values for comparing the characteristics of zeolites, however, the use for drawing structural conclusion may lead to misunderstandings.

On the basis of the measured concentration of Brönsted and Lewis acid sites on the zeolites, the samples may be ordered into the following main groups.

(i) Highly Brönsted acidic samples, in which Brönsted acid sites predominate over Lewis ones. These are the specimens prepared by conventional ion-exchange procedure [Ga(l)-ZSM-5, In(l)-ZSM-5].

(ii) The H-ZSM-5 sample, which possesses somewhat higher Lewis than Brönsted acidity. It is noteworthy, that the overall acidity does not change after oxidative or reductive treatment.

(iii) In the solid state ion-exchanged materials, the relative amounts of Lewis acidity is higher than Brönsted acidity. Pretreatment conditions were shown to affect the acidity of these samples. The behaviour of Ga_2O_3/ZSM-5 and that of In_2O_3/ZSM-5 and In(s)-ZSM-5 was different. For the former the reductive treatment resulted in gradual increase of Lewis acidity, whereas for the indium containing samples only a slight increase was detected.

The aromatization of propane and butane takes place via general mechanism suggested in the literature [3–5,44]. According to this mechanism alkane molecules are first dehydrogenated to olefins which are then dimerized or oligomerized to form higher hydrocarbons followed by cyclization and aromatization.

The activation of olefins is characteristic of pure oxides and the mixed oxide catalysts used for selective oxidation processes [45]. The olefin dehydrogenation and dimerization steps, accordingly take place over the Ga^{3+} or In^{3+} centers of the catalysts. The centers are assigned to surface gallium or indium species, therefore they should play considerably role only in the further reaction of propene. Rapid paraffin dehydrogenation could be observed only on the samples prepared by solid state reactions with predominating Lewis acid character. Consequently, the first step of alkane activation should involve Lewis acid sites appearing via the formation of carbonium ions. IR measurements prove the presence of these centers are characteristic of Ga_2O_3 or In_2O_3 containing samples and these samples possess the highest aromatic selectivity.

Dehydrogenation and the coupling of the intermediates formed by dehydrogenation could be accounted for by isolated Ga_2O_3 or In_2O_3 assemblies with Lewis acidic character in the zeolite structure [43,46,47], whereas further steps resulting in the formation of benzene and alkylaromatics take place over the zeolite. Brönsted acid sites result in cracking the hydrocarbon molecules and the probable alkylation of the aromatic ring. Synergism, namely intimate contact between the oxide "particles" and the acidic sites of the ZSM-5 structure can be assumed as active sites for the dehydrogenation and aromatization of alkanes.

The increasing activity and aromatic selectivity caused by reductive pretreatment is really effective in the case of Ga_2O_3. It can be explained by the migration of the Ga^{x+} ions to the ion-exchange positions in the zeolite structure and their interaction with Brönsted acid sites. This interaction causes the decrease in Brönsted acidity with simultaneous increase in Lewis acidity. Since the mobility of the larger In ions is limited, the dispersion of In_2O_3 is much smaller and the indium oxide/zeolite assemblies can only be found on the outer surface of the zeolite particles.

5. Conclusions

(i) In-containing ZSM-5 zeolites prepared by different ion-exchange methods are active catalysts in the transformation of propane. Activities are comparable with those of similar Ga-containing samples.

(ii) The acidic character of the samples may be controlled by the ion-exchange procedure and the pretreatment methods.

(iii) High cracking activity is characteristic of the catalysts with high surface Brönsted acidity, while the catalysts having Lewis acidity are effective in the dehydrogenation and aromatization reactions.

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