Propane as alkylating agent for benzene alkylation on bimetal Ga and Pt modified H-ZSM-5 catalysts: FTIR study of effect of pre-treatment conditions and the benzene adsorption

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Abstract

FTIR spectroscopy was used to study the influence of pre-treatment on OH groups of H-ZSM-5, Ga-ZSM-5, Pt-ZSM-5 and GaPt-ZSM-5 catalysts and the confinement of benzene molecules in these catalysts pre-treated under different conditions. Types of the hydroxyl groups in GaPt-ZSM-5 and Ga-ZSM-5 are very sensitive to the pre-treatment of the samples. Besides the IR bands at 3745, 3665 and 3612 cm^{-1} assigned to terminal silanol Si–OH, OH group attached to extra-framework aluminum and bridged Si–(OH)–Al groups, respectively, gallium loaded samples show additional IR band at 3699 cm^{-1} which has been attributed to OH groups attached to Ga, such as $Ga_2(OH)_xO_{3-x}$. Dose-dependent measurements have shown that upon benzene loading of 1.7 molecules/u.c. (m/u.c.) for metal modified H-ZSM-5, the reagent molecules are located in the channel intersection. Above 1.7 m/u.c., part of benzene molecules enter the straight or sinusoidal channels and form pseudo liquid phase. The formation of pseudo liquid phase begins at low benzene loading for H-ZSM-5 zeolite. With increasing concentration of benzene molecules in zeolite channels, each molecule undergoes perturbation from the surrounding molecules and framework, which leads to a modification in electronic state and in the dipole moment of different vibrations. Abnormal adsorption isotherms for pure zeolite and gallium loaded samples have been correlated with this modification. This effect is not observed for Pt loaded samples, probably due to possible adsorption of benzene molecules on platinum particles dispersed on the external surface of zeolite crystals. The present paper provides important information on the effect of pre-treatment on the state of active species and the confinement and interaction of benzene molecules in a series of modified H-ZSM-5 catalysts.
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Keywords: Pre-treatment; H-ZSM zeolite; Modification by Ga and Pt; FTIR study; Ga species; OH groups; Confinement of benzene molecules

1. Introduction

Light alkanes such as methane, ethane, propane and butanes are among the most abundant and inexpensive hydrocarbons available today. Their scientific utilization is one of the most challenging subjects for

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21st century. There has been no efficient commercial process for alkylation of aromatics by using light alkanes up to now. It has been reported that pure propane can be dehydrocyclized and activated on Ga-containing MFI catalyst [1]. Different works were realized to find the efficient catalyst for alkylation of benzene with propane for highly added valuable aromatics. The attention was mainly focused on H-ZSM-5 zeolite usually modified by single metal species as Ga, Pt, and Zn [2–15]. Incorporation of Pt in the MFI catalysts resulted in a significant increase of the overall conversion and selectivity to propylbenzenes [8]. The presence of Pt can also reduce the coke formation, because of its role of the entrance of H_2 spill-over. It is well known that Pt has high activity for dehydrogenation of paraffines, but it is also active hydrogenolysis catalyst. While Ga is assumed to have moderate or low activity in the hydrogenolysis. It is therefore of important interest to examine the effect of a bimetallic combination of Pt and Ga to modify H-ZSM-5 in alkylation of benzene with propane.

It is the common point of view of the catalysis community that the pre-treatment conditions will strongly affect the catalytic behavior of catalysts in the reaction. The choice of the pre-treatment conditions is therefore crucial. It is also well known that two elemental steps occur in the catalytic processes based on zeolites: the diffusion of reactants or products within cavities of zeolites and their adsorption on active sites. The understanding the host–guest interaction may lead to a better knowledge on the reaction mechanism and to developing new highly selective catalysts.

The aim of our investigation is the preparation of catalysts with high activity and selectivity in the benzene alkylation with propane as alkylating agent, using a combination of Pt and Ga in H-ZSM-5 zeolites. The present paper deals with the first part of our work concerning the changes in active sites and the identification of the different Ga species in a series of Ga and Pt modified ZSM-5 catalysts upon different pre-treatment conditions. We try to shed some light in molecule level on to reagent–catalysts interaction and to establish the relation between pre-treatment, chemical states of catalysts, their catalytic properties and the confinement of reagent molecules to find the best pre-treatment conditions of catalysts for catalytic reactions.

2. Experimental

2.1. Sample preparation

Na-ZSM-5 zeolite was prepared in our laboratory using hydrothermal synthesis method according to the procedure described in the literature [16]. Aluminium nitrate (Riedel de Haen; 98.5%), Aerosil, NaOH (Merk) and tetrapropylammonium bromide (TPAB) as template agent were used. The as-synthesised zeolite was calcined under N_2 flow from room temperature up to 773 K with heating rate of 2 K/min and then under air flow for 6 h to burn off the organic template in order to obtain Na-ZSM-5. The calcined zeolite was ion-exchanged with ammonium chloride during 3 h at room temperature to obtain NH_4^+ form. This procedure was repeated three times. The proton form (H-ZSM-5) was obtained after deammonization (calcination in O_2 during 5 h at 773 K).

The gallium incorporation in the zeolite was performed by ion exchange using aqueous solution of gallium nitrate (Aldrich, 99.9% purity) at a concentration of 0.05 M. The pH was adjusted to 2–2.5 by adding diluted HCl. The mixture was stirred and refluxed for 3 h at 353 K. The exchange was followed by filtering, washing with demineralized water, drying and calcination in air 10 h at 573 K.

Platinum was introduced in to H-ZSM-5 or Ga-ZSM-5 by ion exchange using a dilute aqueous solution (5×10^{-3} M) of Pt $(NH_3)_4$Cl salt. The suspension was stirred at room temperature for 24 h and then filtered. The filtrate was washed with abundant bi-distillated water to free of Cl^- ions and dried overnight at 373 K. The samples were calcined in O_2 flow by increasing temperature from room to 473 K with heating rate of 2 K/min and then under the same atmosphere 2 h at this temperature. To provide high dispersion of Pt particles, the reduction of platinum containing catalyst was made by a special procedure: first temperature was increased from room to 573 K with a rate of 2 K/min, followed by a rate of 1 K/min to 673 K. The reduction in hydrogen atmosphere was then carried out at 673 K for 1 h.

2.2. Sample characterization

Bulk compositions of materials were obtained by chemical analysis. X-ray diffraction (XRD) patterns

Table 1
Description on pre-treatment conditions of samples

Sample	Pre-treatment
H-ZSM-5	Evacuation 2 h at 673 K
Ga-ZSM-5Ox	Oxidation 6 h at 723 K in air flow and evacuation 2 h at 673 K
Ga-ZSM-5R	Reduction 2 h at 673 K in H_2 flow
Ga-ZSM-5E	Evacuation 2 h at 723 K
Ga-ZSM-5EOx	Evacuation 2 h at 723 K and then oxidation in air 6 h at 723 K
GaPt-ZSM-5Ox	Oxidation 6 h at 723 K in air flow and evacuation 2 h at 673 K
GaPt-ZSM-5OxR	Oxidation 6 h at 723 K in air flow, evacuation 2 h at 673 K and reduction in H_2 flow
GaPt-ZSM-5R	Reduction in H_2 flow
Pt-ZSM-5	Reduction in H_2 flow

were collected on a Philips PW3710 diffractometer using Cu Kα radiation. Crystallinity was calculated by summation of the intensity of eight diffraction peaks at values of 2θ equal to 7.875, 8.800, 9.05, 23.05, 23.675, 23.900 and 24.350° [17]. As a reference was used the as-synthesized Na-ZSM-5.

IR spectra in the framework vibrations region were recorded to check the crystallinity and the nature of materials using Perkin-Elmer FT spectrum 2000 and KBr wafer technique. Solid state ^{29}Si and ^{27}Al MAS NMR spectra were collected on Bruker MSL-400 spectrometer.

Brönsted acidity was determined by TPD of ammonia [18]. Prior to NH_3-TPD analysis the samples were exchanged with ammonia buffer solution (NH_4Cl/NH_3, pH = 9.5, 1 M). Thermal analysis was performed using Setaram TG–DTG DSC111 thermobalance coupled with automatic ammonia Metronm titrator. About 50 mg of the sample were heated from

293 to 923 K at the rate 5 K/min under dry helium flow. The ammonia formed was automatically titrated with sulfonic acid solution (3.32×10^{-3} M).

For IR investigation of benzene adsorption, a self-supported wafer from different samples were prepared and placed in a Pyrex IR cell with NaCl windows. All procedures of pre-treatment were conducted in situ. Pre-treatment procedures are given in Table 1.

3. Results and discussion

3.1. Characterization of prepared samples

The chemical composition of starting zeolite after removal of template agent by calcination is $Na_{4.7}[Al_{4.7}Si_{91.3}O_{192}]$ with Si/Al = 19.6 (Table 2). The prepared catalysts were well crystallized according to XRD (Fig. 1) and IR data (Fig. 2 and Table 2). XRD patterns, the morphology studied by SEM (Fig. 3) and IR spectrum are closely similar to those reported elsewhere for ZSM-5 materials. Gallium and platinum incorporation did not induce any changes in the morphology. Chemical composition by elemental analysis and NMR technique, crystallinity deduced from X-ray and IR data and Brönsted acidity determined by TPD of NH_3 of all the prepared catalysts are collected in Table 2.

Fig. 4 reports the ^{27}Al MAS NMR spectra of pure zeolite and Ga modified H-ZSM-5. Sharp signal at 54 ppm is assigned to the tetrahedral co-ordinated framework Al. Very low intensity signal at 0 ppm observed after gallium deposition and calcination is attributed to the octahedral extra-framework Al. This result indicates that in Ga modified samples a very slight dealumination during the preparation occurred

Table 2
Physico-chemical characteristics of catalyst samples

Sample	RC	I_{450}/I_{550}[a]	NH_3/u.c.[b]	Ga[c] (wt.%)	Pt[c] (wt.%)	Si/Al NMR	Si/Al[c]
H-ZSM-5	100	0.7	3.34	–	–	21	19.5
Ga-ZSM-5	97	0.7	2.98	0.37	–	–	19.6
Pt-ZSM-5	98	0.67	2.24	–	0.57	–	19
GaPt-ZSM-5	98	0.68	3.07	0.35	0.55	–	17

RC: relative crystallinity.

[a] Ratio of the optical density of the bands located at 450 and 550 cm^{-1} (I_{450}/I_{550} = 0.8 for 100% crystallinity).

[b] Total number of NH_3 described per unit cell.
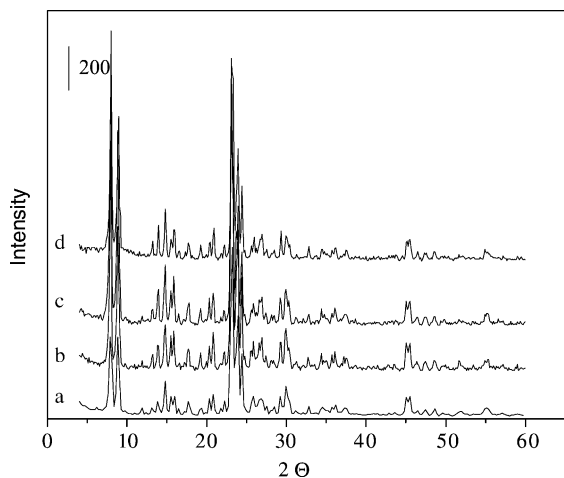
[c] Elemental analysis.

Fig. 1. XRD spectra of different samples: (a) Na-ZSM-5; (b) H-ZSM-5; (c) Ga-ZSM-5 and (d) PtGa-ZSM-5.

leading to the presence of a small amount of extra-framework Al species in the channels of zeolites.

3.2. FTIR study of OH groups of catalysts under various pre-treatments

Figs. 5 and 6 show the infrared spectra in the range of stretching OH vibrations of the H-ZSM-5 (Fig. 5a),
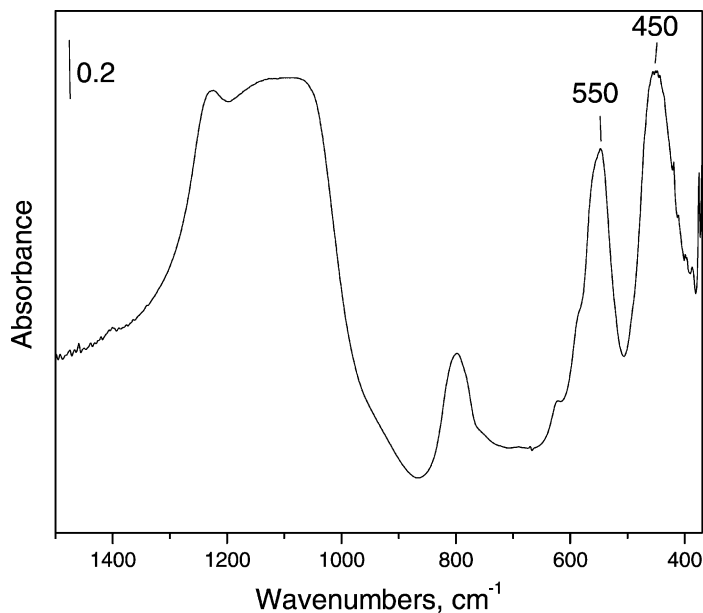
Table 3
IR relative absorbancy of samples at $3612\,cm^{-1}$

Sample	Relative absorbency of $3612\,cm^{-1}$ (A/mg)
H-ZSM-5	0.74 (Fig. 5a)
Ga-ZSM-5Ox	0.55 (Fig. 5b)
GaPt-ZSM-5Ox	0.59 (Fig. 6a)
GaPt-ZSM-5OxR	0.37 (Fig. 6b)
GaPt-ZSM-5R	0.78 (Fig. 6c)
Pt-ZSM-5	0.94

Ga-ZSM-5 (Fig. 5b–e) and GaPt-ZSM-5 (Fig. 6) catalysts. Table 3 reports the relative absorbencies of the IR band at $3612\,cm^{-1}$ determined for the samples, after a series of activation treatment.

H-ZSM-5 exhibits two intensive IR bands at 3745 and $3612\,cm^{-1}$ (Fig. 5a) and two shoulders at 3724 and $3665\,cm^{-1}$. They are assigned to terminal silanol Si–OH, bridged Si–(OH)Al groups, isolated internal silanols and OH groups linked to extra-framework aluminum, respectively [16,19,20]. The broad band in the rang of 3745–$2900\,cm^{-1}$ in all samples is attributed to hydrogen bond formed by the internal silanols.

Gallium modified H-ZSM-5 sample has very different behavior depending on the activation procedures. If the sample was pre-treated in air at 723 K
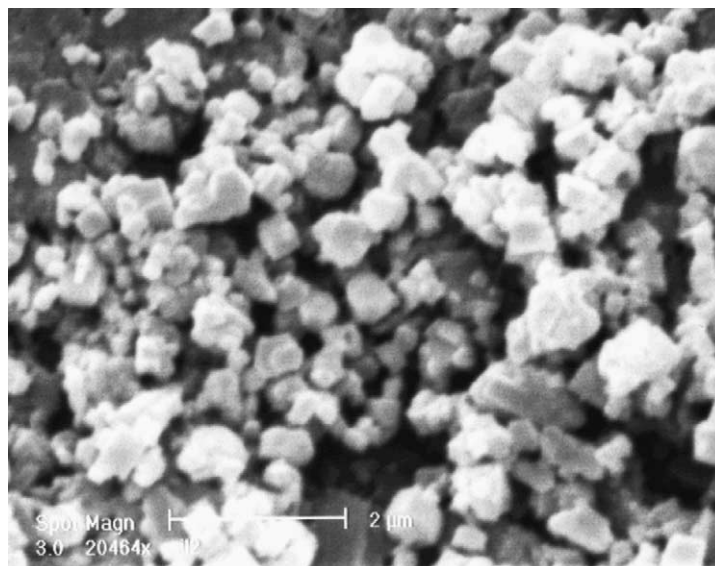

Fig. 2. IR spectrum of H-ZSM-5 zeolite.

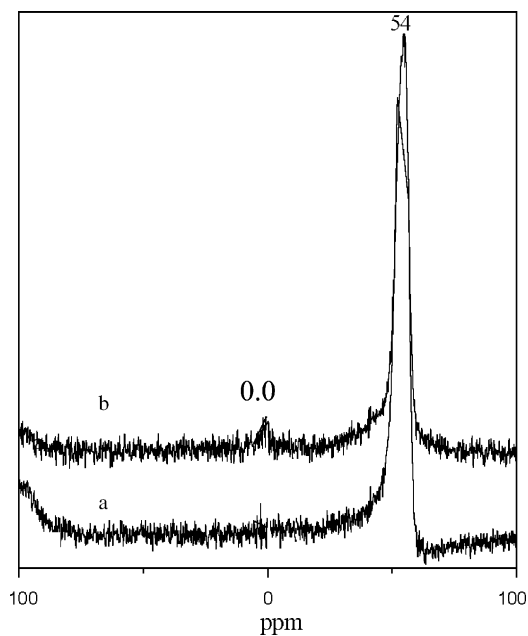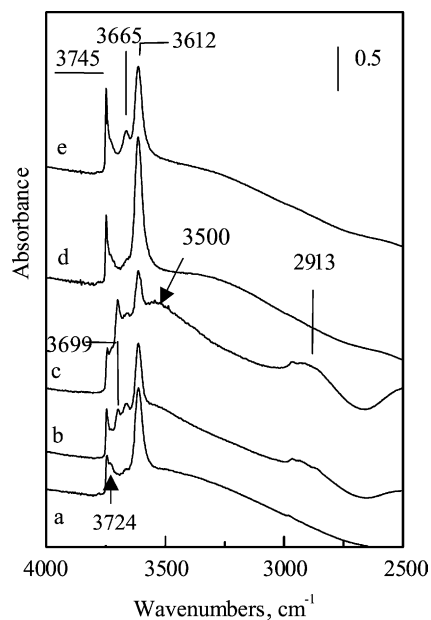Fig. 3. SEM photograph of the H-ZSM-5 sample.

Fig. 4. ^{27}Al MAS NMR spectra of (a) ZSM-5 and (b) Ga-ZSM-5 samples.

Fig. 5. Infrared spectra of Ga-ZSM-5: (a) H-ZSM-5 after evacuation 2 h at 673 K; (b) pre-treated in air 6 h at 723 K (Ga-ZSM-5Ox); (c) pre-treated in hydrogen flow 2 h at 673 K (Ga-ZSM-5R); (d) pre-treated in vacuum 2 h at 723 K (Ga-ZSM-5E) and (e) pre-treated in air 6h at 723K after (c) (Ga-ZSM-5EOx).
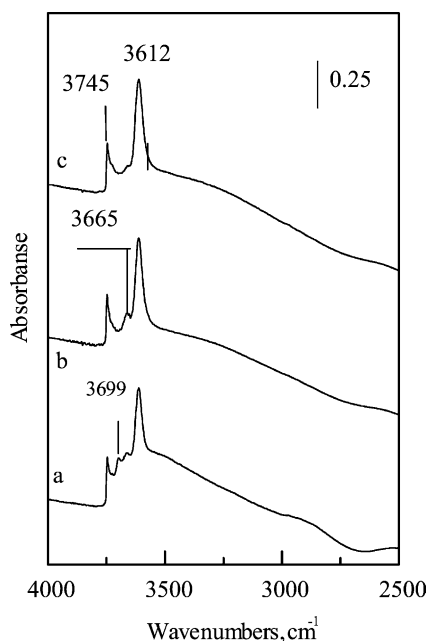
Fig. 6. Infrared spectra of GaPt-ZSM-5: (a) pre-treated 6 h in air at 723 K (GaPt-ZSM-5Ox); (b) pre-treated in hydrogen flow 2 h at 673 K after (a) (GaPt-ZSM-5 OxR) and (c) pre-treated only in hydrogen 2 h at 673 K (GaPt-ZSM-5R).

and then in vacuum at 673 K (Fig. 5b), the intensity of the peak at $3612 \, cm^{-1}$ is lowered compared with that of H-ZSM-5 sample. The vibration bands at 3745 and $3665 \, cm^{-1}$, are also present and a new vibration band at $3699 \, cm^{-1}$ is detected. When this sample is pre-treated directly in H_2 flow at 673 K (Fig. 5c), peaks at 3745, 3699, 3665 and $3612 \, cm^{-1}$ are still present. Only the intensity of peak at $3699 \, cm^{-1}$ becomes very intense and that of 3612 and $3745 \, cm^{-1}$ relatively low. In addition, two new broad bands centered at around 3500 and $2913 \, cm^{-1}$ appear. The vibration band at $3699 \, cm^{-1}$ disappears completely after pre-treatments at 723 K (Fig. 5d and e). It is very possible that the band at $3699 \, cm^{-1}$ is originated from OH groups attached to Ga, such as $Ga_2(OH)_xO_{3-x}$. In fact, it is well know that the OH groups of zeolite framework can be eliminated only at relatively high temperatures [21,22]. The complete elimination of OH groups at 723 K indicates that these groups are not directly linked to zeolite framework. The lower intensity of the peak at $3699 \, cm^{-1}$ after oxidation at 723 K (Fig. 5b) than that after reduction at 673 K

(Fig. 5c) is therefore very probably due to the partial dehydroxylation of $Ga_2(OH)_xO_{3-x}$. It is obvious that the sever pre-treatments can eliminate almost OH groups from such species to give an oxide form such as Ga_2O_3 (Fig. 5d and e).

Under reduction atmosphere, Ga species such as Ga_2O_3 can be reduced to lower oxidation degree state according to the reaction:

$$Ga_2O_3 + H_2 \rightarrow Ga_2O + H_2O$$
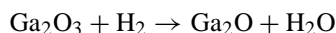
This was previously observed [23]. The decrease in intensity of bridged framework OH at $3612 \, cm^{-1}$ is due to the interaction between Ga species and OH group via the reaction:

$$Ga_2O + H^+Z^- \rightarrow Ga^+Z^- + H_2O$$
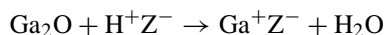
This solid state reaction was previously reported in [23,24]. Appearance of two broad bands centered at 3500 and $2913 \, cm^{-1}$ (Fig. 5c) are a direct proof of the formation of water molecules. Since this small amount of water molecules formed can interact with silanols at $3745 \, cm^{-1}$ and bridged framework OH groups at $3612 \, cm^{-1}$ which are displaced to lower wave-numbers, 3500 and $2913 \, cm^{-1}$, respectively. This phenomenon was largely reported [21,22,26]. The decrease in intensity of peaks at 3745 and $3612 \, cm^{-1}$ is the result of the interaction of part of silanols and bridged framework OH groups with the small amount of water molecule formed. If the sample was directly pre-treated under vacuum at high temperature as 723 K (Fig. 5d), no OH groups attached to Ga species can remain and no interaction between Ga species and bridged framework OH group occurs since all the Ga species are present in higher oxidation degree state. The intensity of $3612 \, cm^{-1}$ is therefore high. A further sever activation at 723 K in air can start to dehydrolyze the OH groups and can dealuminate zeolite [21,22]. The intensity of peak at $3612 \, cm^{-1}$ is reduced and that at $3665 \, cm^{-1}$ is increased. Concerning the peak at $3665 \, cm^{-1}$, Meriaudeau and Naccache attributed it to the OH groups on Ga^{x+} ions in the framework position [24]. From our present study and other work in literature [26,37], we believe that this peak is related to the extra-framework Al species. Our ^{27}Al NMR study confirms the presence of small amount of extra-framework Al after gallium deposition and calcination (Fig. 3).

Concerning bimetal Ga and Pt modified H-ZSM-5, very similar evolution has been observed. For example after a sever oxidation at 723 K, the spectrum obtained (Fig. 6a) is almost identical to that of Ga modified H-ZSM-5 upon same pre-treatment (Fig. 5b). After a further reduction (Fig. 6b), the peak at $3699\,cm^{-1}$ disappears completely and the intensity of band at $3612\,cm^{-1}$ decreases. The complete disappearance of peak at $3699\,cm^{-1}$ suggests the complete elimination of OH group on Ga species due to further reduction treatment. In fact owing to the presence of Pt particles, the reduction of high oxidation Ga species is much easier due to spill-over effect. The low oxidation state Ga species interacting with bridged OH groups results in the decrease in intensity of peak at $3612\,cm^{-1}$. If GaPt-ZSM-5 was directly pre-treated in hydrogen flow, a spectrum (Fig. 6c) very similar to that of Fig. 5d is obtained.

Above results show clearly the effect of pre-treatment of catalysts on the chemical state of catalysts, which will certainly influence their catalytic properties.

3.3. Confinement of benzene molecules

3.3.1. Interaction of –OH groups with benzene

Fig. 7A–C shows the changes in IR absorbency of OH groups of H-ZSM-5 (Fig. 7A), Pt-ZSM-5OxR (Fig. 7B) and Ga-ZSM-5 (Fig. 7C) upon benzene adsorption. As can be seen, the intensity of the peak of $3612\,cm^{-1}$ decreases continuously with introduction of benzene and a new broad band centered at $3246\,cm^{-1}$ appear simultaneously. The broad band shifts very slightly toward a lower wave-numbers with increasing the benzene amount and reaches maximum intensity after benzene loading of 3.6 m/u.c. for H-ZSM-5 (Fig. 7A, curve (e)), 2.6 m/u.c. for Pt-ZSM-5 (Fig. 7B, curve (d)) and 2.7 m./u.c. for Ga-ZSM-5 (Fig. 7C, curve (f)). At these values, the peak at $3612\,cm^{-1}$ disappears completely. These values correspond closely to the acidity determined by TPD of ammonia (Table 2) and suggest that all bridged hydroxyl groups (Al–OH–Si) are accessible for benzene molecules and saturated. After introduction of benzene in excess, the band centered at $3246\,cm^{-1}$ remains unchanged for platinum-loaded samples while decreases in intensity for pure zeolite phase and Ga-ZSM-5. The intensity of band assigned to the silanol groups ($3745\,cm^{-1}$) starts to decrease

and three new poorly resolved bands at 3426, 3498 and $3605\,cm^{-1}$ are generated and are independent of sample preparation.

Simultaneously with decreasing in the intensity of the band at $3246\,cm^{-1}$, the decrease in the intensity of the C–C vibrations of benzene molecules in the region $3200–3000\,cm^{-1}$ (Fig. 7A and C) and also in the fundamental ν_{19} C–C stretching vibration can be seen (Fig. 8). These changes will be discussed further.

The interaction between the protons of the hydroxyls and the π electrons of the benzene ring has been proposed to explain the disturbances of the infrared spectra of OH groups. The extent of the shift is characteristic of the strength of Brönsted acidic sites [21,22]. It was estimated that the shift of the band at $3612\,cm^{-1}$ is about $350\,cm^{-1}$ upon benzene adsorption on ZSM-5 [25,26]. The band at $3246\,cm^{-1}$ ($\Delta\nu = 366\,cm^{-1}$) should therefore correspond to the interaction of benzene with the bridged Si–(OH)–Al groups. The bands at 3498 and $3605\,cm^{-1}$ correspond to the interaction of benzene with OH groups of extra-framework Al ($\Delta\nu = 167\,cm^{-1}$) and Si–OH ($\Delta\nu = 140\,cm^{-1}$), respectively. The shift extents for these two bands are in good accordance with the results reported in literature [21,22]. These two hydroxyls have a relatively low acidity compared with that of Si–(OH)–Al. The broad band at $3345\,cm^{-1}$ appeared from first benzene molecules introduced could be also attributed to bridged framework OH groups with different Brönsted acidity, suggesting the heterogeneity of zeolites in Brönsted acidity.

3.3.2. Type and amount of adsorbed benzene

Out-of-plane C–H vibrational bands: Benzene adsorption on zeolites has been widely investigated [26,28–30], but works about benzene adsorption on ZSM-5 are few [31–35]. It is well known that in the C–H out-of-plane vibrations range liquid benzene gives a pair of bands at 1960 and $1815\,cm^{-1}$ due to ($\nu_5 + \nu_{17}$) and ($\nu_{10} + \nu_{17}$) bending vibrations, respectively. It was shown that this pair of bands can be shifted toward higher wave-number or can split in two pair of bands. The shift of the bands at 1960 and $1815\,cm^{-1}$ towards higher wave-numbers by around of $10–40\,cm^{-1}$ is a result of the interaction between the π electron cloud of benzene and the cations or protons. The shift is small since the interaction of protons with the π-cloud of benzene rings affect indirectly
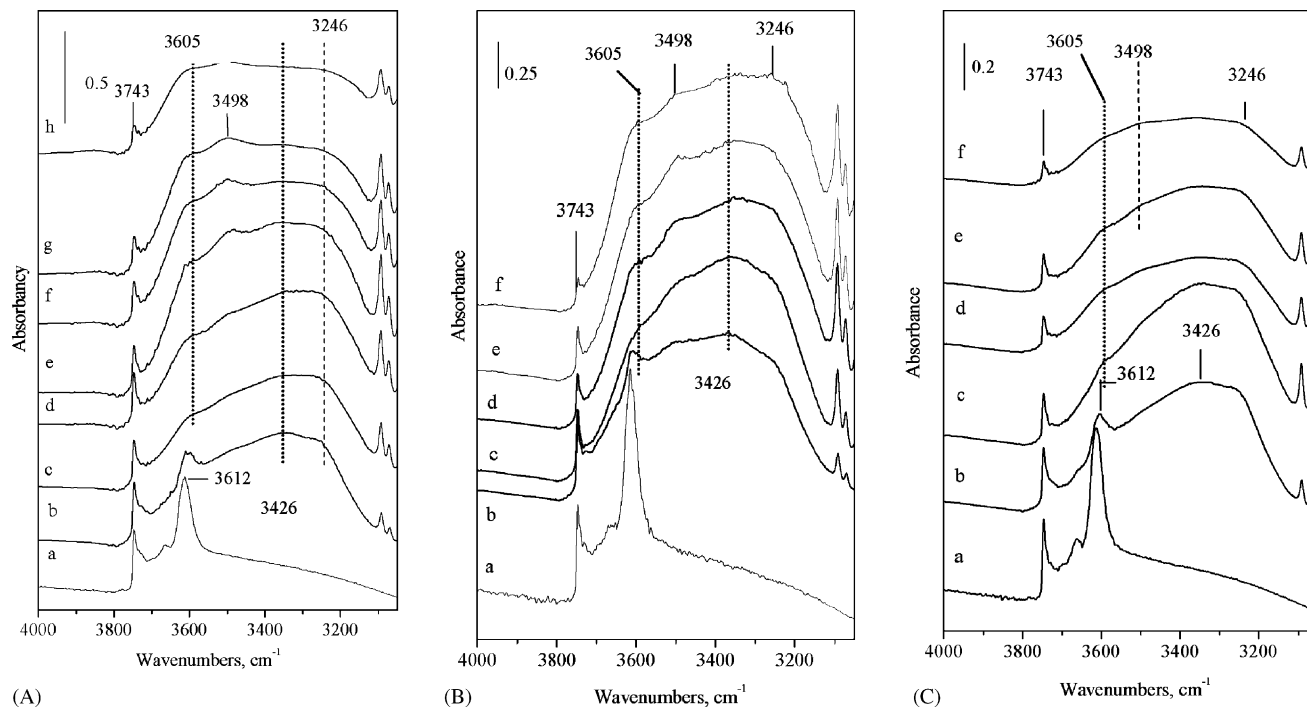
Fig. 7. Changes in the infrared absorbance spectra of hydroxyl groups upon adsorption of increasing amounts of benzene (molecules/u.c.). (A) H-ZSM-5: (a) 0.0, (b) 0.5, (c) 0.95, (d) 1.4, (e) 3.6, (f) 4.6, (g) 6.2, (h) 9.8; (B) Pt-ZSM-5OxR: (a) 0.0, (b) 0.8, (c) 1.7, (d) 2.6, (e) 5.6, (f) 25.9 and (C) Ga-ZSM-5OxR: (a) 0.0, (b) 0.9, (c) 2.7, (d) 5.5, (e) 10, (f) 30.
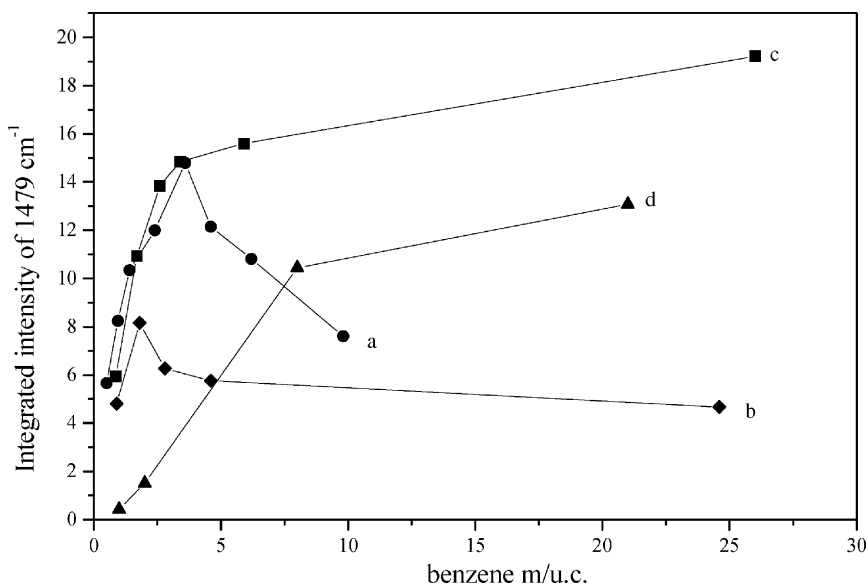
Fig. 8. Relative absorbance of $1479\,cm^{-1}$ bands as a function of benzene loading in (a) H-ZSM-5 (●); (b) Ga-ZSM-5-Ox (◆); (c) Pt-ZSM-5-R (■); (d) GaPt-ZSM-5-OxR (▲).

and only weakly on the C–H vibrations. The shift of C–H out-of-plane vibrations ($\nu_5 + \nu_{17}$) and ($\nu_{10} + \nu_{17}$) of ca. 40–$100\,cm^{-1}$ is attributed of the benzene molecule interacting with 12R windows of zeolites [26,28,29].

ZSM-5 has three-dimensional pore system and three possible adsorption location: the intersection between the straight and zigzag channels and the midsection of either straight or zigzag channels. Goyal et al. [31] have demonstrated using X-ray diffraction that below 4 molecules/u.c. (m/u.c.), benzene molecules are confined in the intersection of straight and sinusoidal channels. Above 7.6 m/u.c., benzene molecules are located at intersection in the sinusoidal channels and in the straight channels. Huang and Havenga [32] in FT-Raman spectroscopy study demonstrated similarly that in the range of 1–4 m/u.c., guest molecules are in the channel intersection. At the high loading, the rest of benzene moves to the midsection of the straight channels. However, Sahasrabudhe et al. [33] concluded that at the loading of 1.6 m/u.c., benzene cluster might be formed and the large fraction of them is located at intersection sites. At the same time the small fraction exists in the straight and sinusoidal channels. Upon increasing benzene loading, the other sites are occupied. Portsmouth et al. [34]

and Shah et al. [35] reported same contrary observations. According to these authors, at low benzene loading (≤ 4 m/u.c.) the guest molecules are situated in straight channels. Above 4 m/u.c., the benzene molecules migrate to the channel intersection.

Simultaneously with the changes in the hydroxyl spectra upon benzene adsorption, the changes in the spectra of C–H out-of-plane vibrations were studied. Upon benzene adsorption up to 0.9 m/u.c. on H-ZSM-5 (spectrum (b) of Fig. 9A), Pt-ZSM-5 (spectrum (a) of Fig. 9B), Ga-ZSM-5Ox (spectrum (a) of Fig. 10A), GaPt-ZSM-5OxR (spectrum (a) of Fig. 10B), the bands at 1830 and $1970\,cm^{-1}$ have appeared. Small bands at around 2002 and 1860 can be seen at this benzene loading. The position of these two pairs of bands is independent of metal present, suggesting that specific interaction between metal and benzene molecules is small. All bands do not change their position upon increasing benzene in the IR cell.

According to the shift value of around 11–$28\,cm^{-1}$ compared with that of liquid benzene, the bands at around 1830 and $1970\,cm^{-1}$ should be assigned to the interaction of the zeolitic protons and/or cations with the π-cloud system of benzene [26,28,29]. The band intensity increases up to benzene loading of 3.6 m/u.c. (spectrum (e) of Fig. 9A) for H-ZSM-5 and 2.6 m/u.c.
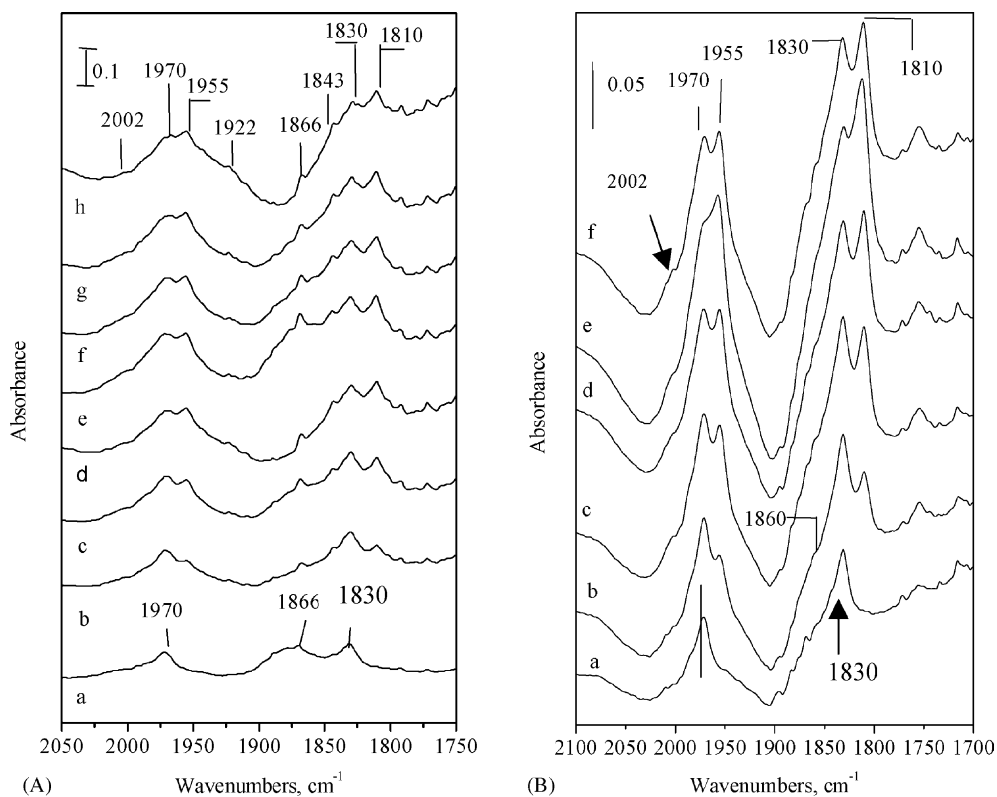
Fig. 9. Changes in the infrared absorbance spectra of the C–H out-of-plane vibrations of benzene adsorbed on H-ZSM-5 and Pt-ZSM-5 as a function of the amount of benzene introduced (molecules/u.c.) in the IR cell: (A) H-ZSM-5: (a) 0.5, (b) 0.95, (c) 1.45, (d) 2.4, (e) 3.6, (f) 4.6, (g) 6.2, (h) 9.8; (B) Pt−ZSM-5: (a) 0.86, (b) 1.7, (c) 2.63, (d) 3.4, (e) 5.9, (f) 25.9.
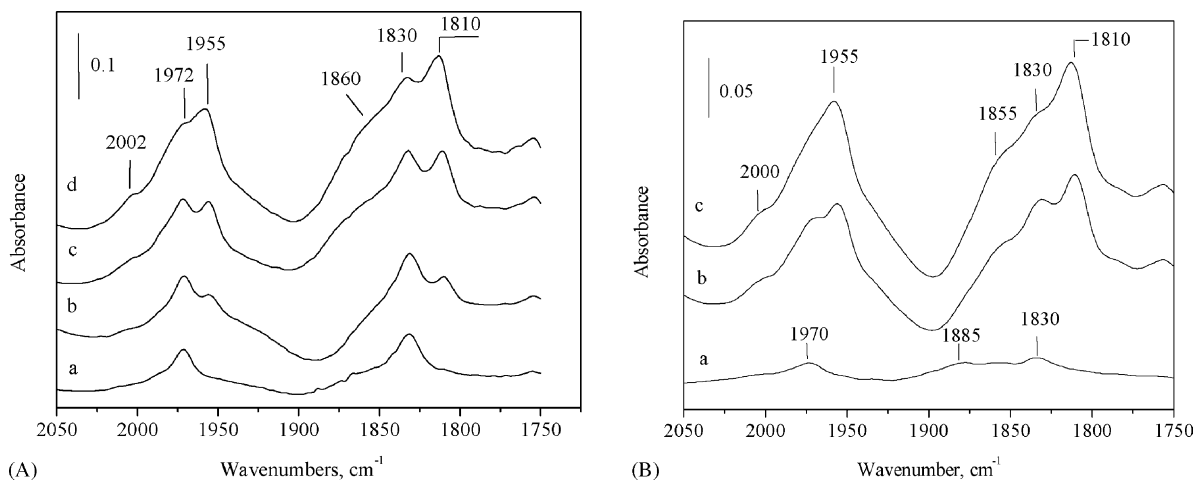

Fig. 10. Changes in the infrared absorbance spectra of the C–H out-of-plane vibrations of benzene adsorbed a function of the amount of benzene introduced (molecules/u.c.) in the IR cell: (A) Ga-ZSM-5: (a) 0.9, (b) 2.8, (c) 9.8, (d) 10, and (B) GaPt-ZSM-5-OxR: (a) 2, (b) 11, (c) 3.

(spectrum (c) of Fig. 9B) for platinum modified sample, indicating saturation of all framework protons. This result is in good agreement with Brönsted acidity determined from ammonia desorption (Table 2). The bands at 1810 and 1955, attributed to pseudo liquid phase [26,28,29] can be seen in IR spectra after 1.7 m/u.c. (spectra (b) of Figs. 9B, 10A and B) for gallium and platinum loaded samples and after 0.9 m/u.c. for H-ZSM-5 (spectrum (b) of Fig. 9A). Most probably these two bands are the result of the condensation of benzene in the zeolite channels and intersections. The presence of small pair of bands at around 1860 and 2002 cm^{-1} is also noted at any benzene loading in the spectra of all samples (shift around of 40–60 cm^{-1}). They appeared simultaneously with bands for pseudo liquid phase for metal modified samples (spectra (b) of Figs. 9B, 10A and B), but can be seen in the spectra of pure zeolite before the appearance of the pseudo liquid phase bands (spectrum (a) of Fig. 9A). The intensity of high frequency bands (1860 and 2002 cm^{-1}) increases slightly with increasing benzene concentration. The shift of C–H out-of-plane vibrations ($\nu_5 + \nu_{17}$) and ($\nu_{10} + \nu_{17}$) of ca. 40–100 cm^{-1} is generally attributed to the benzene molecule interaction with 12R windows of a zeolites [26,27–29]. However, ZSM-5 does not contain 12R.

In our opinion, the bands with high frequency shift could result from the interaction of benzene molecule with the zeolite channels if assumed that the ring of benzene molecule is perpendicular to the surface of the walls of zeolite channels. The amount of benzene adsorbed in this position is low, because of low intensity of bands. The benzene molecule dimension (diameter $\cong 5.85$ Å) [32] is near to that of the channel (5.5 Å) [33] and surrounding framework can compress the C–H bond. This leads to increase in the effective force constant, resulting in frequency shifted toward higher wave-number. The same explanation is given by Huang and Havenga [32] for shift of benzene Raman frequencies at 3059 and 3047 cm^{-1} to high wave-numbers after adsorption on ZSM-5. As mentioned above, bands at 1810 and 1955 cm^{-1} can be seen in spectra of metal modified samples at benzene loading of 1.7 m/u.c. (spectra (b) of Figs. 9B and 10) and at 0.9 m/u.c. for pure zeolite. With increasing benzene concentration, pseudo liquid phase increases in intensity because of stacked benzene molecules in the zeolite channels. This means that part of benzene enter

in the zeolite channels and form the pseudo liquid phase. The formation of pseudo liquid phase for pure zeolite starts at low benzene concentration. The difference between H-ZSM-5 and gallium and platinum loaded catalysts can be explained by hindered transport of benzene molecules in the metal modified samples as a result of partial blockage of channel by metal particles or exchanged cations and possible adsorption of benzene molecules on Pt particles dispersed on external surface of zeolite crystals, which prevent the aggregation of benzene molecules. A more important amount of benzene molecules is necessary for the formation of benzene clusters. Our observation for metal loaded samples are in a good accordance with the conclusion made by Sahasrabudhe et al. [33] that benzene cluster is formed above 1.6 m/u.c.

Fundamental ν_{19} C–C stretching vibration: The variation of this band was closely followed because of the high sensitivity of this IR band to the chemical and geometrical nature of zeolite [30]. No frequency shift or band splitting are observed upon adsorption of benzene.

Fig. 8 shows the relative absorbance of 1479 cm^{-1} bands as a function of benzene loading on pure zeolite and metal modified samples. As can be seen with increasing benzene amount, the intensity of band at 1479 cm^{-1} increases for platinum containing samples. Abnormal adsorption isotherm is observed for H-ZSM-5 and Ga-ZSM-5 catalysts that upon adsorption of increasing and known amount of benzene, the intensity increases first then decreases. The decrease is more pronounced for a pure zeolite (Fig. 8b). A Similar phenomenon was observed during the adsorption of CO on platinum catalysts [27]. With increasing the coverage the absorbance of linear CO species decreases as result of decreasing in the extinction coefficient.

With increasing the benzene loading, molecule concentration in the zeolite channels and intersection rises and molecules packed closely. Each benzene molecule undergoes perturbation from the surrounding framework and other benzene molecules. These interactions most probably lead to the change in the electronic state of benzene molecule and in the dipole moment of different vibration. It is well known that integrated band intensity is proportional to the square of change in the dipole moment with respect to the

normal coordinate [36].

$$A = 304.75 \frac{\partial \mu}{\partial q}$$

This means that small changes in dipole moment and electronic state in molecule will cause the change in the integrated intensity.

In the case of platinum loaded sample part of metal particles are dispersed on the external surface of zeolite crystals. These Pt particles can be adsorption sites for benzene molecules. At high loading of benzene, after saturation of Brönsted acid sites, the benzene adsorption on these Pt particles occurs, leading to the normal isotherm (Fig. 8c and d).

Considering the above results we can conclude that up to benzene loading 1.7 m/u.c., the guest molecules occupied the channels intersection. Above 1.7 m/u.c. part of benzene molecules enter the straight or sinusoidal channels and form pseudo liquid phase. Interaction of benzene with framework protons gives raise band at 1970 and 1830 cm^{-1}. Above 3.0 m/u.c., all framework protons are occupied. High concentration of benzene molecules in zeolite channels (for H-ZSM-5 and Ga-ZSM-5) leads to change in dipole moment of different vibrations and intensity of the band at 3246, 3200–3000 and 1479 cm^{-1} decreases.

4. Conclusion

The type of the hydroxyl groups on GaPt-ZSM-5 and Ga-ZSM-5 is very sensitive to the pre-treatment of the samples. Besides the IR bands at 3746, 3612 cm^{-1} 3665 cm^{-1} assigned to terminal silanol Si–OH, bridged Si–(OH)–Al groups and OH group attached to extra-framework aluminium, gallium loaded samples show additional IR band at around 3699 cm^{-1}. It is attributed to OH groups attached to Ga, such as Ga$_2$(OH)O$_{3-x}$, which is reduced in H$_2$ flow. Upon benzene adsorption, the hydroxyl groups linked to Ga species shift toward lower wave-numbers with a lower extent compared with that of bridged hydroxyls. This means that the last hydroxyls have relatively low acidity compared with Si–(OH)–Al.

Upon benzene loading of 1.7 m/u.c., for metal loaded samples and 0.5 m/u.c. for pure zeolite, the guest molecules occupied the channels intersection. Above these loading part of benzene molecules enters

the straight or sinusoidal channels and form pseudo liquid phase. Interaction of benzene with framework protons gives raise band at 1970 and 1830 cm^{-1}. At a loading of around 2–3.6 m/u.c., all framework protons are occupied. Above these loadings, the concentration of benzene molecules in zeolite channels increases and each molecule undergoes perturbation from the surrounding molecules and framework, which lead to a change in electronic state of molecules and in dipole moment of different vibrations. Changing in dipole moment causes abnormal absorption isotherm for pure zeolite and gallium loaded samples. This effect is not observed for Pt loaded samples, probably due to adsorption of benzene molecules platinum particle dispersed on the external surfaces of zeolite crystals.

References

[1] I. Ivanova, D. Brunel, J.B. Nagy, E. Derouana, J. Mol. Catal. A: Chem. 95 (1995) 243.

[2] A. Angelis, St. Amarilli, D. Berti, L. Montarani, C. Pergo, J. Mol. Catal. A: Chem. 146 (1999) 37.

[3] S. Siffert, L. Gaillard, B.L. Su, in: Proceedings of the 12th International Zeolite Conference, Materials Research Society, Warrendale, PA, 1999, p. 1121M.

[4] S. Siffert, L. Gaillard, B.L. Su, J. Mol. Catal. A: Chem. 153 (2000) 267.

[5] I. Ivanova, E.B. Pomakhina, A.I. Rebrov, E.G. Derouane, Top. Catal. 6 (1998) 49.

[6] E. Derouane, H. He, Sh. Derouane-Abd. Hamid, D. Lambert, I. Ivanova, J. Mol. Catal. A: Chem. 159 (2000) 5.

[7] C. Bigey, B.L. Su, Ind. Appl. Zeolites, Technologisch Instituut vzw, Brugge, Belgium, 2000, pp. 193–204.

[8] A. Smirnov, E.V. Mazin, V.V. Juschenko, E. Knyareva, S.N. Nesterenko, I. Ivanova, L. Galperin, R. Jansen, S.T. Bradly, J. Catal. 194 (2000) 266.

[9] S. Siffert, B.L. Su, Reac. Kinet. Catal. Lett. 68 (2000) 191.

[10] I. Ivanova, N. Blom, E. Derouane, J. Mol. Catal. A: Chem. 109 (1999) 157.

[11] A. Smirnov, A.A. Shaskov, I. Ivanova, B.V. Romanovsy, Z. Gabelica, in: Proceedings of the 12th International Zeolite

Conference, Materials Research Society, Warrendale, PA, 1999, p. 1207.

[12] I. Ivanova, F. Fajula, in: Proceedings of the 12th International Zeolite Conference, Materials Research Society, Warrendale, PA, 1999 p. 2273.

[13] O.V. Chetina, T.V. Vasina, V.V. Lunin, O.V. Bragin, Catal. Today 13 (1992) 639.

[14] J.A. Biscardi, G.D. Meitzen, En. Iglesia, J. Catal. 179 (1998) 192.

[15] J.A. Biscardi, En. Iglesia, J. Catal. 182 (1999) 117.

[16] B.L. Su, D. Jaumain, in: Proceedings of the 12th Intern. Zeolite Conference, Materials Research Society, Warrendale, PA, 1999, p. 2689.

[17] E.G. Derouane, S. Determmerie, Z. Gabelica, N. Bom, Appl. Catal. 1 (1981) 211.

[18] S.B. Abdul Hamid, Doctorate of Science Thesis, The University of Namur, Belgium, 1993.

[19] S. Kotrel, J.H. Lunsford, H. Knõzinger, J. Phys. Chem. B 105 (2001) 3917.

[20] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Petrini, G. Leofanti, M. Padovan, C. Otero Arean, J. Chem. Soc., Faraday Trans. 88 (19) (1992) 2959.

[21] B.L. Su, D. Barthomeuf, Zeolites 13 (1993) 6269.

[22] B.L. Su, D. Barthomeuf, J. Catal. 139 (1993) 81.

[23] G.L. Price, V. Kanazirev, J. Catal. 126 (1990) 267.

[24] P. Meriaudeau, C. Naccache, Appl. Catal. 73 (1991) L13.

[25] L.M. Kustov, V.B. Kazansfy, P. Ratnosamy, Zeolites 7 (1987) 79.

[26] B.L. Su, V. Norberg, Zeolites 19 (1997) 65.

[27] G. Kadinov, A. Palazov, in: L. Petrov, A. Andreev, G. Kadinov (Eds.), Proceedings of the 7th International Symposium on "Heterogeneous Catalysis", Part I, Bourgas, Vratza, 1991, p. 125.

[28] B.L. Su, J. Chem. Soc., Faraday Trans. 93 (7) (1997) 1449.

[29] V. Norberg, F. Docquir, B.L. Su, Stud. Surf. Sci. Catal. 125 (1999) 253.

[30] D. Barthomeuf, Catal. Rev.-Sci. Eng. 38 (1996) 521.

[31] R. Goyal, A.N. Fitch, H. Jobic, J. Phys. Chem. B 104 (2000) 2878.

[32] Y. Huang, E.A. Havenga, J. Phys. Chem. B 104 (2000) 5084.

[33] A. Sahasrabudhe, V.S. Kamble, A.K. Tripathi, N.M. Gupta, J. Phys. Chem. B 105 (2001) 4374.

[34] R.L. Portsmouth, M.J. Duer, L.F. Gladden, J. Chem. Soc., Faraday Trans. 91 (1995) 559.

[35] D.B. Shah, C.J. Guo, D.T. Hayhurst, J. Chem. Soc., Faraday Trans. 9 (1995) 1143.

[36] N.B. Colthup, St.E. Wiberley, L.H. Daly, Introduction to Infrared and Raman Spectroscopy, Academic Press, San Diego, 1990, p. 101.

[37] B.L. Su, D. Jaumain, Catal. Today 73 (2002) 178.