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Effects of acidity and combination of Ga and Pt on catalytic behavior of Ga-Pt modified ZSM-5 catalysts in benzene alkylation with pure propane

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Abstract

Alkylation of benzene with pure propane under flow condition has been investigated on a series of monometal gallium and bimetal gallium-platinum modified H-ZSM-5 zeolites with different acidity. The catalysts have been intensively characterized by XRD, XPS, TPR and IR spectroscopy. The chemical states of Ga and Pt have been studied and correlated with catalytic performances of these materials. The coke deposition on catalysts has been evaluated. It was found that the catalytic activity, product distribution and reaction path depend strongly on zeolite acidity and Pt content. With increasing the Si/Al ratio, the benzene conversion decreases and products distribution changes. Main reaction products for high acidity catalysts (lower Si/Al ratio) are toluene, ethylbenezene (EB) and xylenes, indicating that the cracking of propane is favored over its dehydrogenation. For the samples with low acidity, the formation of cumene and propylbenzenes (PrBz) is enhanced. Bimetal GaPt samples show high catalytic activity and selectivity to cumene. Pt promoted Ga-ZSM-5 catalysts show low concentration of coke like polyolefines and polycondensed aromatics, because platinum has a role of the entrance for hydrogen spillover which prevents or moderates coke deposition. Bimetal GaPt samples could be very efficient catalysts for cumene production from benzene alkylation using propane as alkylating agent. It is established that part of platinum in the bimetal samples is in zero valent state and most probably form big metal particles.

Keywords: Benzene alkylation; Propane; Ga-ZSM-5; GaPt-ZSM-5; XPS

1. Introduction

Alkylation of benzene with light alkanes can be considered as perspective way for synthesis of high value alkylaromatics and light alkanes upgrading. The production of cumene from benzene and propane is a great challenge for, at least, the beginning of 21st century. Zeolite type solid acids were reported to be potential catalysts active for production of alkylbenzenes from benzene and pure propane [1–3]. Due to the low reactivity of propane, the alkylation of benzene with propane on zeolites requires high reaction temperature and the set of side reactions led to formation of different condensed aromatics [2–4]. Ga species were added in zeolites to enhance the catalytic activity due to their good performance in activation of propane. Gallium ions on acid support (e.g. H-ZSM-5) promote dehydrogenation steps more effectively that bather dehydrogenation catalyst. Addition of Pt to the Ga promoted catalysts leads to increasing of conversion of low alkenes to aromatics [4]. It was reported that Pt incorporation in the MFI with low acidity resulted in a significant increase in selectivity to propylbenzenes (PrBz) at mild reaction temperature (573–723 K) [5]. It is therefore of important interest from scientific and industrial point of view to examine the effect of bimetal combination of Ga and Pt in benzene alkylation reaction.

Here we report the alkylation of benzene with pure propane on a series of bimetal (gallium and platinum) modified MFI catalysts.

2. Experimental

2.1. Sample preparation

The starting ZSM-5 materials with different Si/Al ratio were kindly provided by SUD-CHEMIE AG (H-MFI-90,

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Si/Al = 50 and H-MFI-240, Si/Al = 100) and ALSI PENTA zeolite GmbH (SH-27, Si/Al = 23), respectively.

Gallium was incorporated by ion exchange followed by filtering, washing with demineralized water, drying and calcination in air flow firstly 5 h at 573 K and then 15 h at 823 K. The obtained sample was exchanged with dilute aqueous solution of Pt $(NH_3)_4Cl_2$ salt to obtain different Pt content. The solution was stirred at room temperature for 24 h and then filtered, washed with abundant bidistillated water to free Cl^- ions and dried overnight at 373 K. Samples were calcined 6 h in air at 723 K. The characteristics of prepared catalysts are given in Table 1.

2.2. Sample characterization

XRD patterns were collected on a Philips PW3710 diffractometer using Cu Kα radiation. IR spectra in the region of 1200–4000 cm^{-1} were recorded using Perkin-Elmer FT spectrum 2000 and KBr wafer technique for coke formation study. The solid-state ^{71}Ga MAS NMR spectra were collected on Bruker MSL 400 Hz NMR spectrometer. Prior to the ^{71}Ga MAS NMR measurements samples were exchanged with an aqueous solution of NH_4NO_3 to minimize quadruple effects [2,6].

XPS spectra were recorded on ESCALAB-MkII (VG Scientific) electron spectrometer with a vacuum of 10^{-8} Pa as described in [7]. The energy position of photoelectron line was determined with respect to the reference C 1s line (BE 285 eV).

Temperature programmed reduction (TPR) analysis was conducted with an equipment described elsewhere [8], using a flow mixture of 10% H_2 in Ar at 10 ml/min, with a temperature rate of 10 K/min from room temperature to 973 K. Prior to the TPR experiment the sample was treated 1 h at 393 K.

2.3. Catalytic experiment

Catalytic activity of the samples was determined using continuous flow under atmospheric pressure. Mass flow controllers were used to regulate nitrogen and propane flows. Benzene (Merck, 99.9%) was introduced by bubbling N_2 in a saturator-condensation device where the temperature was carefully regulated by cryostat. A 100 mg of catalyst was charged in quartz reactor. In order to prevent condensation of products, all feed lines after reactor were heated. The products were analyzed on line by gas chromatography (Perkin-Elmer Autosystem XL) equipped with 30 m AT-WAX capillary column and flame ionization detector. Gases (N_2, O_2 and H_2) were purified by gas clean filter system in order to remove traces of moisture and/or oxygen.

Prior to catalytic test the samples were calcined in air 15 h at 823 K. The platinum containing samples were reduced 2 h at 723 K after calcination. The catalyts were purified in N_2 flow at reaction temperature for 2 h after calcination in O_2 or reduction in H_2. The catalytic activity was obtained for a benzene/propane molar ratio (Bz/Pr) of 1 and the WHSV fixed at 5.4 h^{-1}. The effect of reaction temperature on the catalytic activity was first studied in a temperature range of 573–823 K after standard treatment. Between two catalytic measurements, samples were maintained in pure N_2 flow at reaction temperature. Influence of time on stream on the activity and selectivity was determined at 673, 723 and 823 K under reaction flow.

Conversion is defined as the amount (moles) of benzene converted over that introduced since propane is used in excess. The selectivity (*S*%) of one defined product is expressed as the percentage of this product among all products.

3. Results and discussion

3.1. Characterization of prepared samples

XRD patterns showed that gallium and platinum incorporation did not induce any change in crystallinity compared with that of starting materials (Fig. 1).

The effects of Ga deposition on the intensity of –OH groups in IR are shown in Fig. 2. Only spectra in hydroxyl region in the zone of 3000–4000 cm^{-1} for samples with high Si/Al ratio are given. Pure zeolite exhibit three bands at 3743, 3700 and 3612 cm^{-1} assigned, respectively, to ter-

Table 1
Characteristics of the prepared catalysts

Sample	Name	Si/Al	Ga[a] (wt.%)	Pt (wt.%)
0.7Ga-SH-27	Ga-SH-27	23	0.75	–
0.7Ga + 0.1Pt-SH-27	GaPt1-SH-27	23	0.75	0.14
0.7Ga + 0.2Pt-SH-27	GaPt2-SH-27	23	0.71	0.20
0.7Ga-MFI-90	Ga-MFI-90	50	nd[b]	–
0.7Ga + 0.1Pt-MFI-90	GaPt1-MFI-90	50	nd	nd
0.7Ga + 0.2Pt-MFI-90	GaPt2-MFI-90	50	nd	nd
0.7Ga-MFI-240	Ga-MFI-240	100	0.7	–
0.7Ga + 0.1Pt-MFI-240	GaPt1-MFI-240	100	0.002	0.17
0.7Ga + 0.2Pt-MFI-240	GaPt2-MFI-240	100	0.005	0.27

[a] Elemental analysis.
[b] No data.

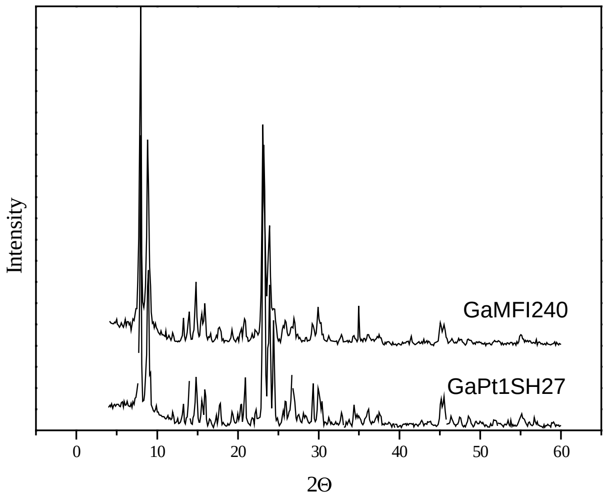


Fig. 1. XRD spectra of different samples after gallium deposition.

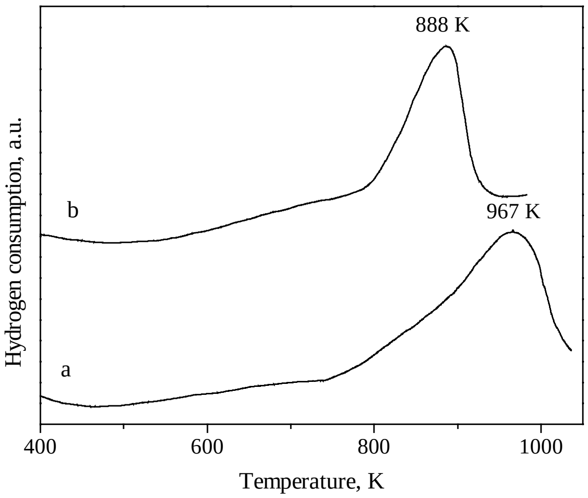


Fig. 3. TPR profiles of (a) physical mixture of Ga_2O_3 and MFI-240 and (b) Ga-MFI-240.

minal silanol Si–OH, isolated internal silanols and bridged Si–(OH)–Al [9]. The intensity of band at 3612 cm^{-1} decreases sharply after gallium deposition and new band at 3669 cm^{-1} appears. The decrease in intensity of bridged framework OH is due to removal of several Si–(OH)–Al groups during calcination as the result of solid-state reaction. This solid state reaction was previously detailed [9–11]. The peak at 3669 cm^{-1} could arise from OH groups attached to extra-framework aluminum species whose amount increases in the sample after Ga deposition [9].

^{71}Ga NMR spectra show that no gallium signals are visible, suggestive of the absence of framework gallium species for all studied samples. Previous works demonstrated [5] that non-framework gallium species are undetectable by ^{71}Ga NMR experiment. To study these non-framework species, TPR and XPS experiments were performed.

Fig. 3 presented TPR profiles of GaMFI240 samples and physical mixture from Ga_2O_3 and MFI240. The weight percent of Ga in these two samples are the same. It was reported that the pure Ga_2O_3 can be reduced by H_2 above 873 K to form Ga_2O [12,13] and that the reduction of gallium in the zeolite occurred in a temperature range of 760–873 K [11,14,15]. The reduction peak at 888 K observed on Ga-MFI-240 catalyst results probably from the reduction of Ga_2O_3 interacting weakly with zeolite framework. According to our previous investigations, concerning the nature of Ga species, gallium in the samples with high acidity is present in two oxide phases—phase I: Ga_2O_3 weakly interacting with zeolite with a reduction temperature of 858 K and phase II: Ga_2O_3 interacting strongly with zeolite with a reduction temperature of 973 K. Sharp signal in XPS spectra (Fig. 4) at 1118.8 eV (Ga $2p_{3/2}$) confirms the 3+ valent state of gallium. Most probably Ga_2O_3 species are located on the external zeolite surface. This proposition is in agreement with the previous work that ion exchange procedures lead to the preferential deposition of Ga^{3+} species on the outer surface of zeolite [10,16,17]. Hydrated Ga^{3+} cations cannot enter the channels (0.55 nm × 0.27 nm) of MFI during ion exchange. The calcination led to the conversion of these gallium species to Ga_2O_3 [10,16,17].

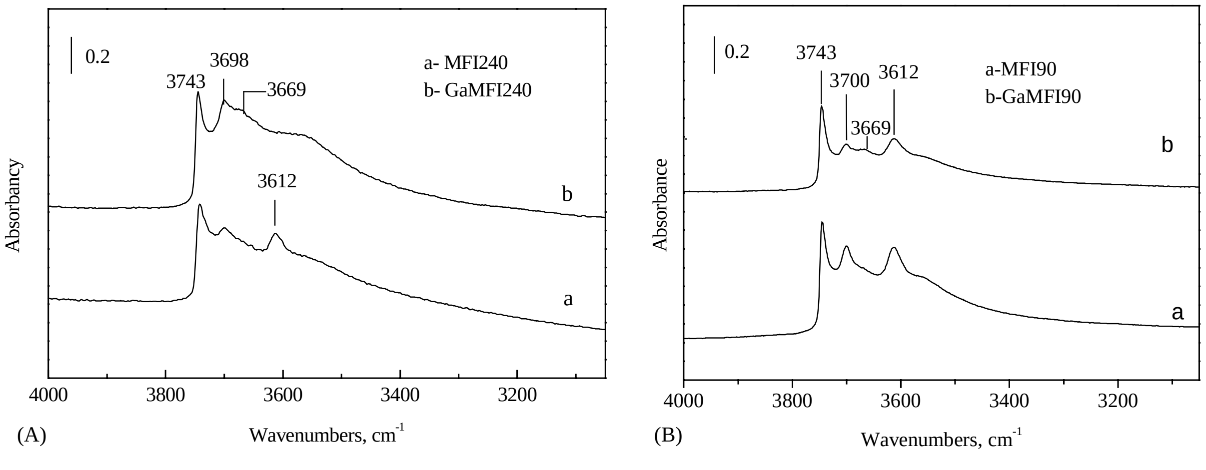


Fig. 2. IR spectra in the –OH region after evacuation 2 h at 723 K for: (A) Ga-MFI-240; (B) Ga-MFI-90.

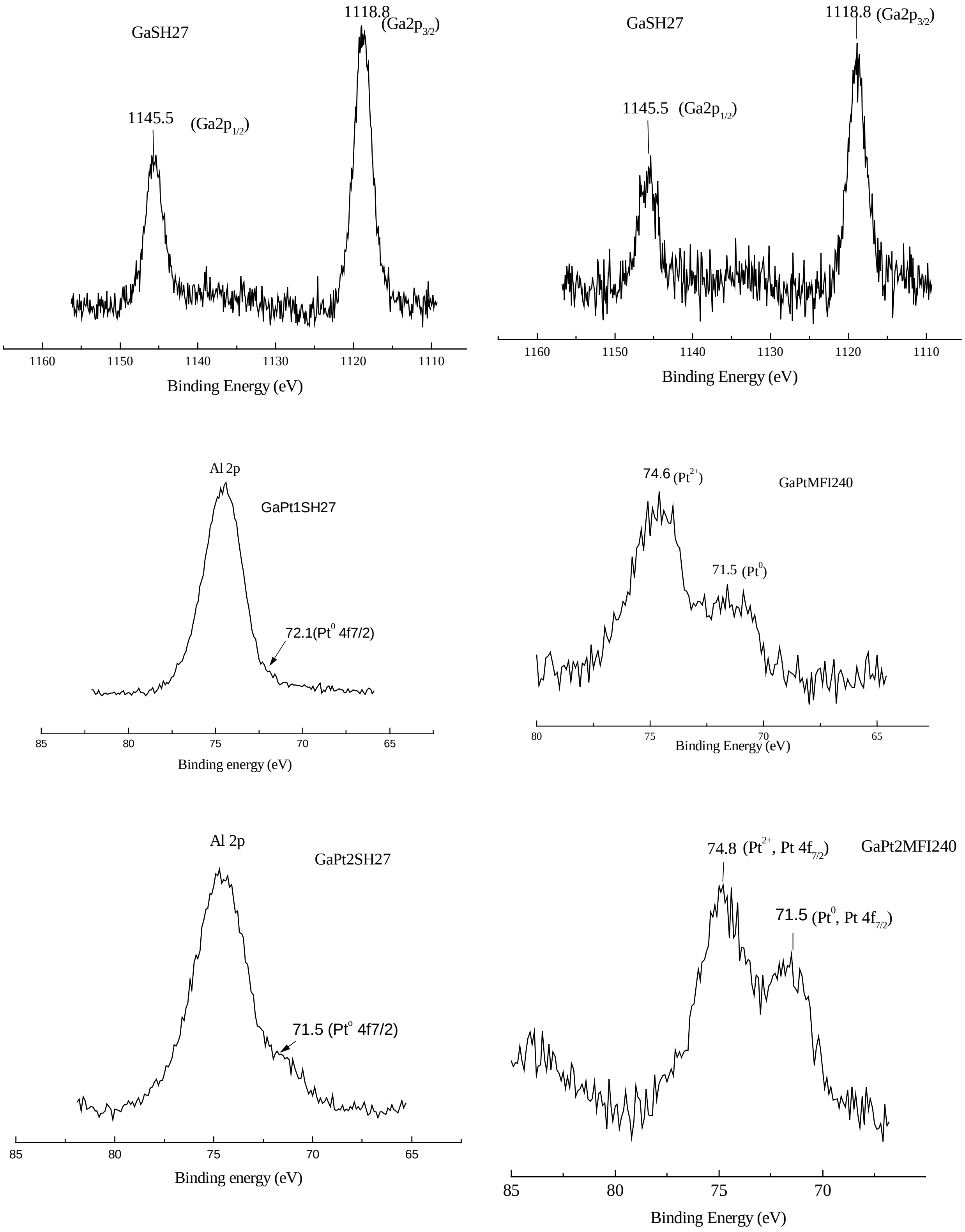


Fig. 4. XPS spectra from bimetal samples with different acidity.

XPS spectra of the calcined bimetal samples show a doublet in the region of Pt $4f_{7/2}$ eV (Fig. 4). The peak at 74.6 eV is attributed to Pt $4f_{7/2}$ of Pt^{2+} and that at 71.5 eV to Pt^0 [18,19]. Binding energies of Pt $4f_{7/2}$ in the range of 71.6–72.1 eV are typical for large platinum particles [19]. The weak signal at 71.5 eV for high acidity samples (GaPt1-SH-27 and GaPt2-SH-27) results most probably from the low quantity of platinum in zero valent state. It is possible that the strong interaction between high acidity zeolite and $[Pt(NH_3)_4]Cl_2$ hinders the decomposition of platinum complex during oxidation. Our data confirm the results of Raddi de Araujo and Shamal [18] that high calcination temperature promoted a great reduction of Pt^{2+} to Pt^0 according to the following reactions:

$$[Pt(NH_3)_4]^{2+} \rightarrow Pt^{2+} + 4NH_3$$

$$2NH_3 \rightarrow N_2 + 3H_2$$

$$Pt^{2+} + H_2 \rightarrow Pt^0 + 2H^+$$

A very interesting phenomenon is observed after Pt deposition into Ga-MFI that Ga content decreases sharply from 0.7 wt.% to only 50 ppm. This can be explained by taking into account the reaction shown above. Upon thermal treatment, $[Pt(NH_3)_4]^{2+}$ ions decompose, giving Pt^{2+}, N_2 and H_2 [18]. A part of H_2 is consumed for Pt^{2+} reduction to Pt^0 and another part for Ga_2O_3 reduction to Ga_2O, which is volatile. That is, why we observed an important lose of Ga quantity.

On the basis of results discussed above we can conclude that the state of gallium species depend strongly on the zeolite acidity. Ga_2O_3 in the catalysts with high Si/Al ratio present as one oxide phase, in the high acidity samples Ga_2O_3 form two oxide phases. Part of Pt in the calcined bimetal samples is in the zero valent state and forms large platinum particles.

3.2. *Catalytic activity*

The conversion increases in general with temperature (Table 2). The reaction starts at about 623 K. Very low activity (<5% in conversion) is observed on HZSM-5 below 823 K. The low benzene alkylation is mainly due to thermodynamic factors, because propane dehydrogenation is strongly endothermic. The conversion on metal modified catalysts reaches maximum after 47 min in reaction mixture, most probably as results of additional redistribution and redispersion of gallium species under reaction conditions [20]. Tables 3 and 4 report products distribution and conversion in reaction mixture on monometalic gallium and bimetal gallium-platinum samples at 723 and 823 K. The major products observed at 823 K are toluene, ethylbenzene (EB) and xylenes.

Table 2
Benzene conversion on a series of catalysts at different temperatures

Sample	623 K	673 K	723 K	823 K
Ga-SH-27	5	12	30	53
GaPt1-SH-27	2	10	43.5	60
GaPt2-SH-27	nd[a]	nd	nd	71
Ga-MFI-240	<1%	<1%	<1%	2.7
GaPt1-MFI-240	<1%	10	11	10
GaPt2-MFI-240	<1%	17	23	nd
Ga-MFI-90	nc[b]	nc	nc	5.9
GaPt1-MFI-90	<1%	<1%	4.5	13
GaPt2-MFI-90	<1%	<1%	<1%	9

Bz/Pr = 1, WHSV = $5.4\,h^{-1}$.

[a] No data.

[b] No conversion.

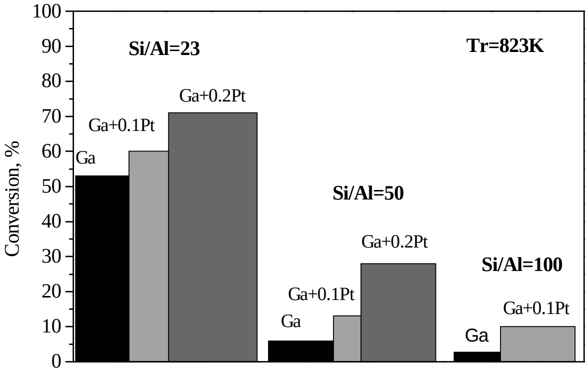
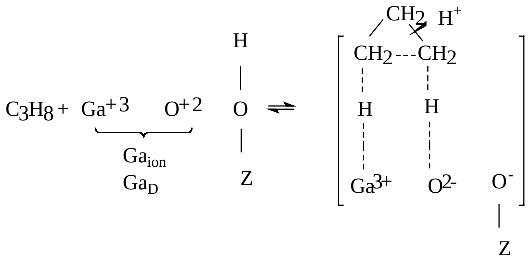


Fig. 5. Conversion on samples with different acidity after 47 min on stream (reaction temperature: 823 K).

The product distribution and reaction path depend strongly on zeolite acidity and Pt content. With increasing Si/Al ratio, the conversion decreases (Fig. 5) and products distribution changes. Main reaction products for lower Si/Al ratio catalysts are toluene, ethylbenzene and xylenes (Table 3), which means that creaking of propane is favored over its dehydrogenation. The formation of cumene and propylbenzenes is enhanced for the samples with high Si/Al ratio.

A bifunctional mechanism for propane activation on Ga modified HZSM-5 was previously postulated, involving double sites: Ga^{x+} sites acting as Lewis sites and protons as Brönsted sites and formation of pseudo protonated cyclopropane (PPCP) species (Scheme 1) [21].

The decomposition of PPCP gives different carbenium ions, which can interact with benzene and form different substituted benzene products. The reaction path depends



Scheme 1. Formation of PPCP via a bifunctional mechanism [21].

Table 3
Conversion and selectivity at 723 K after 47 min on stream

	Ga-SH-27	Ga-MFI-90	Ga-MFI-240	GaPt1-SH-27	GaPt1-MFI-90	GaPt1-MFI-240
Conversion (%)	30	nc	nc	43.5	4.5	11
Selectivity (%)						
Toluene	66.5	0	0	43.42	1.25	14
EB	13.04	–		9.39	0.24	0.04
p-Xylene	5.36	–		8.86	5.25	0.11
m-Xylene	9.74	–		12.21	0.36	14.77
cumene	0.28	–		4.45	28.52	14.03
o-Xylene	2.8	–		8.21	1.16	0.11
NPBz	0.4	–		7.91	3.4	21.53
4-EtTol	–	–			6.16	–
135-TrMBz	0.28	–		1.39	53.99	13.6
2 and 3-tol	0.0	–		1.81	–	12.13
124TrMBz	–	–		0.31	–	–
1-3DIPB	0.21	–		0.07	–	3.4
1-4DIPB	0.02	–		1.53	–	–
1235-TMeBz	0			0.13	–	3.81
1234-TMeBz				0.31	–	2.54

Bz/Pr = 1, WHSV = $5.4\,h^{-1}$.

Table 4
Conversion and selectivity at 823 K after 47 min on stream on fresh samples

	Ga-SH-27	Ga-MFI-90	Ga-MFI-240	GaPt1-SH-27	GaPt1-MFI-90	GaPt1-MFI-240
Conversion (%)	53	5.9	2.7	45.63	13	10
Selectivity (%)						
MeBz	58	100	27.18	69.28	42.98	15.92
EtBz	9.05	–	34.66	3.19	19.89	0.07
p-Xylene	6	–	0.00	5.15	6.47	0.11
m-Xylene	10.55	–	2.07	8.92	13.43	22.92
cumene	0.48	–	9.05	1.37	2.35	12.10
o-Xylene	4.54	–	1.35	3.77	5.44	0.42
NPBz	–	–	6.10	0.75	1.25	14.59
4-EtTol	–	–	0.00	–	8.19	–
135-TrMBz	1.43	–	3.26		–	0.8
2 and 3-tol	1.52	–	0.00		–	13.58
124TrMBz	–	–	0.00		–	–
1-3DIPB	1.13	–	1.23		–	0.5
1-4DIPB	0.96	–	14.67		–	15.21
1235-TmeBz	5.3		0.43		3.81	1.4
1234-TmeBz			0.00		2.54	3.08

Bz/Pr = 1, WHSV = $5.4\,h^{-1}$.

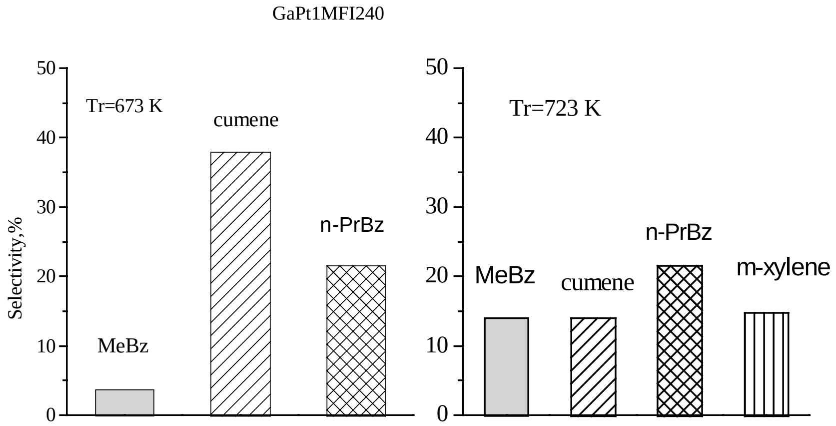
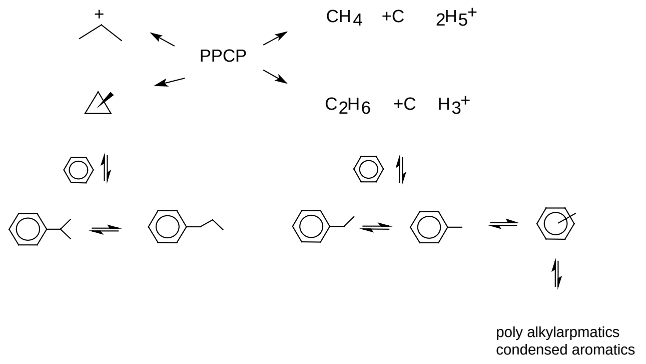


Fig. 6. Selectivity on bimetal GaPt1-MFI-240 samples after 47 min on stream.



Scheme 2. Schematic reaction pathways for benzene alkylation with pure propane.

strongly on the zeolite acidity and on the Lewis/Brönsted balance (Ga^{x+}/H^+). In the case of high acidity samples the cracking activity is favored over dehydrogenation, probably due to a high density of H^+ acidic sites. This is in accordance with the products distribution showing an increase in toluene percentage with the temperature and with increasing sample acidity (lowering the Si/Al ratio). The conversion over monometal Ga and bimetal GaPt modified zeolites is higher than that on pure zeolite. The possible reaction pathways for benzene alkylation on Ga and GaPt modified H-ZSM-5 under our conditions are illustrated in Scheme 2.

Addition of Pt to the Ga modified samples can improve catalytic activity and modify strongly the selectivity of reaction. It is observed that higher Pt content, higher conversion, whatever the Si/Al ratio is. For example, Ga modified ZSM-5 (Si/Al = 100) shows the lowest catalytic activity among all metal modified catalysts (Fig. 5, Table 4). The main reaction products are toluene, xylenes and EB (Table 4). The selectivity changes to cumene and *n*-PrBz at 673 and 723 K after Pt deposition (Fig. 6). It is well known that Pt has high activity in dehydrogenation of paraffins. The incorporation of Pt shifts the reaction path to dehydrogenation and the activation of propane leads to the formation of $C_3H_7^+$ ions, which attack benzene molecules, giving cumene and *n*-PrBz. Increasing reaction temperature can reinforce the conversion, however, decrease simultaneously the selectivity to cumene and increase the production of toluene and EB (Fig. 6), most probably because of fragmentation of cumene and *n*-PrBz at higher temperatures since it is known that cumene and *n*-PrBz may easily be converted to toluene and EtBz over acidic zeolites [4]. All studied monometal and bimetal GaPt samples demonstrate good stability with time on stream (Fig. 7). In our previous investigation on gallium and platinum modified H-ZSM-5 (Si/Al = 20) was established that activity drop quickly after 300 min time on stream (Fig. 7C upper right corner). Coke formation is responsible for quick deactivation of the samples. Better dispersion of the gallium species significant decreases coke formation. We suppose that upon activation condition used in this study (15 h at 823 K) and after Pt addition, gallium species are well dispersed in the zeolite framework. Additional redistribution and redispersion of gallium species under reaction conditions in the first reaction minutes take place and the conversion first increases and then reaches a constant.

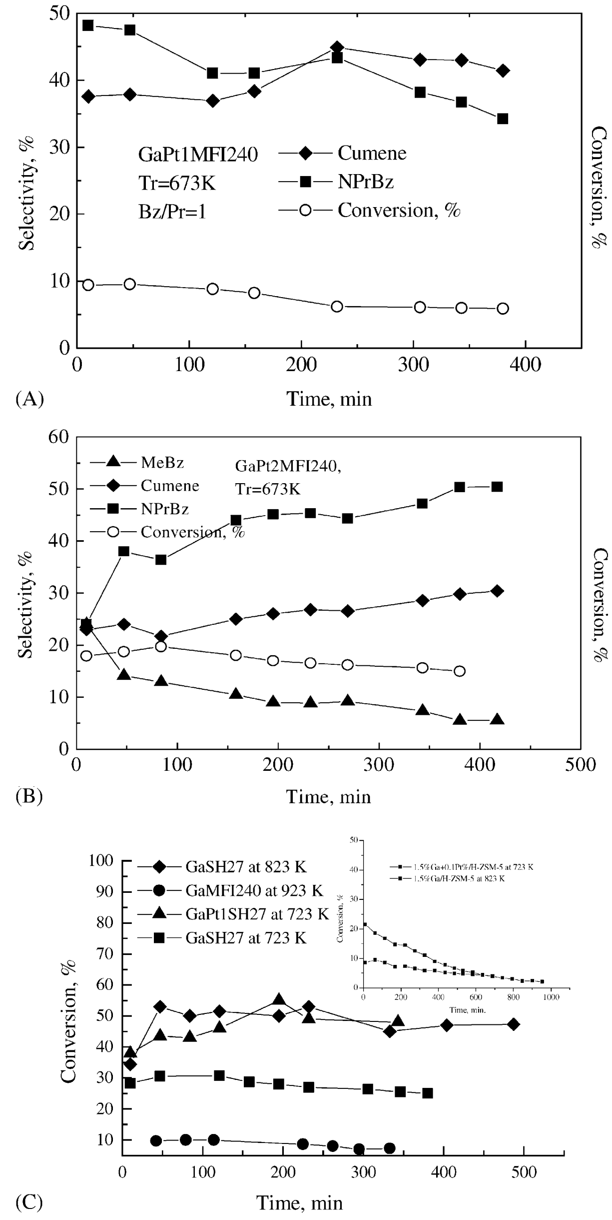


Fig. 7. Conversion and selectivity with time on stream for sample with different acidity and Ga/Pt ratio: (A) GaPt1-MFI-240, (B) GaPt2-MFI-240, (C) conversion with time on stream on monometal and bimetal samples.

Monometal Ga-MFI-90 and Ga-MFI-240 show high conversion and good stability with time on stream at high temperature (923 K) (Fig. 7C). After 6 h reaction the conversion decreases only about 5–10%. This is because of low acidity of these samples, the coke formation is suppressed.

3.3. Coke formation

The IR spectra of discharged catalysts in KBr were recorded to understand the type of coke produced during

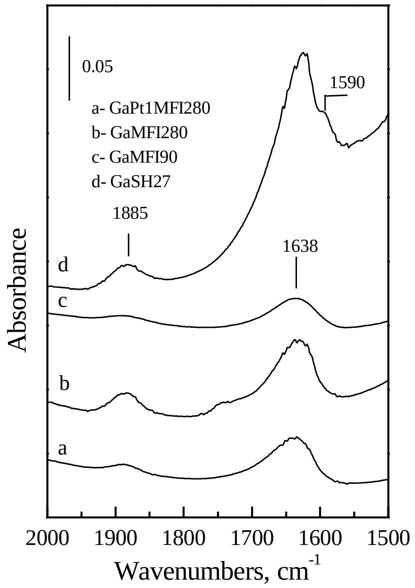


Fig. 8. IR spectra after reaction at different temperature on gallium loaded samples with different Si/Al ratio.

reaction (Fig. 8). Samples with high Si/Al ratio exhibit band at 1638 cm^{-1} (Fig. 8a and b) and the samples with low Si/Al ratio (Fig. 8d) show additional band at 1590 cm^{-1}. which arises from the heavy polyolefines and/or polycondensed aromatics [22]. The band 1638 cm^{-1} is so-called coke band which originates from δ (C–H) modes of complex mixture of carbonaceous, hydrogen-deficit deposits, polyethens and/or aromatics [22]. Very probably high acidic zeolites provoke the deposition of polyolefines and/or polycondensed aromatics on the catalysts surface [23]. The presence of platinum particles decreases the deposition of polyolefines and increase catalytic activity and stability (Fig. 8a and b).

4. Conclusion

Ga- and GaPt-modified H-ZSM-5 zeolites are efficient catalysts for benzene alkylation with pure propane. The catalytic activity, products distribution and reaction path depend strongly on zeolite acidity and Pt content. The conversion decreases and products distribution changes with increasing Si/Al ratio. Main reaction products for high acidity catalysts (lower Si/Al ratio) are toluene and xylenes, which means that creaking of propane is favored over its dehydrogenation. For the sample with low acidity, the formation of ethylbenezene (EtBz) and propylbenzenes (PrBz) is enhanced.

Bimetal GaPt samples could be very efficient catalysts for cumene production from benzene alkylation using propane as alkylating agent. Pt promoted Ga-ZSM-5 catalysts show low concentration of coke like polyolefines and polycondensed aromatics, because of platinum has a role of the entrance for hydrogen spillover, which prevents or moderates, coke deposition.

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References

[1] S. Siffert, B-L Su, React. Kinet. Catal. Lett. 68 (1999) 191–195.
[2] C. Bigey, B.L. Su, J. Mol. Catal. A: Chem. 209 (2004) 179–187.
[3] I. Ivanova, N. Blom, E. Derouane, J. Mol. Catal. A: Chem. 109 (1999) 157–168.
[4] I.I. Ivanova, D. Brunel, J.B. Nagy, E.G. Derouane, J. Mol. Catal. A: Chem. 95 (1995) 234.
[5] 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.
[6] A. Montes, Z. Gabelica, A. Rodriquez, G. Gianetto, Appl. Catal. A 169 (1998) 82.
[7] V. Kanazirev, G.L. Price, G. Tyuliev, Zeolite 12 (1992) 846.
[8] Ek. Zhecheva, R. Stoyanova, G. Tyuliev, K. Tenchev, M. Mladenov, S. Vassilev, Solid-State Sci. 5 (2003) 711.
[9] S. Todaorova, B.L. Su, J. Mol. Catal. A: Chem. 201 (2003) 223–235.
[10] G.L. Price, V. Kanazirev, J. Catal. 126 (1990) 267.
[11] P. Meriaudeau, C. Naccache, Appl. Catal. 13 (1991) L13.
[12] I.A. Sheka, I.S. Chaus, I.I. Mityureva, The Chemistry of Gallium, Elsevier, Amsterdam, 1966.
[13] S.B. Abdul Hamid, Dr. Sc. Thesis, University of Namur, Belgium, 1993.
[14] R.S. Kwak, W.M.N. Sachtler, J. Catal. 145 (1994) 456.
[15] T.J.G. Kolke, K.J. Gortek, G.T. Kokotailo, Appl. Catal. 54 (1989) 177.
[16] K.M. Dooley, C. Chang, G.L. Price, Appl. Catal. 84 (1992) 17.
[17] P. Meriaudeau, S.B. Abdul Hamid, C. Naccache, J. Catal. 139 (1993) 683.
[18] L.R. Raddi de Araujo, M. Shamal, Appl. Catal. A: Gen. 203 (2000) 275.
[19] E.S. Shpiro, D.P. Shavchenko, O.P. Tkachenko, R.V. Dmitriev, Appl. Catal. 107 (1994) 147.
[20] R. Fricke, H. Kosslick, G. Lischke, M. Richter, Chem. Rev. 100 (2000) 2303.
[21] E.G. Deurouane, S.B. Abdul Hamid, I.I. Ivanova, N. Blom, P.E. Hojlund-Nielsen, J. Mol. Catal. 86 (1994) 371.
[22] V.M. Choudhary, C. Sivadinarayana, P. Devadas, S.D. Sansare, P. Magnoux, M. Guisnet, Mesopor. Mesopor. Mater. 21 (1998) 91.
[23] H.G. Karge, Appl. Catal. A: Gen. 146 (1996) 33.