Shape selectivity of ZSM-5 zeolite modified with chemical vapor deposition of silicon and germanium alkoxides

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Abstract

The shape selectivity of ZSM-5 zeolite was modified with the chemical vapor deposition of silicon and germanium ethoxides. Both Si and Ge modifications were carried out by using one and three CVD cycles. Modified zeolites were characterized with FTIR and MAS NMR spectroscopy. The deposition of alkoxides took place mainly on the external surface and therefore no significant changes in strong Brønsted acidity were observed. This was confirmed by IR and ^{1}H MAS NMR spectroscopy as well as with the catalytic cracking of n-hexane over modified zeolites in which no significant loss of activity compared with unmodified zeolite was detected (except in the case of triply silane deposited ZSM-5). The reduction of channel dimensions of modified zeolites was concluded from the reduced chemisorption capacity of pyridine. In the conversion of methanol to hydrocarbons the selectivity of modified zeolites towards aliphatic, linear and small olefinic products increased and the formation of aromatic and branched hydrocarbons decreased. In the cracking of n-hexane the effect of modifications on shape selectivity was less notable. The passivation of external surface was characterized by the cracking of 1,3-di-isopropyl benzene. Both Si and Ge modifications decreased the outer surface acidity but the passivation was concluded to be more complete in silane deposited ZSM-5 zeolites.

Keywords: ZSM-5; CVD; Silicon and germanium alkoxide; Shape selectivity

1. Introduction

One of the most important aims in the industrial catalytic processing of hydrocarbons is the selectivity towards desirable reaction products. The use of zeolites as shape selective catalyst has been under extensive study since the early 1960's [1]. The major progress in the field of shape selective catalysis was the discovery of medium pore zeolite ZSM-5 [2]. The impor-

tance of ZSM-5 is due to its unique channel structure with dimensions approaching those of many organic molecules resulting in diffusional differences between linear and branched hydrocarbons [3].

Although possessing good shape selectivity by themselves, there has been a considerable effort to prepare more selective zeolite catalysts by a number of post synthesis reactions. One interesting method to enhance shape selectivity is the passivation of the non-shape selective acid sites located on the external surface of

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catalyst crystals. This can be carried out by the selective dealumination of zeolite framework with compounds like $(NH_4)_2SiF_6$ [4–6] and $SiCl_4$ [7–9].

Also the chemical vapor deposition (CVD) of tetramethoxy silane $Si(OCH_3)_4$ have been found to be an effective method to tailor the external surface acidity of zeolite materials [10–14]. The effect of CVD modification on selectivity is twofold: it is possible not only to passivate the outer surface acid sites but also to control the dimensions of pore openings by the deposition of inactive silica coating on the external surface of the catalyst crystals.

Due to relative high boiling temperatures of higher silicon alkoxides, the preparation of catalysts modified with e.g. $Si(OC_2H_5)_4$ has usually been carried out by impregnation [15,16] although the use of CVD technique over zeolite Hβ has also been reported [17]. The aim of our present work was to study the shape selective properties of ZSM-5 zeolite modified with the chemical vapor deposition of tetraethoxy silane and germanium tetraethoxide $Ge(OC_2H_5)_4$. Due to the large size of the alkoxides (the longest dimension of tetraethoxy silane ~ 11.5 Å) the modifications were expected to limit only on the external surface of ZSM-5 zeolite.

2. Experimental section

ZSM-5 zeolite with a Si-to-Al ratio of 54.4 and a crystallinity of 99% was prepared according to the literature methods [18]. The ammonium form of ZSM-5 zeolite was converted to the corresponding hydrogen form, HZSM-5, during calcination in air at 813 K for two hours.

The chemical vapor deposition of HZSM-5 with silicon and germanium ethoxide was carried out in a quartz tube reactor at atmospheric pressure. Before the depositions HZSM-5 was dehydrated at 673 K for two hours under a nitrogen flow. The modifications were performed by using one and three CVD cycles. The

number in the catalyst name is referred to the number of deposition cycles during the modifications. Samples Si_1ZSM-5 and Ge_1ZSM-5 were prepared by introducing vaporized alkoxide compounds into the reactor at 388 K by using nitrogen as a carrier gas. Due to relative high boiling points of the silicon and germanium ethoxides (168 and 185°C, respectively) oil bath ($T \sim 150$°C) was used to enhance the vaporization. The volumes of the modifiers were calculated to exceed at least three times the theoretical total number of strong acid sites which was estimated from the aluminium content of the zeolite (1 wt.-%). Deposited catalysts were contacted with water vapor at ambient temperature in order to decompose the organic substituents of the alkoxides. Finally the catalysts were dried and calcined in air at 813 K for two hours.

Samples Si_3ZSM-5 and Ge_3ZSM-5 were prepared by using deposition temperature of 593 K. Water vapor treatment was not carried out after the modifications. Modified zeolites were calcined in air at 673 K for three hours. The CVD process was repeated as above and after third depositions the samples were calcined in air at 813 K for two hours in order to decompose all organic substituents.

The acidic properties of the outer surface modified ZSM-5 zeolites were characterized with Nicolet Magna 750 FTIR spectrometer by using a diffuse reflectance method. Sample chamber was equipped with nitrogen and vacuum line connections. Zeolite samples with a 50 wt.-% diamond powder matrix were dehydrated in a nitrogen flow and under vacuum conditions at 673 K for two hours. Pyridine was contacted with the zeolite for 15 minutes at 388 K at the pressure of 3 Torr. Physisorbed pyridine was desorbed by heating the zeolite at 423 K for two hours under vacuum. All IR spectra were collected at ambient temperature.

NMR measurements were carried out with Bruker AMX-400 FT NMR spectrometer equipped with magic angle spinning probeheads. For ^1H (400.131 MHz, pulse length 2.0

μs, recycle delay 2.0 s) MAS NMR measurements the samples were dehydrated under vacuum conditions at 673 K for 8 hours. Before ^{27}Al (65.177 MHz, pulse length 0.6 μs, recycle delay 0.5 s) MAS NMR measurements the samples were contacted with the vapor of 3 M NH$_4$NO$_3$ solution for three days under vacuum. For ^{29}Si (49.695 MHz, pulse length 5.0 μs, recycle delay 10 s) measurements no sample pretreatments were required. The spinning rate of the spinner (7 mm) was 5 kHz in all measurements. The framework Si-to-Al ratios of the modified zeolite samples were determined from the ^{29}Si MAS NMR spectra by deconvolution.

The effect of the surface modifications on catalytic activity and product selectivity was studied in the crackings of n-hexane and 1,3-di-isopropyl benzene as well as in the conversion of methanol to hydrocarbons. The reactions were studied in a continuous flow reactor. The products were analyzed with a Hewlett-Packard 5890 Series II gas chromatography (on-line system) equipped with a flame ionization detector (FID). The areas of products were integrated and the amounts of products were presented in terms of percentages from the total product feed. The cracking of n-hexane and the methanol conversion reactions were carried out at the temperature of 643 K and the cracking of 1,3-di-isopropyl benzene at 673 K. The WHSV values for n − hexane, methanol and 1,3-di-isopropyl benzene were determined according to a equation WHSV = (g of reactant)h^{-1} (g of zeolite)$^{-1}$.

3. Results and discussion

The modifications of ZSM-5 zeolite were carried out with the chemical vapor deposition of silicon and germanium tetraethoxide by using one and three deposition cycles at 388 and 593 K, respectively. The acidic properties of the surface modified zeolites were studied by FTIR and ^{1}H MAS NMR spectroscopy. Structural transformations were characterized by ^{27}Al and ^{29}Si MAS NMR spectroscopy.

3.1. FTIR measurements

The OH region in the IR spectrum of HZSM-5 zeolite is composed of four bands (Fig. 1). The most dominant bands at 3745 cm^{-1} and 3610 cm^{-1} are due to terminal silanol groups SiOH and strong Brønsted acid sites, respectively. A weak band at 3662 cm^{-1} and a broad band at ca. 3500 cm^{-1} has been assigned to extra-lattice aluminium hydroxide species and hydrogen bonded silanol groups, respectively.

Silicon and germanium modifications resulted in no remarkable changes in the intensity
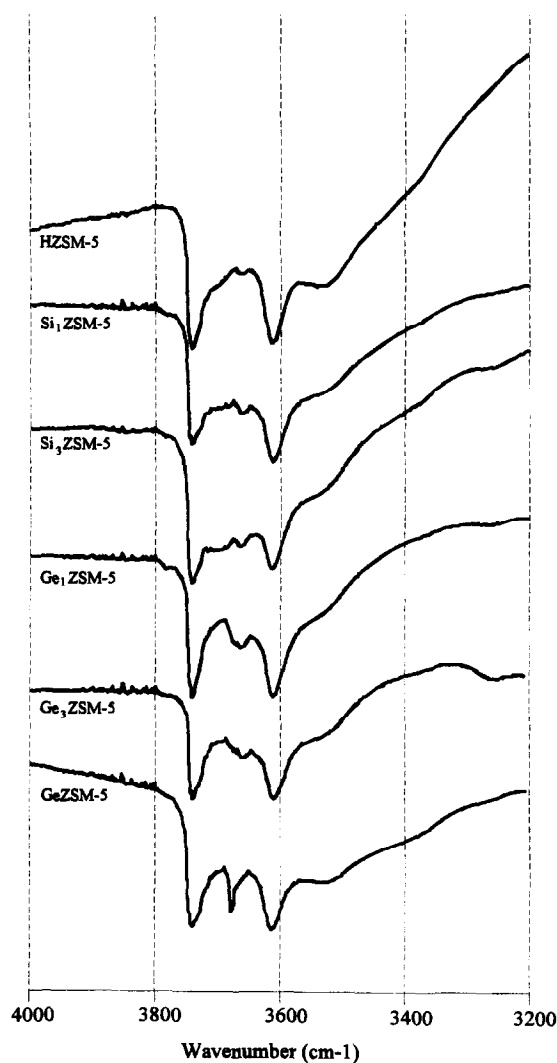

Fig. 1. FTIR spectra of silicon and germanium modified ZSM-5 zeolites on the OH region.

of the band at 3610 cm^{-1} indicating no significant loss of strong Brønsted acid sites. The result confirms that the modifications have limited mainly on the external surface of the catalyst particles which is logical due to the dimensions of silicon and germanium ethoxides larger than the pore openings of ZSM-5 zeolite. X-ray diffraction results have showed decreased crystallinity in triply silane modified ZSM-5 (74%) compared with unmodified zeolite (96%). This may be due to quite severe reaction conditions during CVD resulting in the decomposition of zeolite structure. The dealumination is likely to take place selectively on the outer parts of catalyst crystals because the diffusion of bulky silane molecules into the zeolite channels is not possible. The appearance of new bands in the IR spectrum of Si$_3$ZSM-5 may be due to the presence of extra framework aluminium and silicon species located on the surface or in the zeolite channels.

In the IR spectra of Ge$_1$ZSM-5 and Ge$_3$ZSM-5 a new signal with weak intensity at 3675 cm^{-1} probably due to germanium hydroxyl species was observed. The intensity of this band was relative high after modification with germanium ethoxide carried out in situ in the IR sample chamber followed by calcination under nitrogen at 673 K for 2 hours (GeZSM-5 in Fig. 1). Therefore, it is likely that calcination in air at high temperature results in the conversion of the germanium hydroxyls into germanium dioxide layer on the external surface of the catalyst. The deposited germanium dioxide is composed of tetrahedral GeO$_4$ units and it has been reported to be unstable to moisture [14,19].

The chemisorption of pyridine over unmodified HZSM-5 and outer surface modified ZSM-5 zeolites is presented in Fig. 2. Pyridine chemisorbed on Brønsted acid sites (pyridinium ions PyH$^+$) results in IR bands at 1638 cm^{-1} and 1547 cm^{-1}. Bands due to pyridine on Lewis acid sites are observed at 1625, 1455 and 1450 cm^{-1}. An intense band at 1491 cm^{-1} has been assigned to pyridine on both Brønsted and Lewis acid sites. The intensities of pyridinium ion

signals remained nearly unchanged in once silicon and germanium deposited zeolites (samples Si$_1$ZSM-5 and Ge$_1$ZSM-5). However, modifications enhanced slightly the formation of weak Lewis acid sites which was observed as an increased intensity of the bands at 1491 and 1450 cm^{-1}. According to the above results it seems obvious that in samples Si$_1$ZSM-5 and Ge$_1$ZSM-5 the amount of deposited silicon and
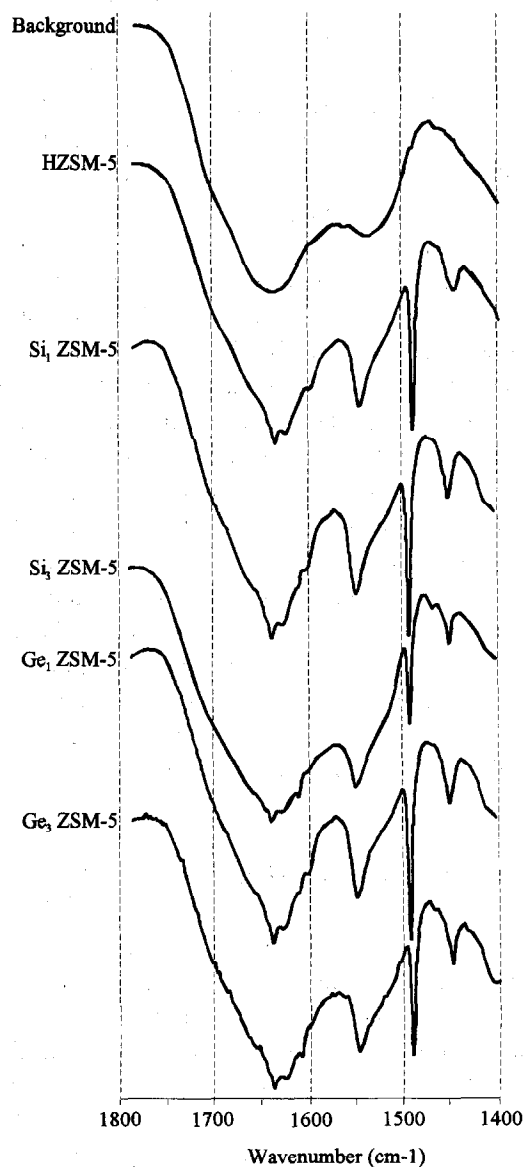

Fig. 2. Effect of silicon and germanium modifications on the chemisorption capacity of pyridine.

germanium is quite small and the effect on reduction of pore openings is not remarkable.

The chemisorption capacity of triply silicon and germanium modified zeolites (samples Si$_3$ZSM-5 and Ge$_3$ZSM-5) decreased notably compared with unmodified HZSM-5 probably due to reduced diffusion rate of pyridine into the intracrystalline acid sites of the zeolite through pore openings with decreased dimensions. The reduction of pore openings seemed to be more drastic in silicon deposited zeolite. This may be explained by the poor stability of deposited germanium oxide to traces of moisture which may be present in the zeolite even after dehydration at 673 K. Enhanced shape selective properties of germanium deposited zeolite has been reported to be due to the formation of an ultrathin germanium oxide layer on the external surface [19]. When exposed to water the ultrathin oxide layer is converted to bulky germanium oxide layer resulting in the blocking of some pore openings and the formation of undeposited areas on the surface.

3.2. MAS NMR measurements

Silicon and germanium modified zeolites were characterized also with ^{29}Si, ^{27}Al and ^{1}H MAS NMR spectroscopy. The Si MAS NMR spectrum of ZSM-5 zeolite is composed of three signals at the chemical shifts of -106, -112 and -115 ppm [20]. An intense signal at -112 ppm as well as a shoulder at -115 ppm are due to silicon tetrahedra SiO$_4$ surrounded by four other silicon tetrahedra. A signal at -106 ppm has been assigned to silicon tetrahedra connected to three other silicon tetrahedra and to one aluminium tetrahedron. The intensity of this signal is low because of the low aluminium content of ZSM-5 zeolite (Fig. 3).

Germanium modifications resulted in a slight dealumination of the zeolite framework. This was concluded from the loss in intensity of the signal at -106 ppm as well as from the increased Si-to-Al ratios of the Ge deposited ZSM-5 (58.8 for Ge$_1$ZSM-5 and 62.2 for

Ge$_3$ZSM-5) compared with unmodified HZSM-5 (Si/Al$_{total}$ = 54.4, Si/Al$_{framework}$ = 52.0) Also the intensity of the signal at -115 ppm decreased remarkably in germanium deposited zeolites. In ZSM-5 modified once with tetraethoxide silane the framework Si-to-Al ratio determined with ^{29}Si MAS NMR increased to 61.7 indicating the minor loss of structural aluminium. However, repeated silane modifications carried out at high temperature (Si$_3$ZSM-5) resulted in the loss of both structural aluminium and silicon atoms. Due to the loss of structural silicon the framework Si-to-Al ratio dropped to 46.8.

The ^{1}H MAS NMR spectrum of unmodified HZSM-5 zeolite presented in Fig. 4 is com-
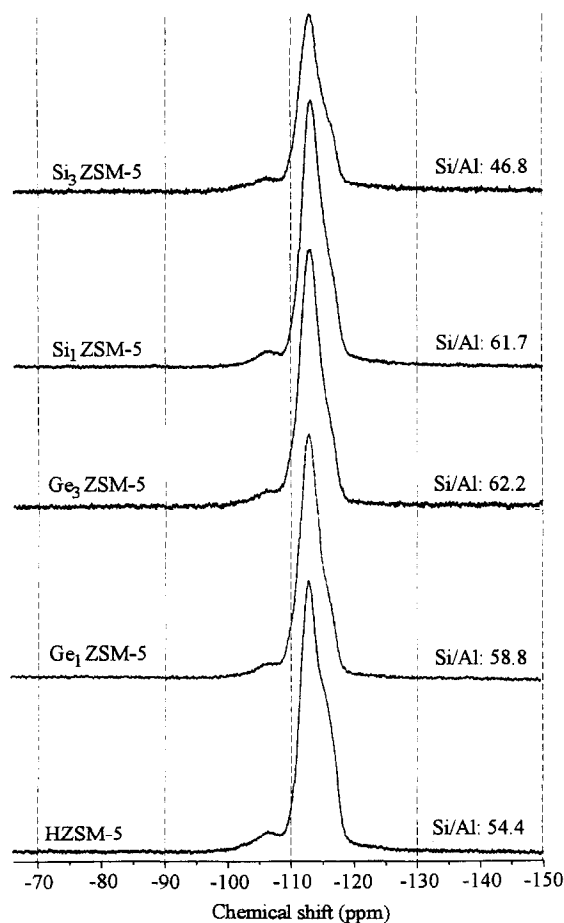

Fig. 3. ^{29}Si MAS NMR spectra and the theoretical Si-to-Al ratios of silicon and germanium deposited ZSM-5 zeolites.

posed of two main signals at the chemical shift of 3.8 and 1.5 ppm due to bridging hydroxyl groups (Brønsted acid sites) and terminal silanol groups, respectively. No significant changes in the intensity of the Brønsted acid site signal of surface modified zeolites were observed indicating only minor loss of strong acid sites. This result is in agreement with FTIR measurements discussed above. The signal of terminal AlOH groups appears in the proton spectra at the region of 2.6–3.6 ppm. Therefore, the slight broadening of the Brønsted acid site signal in Ge_3ZSM-5 and Si_3ZSM-5 may be due to the presence of aluminium hydroxyls groups formed via the dealumination of the zeolite framework. In the spectrum of singly germanium deposited ZSM-5 a new signal appeared at the chemical shift of 6.2 ppm. The origin of this signal is believed to be due to the same species observed at 3675 cm^{-1} in the IR spectrum of Ge_1ZSM-5 assigned to germanium hydroxyl species. The
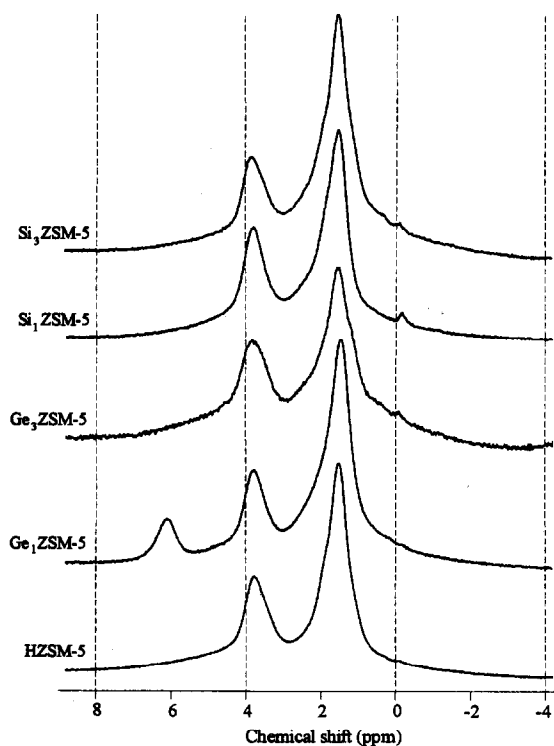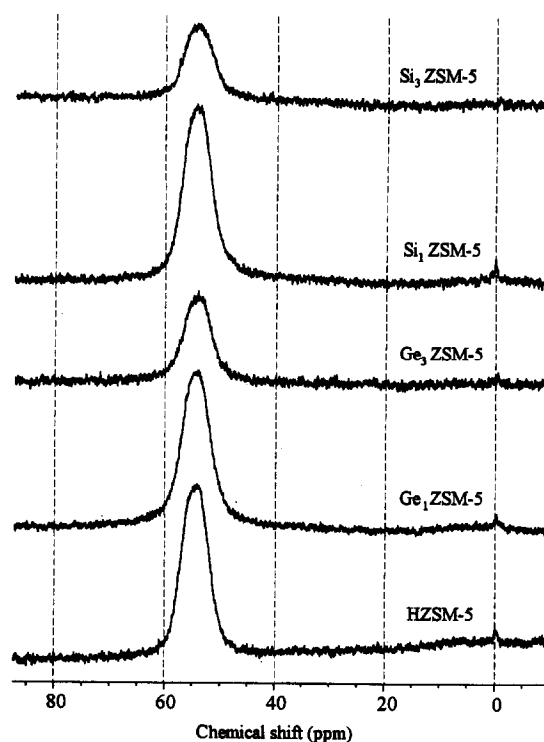

Fig. 5. ^{27}Al MAS NMR spectra of silicon and germanium modified ZSM-5 zeolites.

signal was not detected in Ge_3ZSM-5 which can be explained by the total conversion of the surface GeOH species into germanium dioxide at higher calcination temperature.

^{27}Al MAS NMR spectroscopy was used to characterize the aluminium atoms in different coordination environments. Two signals at 54 and 0 ppm in the ^{27}Al MAS NMR spectrum of HZSM-5 (Fig. 5) have been assigned to tetrahedrally coordinated framework aluminium and octahedrally coordinated extra framework aluminium atoms, respectively. Due to a high Si-to-Al ratio and high crystallinity of HZSM-5 the intensity of octahedral aluminium was low. The intensity of the signal of tetrahedral aluminium was unchanged in Si_1ZSM-5 but was slightly decreased in Ge_1ZSM-5. In triply silicon and germanium deposited zeolites the intensity has decreased drastically indicating the conversion of structural aluminium into extra framework aluminium species. However, there was no evi-

Fig. 4. ^1H MAS NMR spectra of silicon and germanium modified ZSM-5 zeolites.

dence of octahedral extra framework aluminium in Si_3ZSM-5 and Ge_3ZSM-5.

3.3. Catalytic studies

The catalytic activity of zeolite materials in hydrocarbon conversion reactions is based on the presence of acidic centers, especially strong Brønsted acid sites, in zeolite framework. The O–H bond in a Brønsted acid site is mainly covalent in nature and the acid strength is affected by the Si–O–Al angle, the amount of aluminium in the first coordination sphere and the concentration of protons in the framework [21]. Therefore, zeolites with a high Si-to-Al ratio such as HZSM-5 are materials with high acid strength. Due to the low concentration of structural aluminium atoms the acidic centers are isolated leading to low rates of bimolecular hydrogen transfer reactions. This as well as the advantageous channel structure are the main reasons for the large use of ZSM-5 zeolites as an octane boosting component in a modern FCC catalyst.

3.3.1. Cracking of n-hexane and 1,3-di-isopropyl benzene (1,3-DIPB)

The product distribution in the cracking of n-hexane over Si and Ge deposited ZSM-5 was analyzed after 2, 4 and 6 hours from the beginning of the reaction. There was no notable loss of activity after the cracking time of 6 hours and no significant changes in the product distribution were observed. The product composition after the reaction time of 2 hours is presented in Table 1. The catalytic activity of triply silane deposited ZSM-5 decreased drastically compared with unmodified zeolite probably because of the diffusional effects which will be discussed in more detail in Section 3.3.2. However, there was no notable drop in the conversion level over other modified catalysts indicating only minor loss of strong Brønsted acid sites during the depositions. The modifications had no significant effect on the formation selectivity of aliphatic, aromatic, linear or branched hydro-

Table 1

Cracking of n-hexane over HZSM-5 and outer surface modified ZSM-5 zeolites

	Catalyst number [a]				
	1	2	3	4	5
Conversion of n-hexane (%)	23.1	19.7	18.6	21.4	11.5
WHSV [b]	13.9	14.7	14.9	14.1	14.6
Hydrocarbons (%)					
Aliphatics	93.5	94.0	95.5	93.7	93.6
Aromatics	6.5	6.0	4.5	6.3	6.4
Linear	64.7	63.9	67.5	65.1	66.9
Branched	28.8	30.1	28.0	28.6	26.6
Olefins (%)					
C_2	0.6	0.6	1.1	0.8	1.1
C_3	2.2	2.3	4.0	3.1	4.3
C_4	3.7	3.9	6.4	4.8	6.6
C_2–C_4 (total)	6.5	6.8	11.5	8.7	12.0
C_5–C_6 (total)	1.4	1.5	2.6	1.9	2.7
Paraffins (%)					
C_2	0.5	0.4	0.4	0.4	0.4
C_3	29.0	26.4	25.1	26.2	24.5
C_4	20.8	21.1	20.1	20.3	19.5
i-C_4	17.6	17.5	15.5	16.5	14.4
C_2C_4 (total)	67.9	65.4	61.1	63.4	58.8
C_5^+	17.6	18.1	20.2	19.5	20.0

Reaction conditions: $T = 370°C$, $p = 1$ atm.

[a] Catalyst numbers: (1) HZSM-5, (2) Ge_1ZSM-5, (3) GQZSM-5, (4) Si_1ZSM-5, (5) Si_2ZSM-5.

[b] WHSV = (g of n-hexane)h^{-1} (g of catalyst)$^{-1}$.

carbons but the production of small olefins increased slightly over triply Si and Ge deposited zeolites.
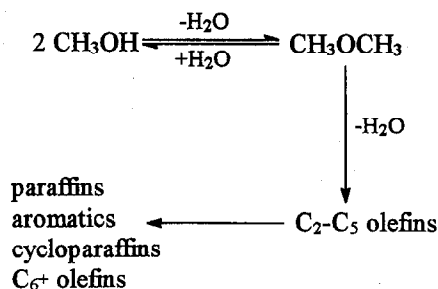
The cracking of 1,3-DIPB was used as a test reaction to characterize the acidity on the external surface. Due to the size of 1,3-DIPB larger than the channel dimensions of ZSM-5 the catalytic activity should be related only to the number of acid sites on the external surface. Reactions were carried out at 673 K and the composition of feed was analyzed after 2 hours from the start. The conversion level dropped from 0.7% (unmodified HZSM-5) to 0.1% and 0.2% over Si_1ZSM-5 and Ge_1ZSM-5, respectively. The low activity of unmodified HZSM-5 indicates that only a small fraction of acid sites is located on the external surface and therefore the catalytic role of these sites is quite negligi-

ble. The conversion of Si_3ZSM-5 and Ge_3ZSM-5 dropped from 1.2% (HZSM-5) to 0.4% and 0.3%, respectively. However, in the case of Si_3ZSM-5 the only product was methane. It was possibly formed via thermal cracking, since its formation was also detected in a blank test (no catalyst in the reactor). Therefore, the passivation of the external surface in the case of Si_3ZSM-5 may be considered complete.

3.3.2. Methanol to hydrocarbons

The conversion of methanol to hydrocarbons is believed to take place according to a reaction path presented in Scheme 1 [22]. Dimethyl ether DME is the intermediate in the reaction. The conversion of DME to hydrocarbons as well as the product distribution are highly depended on the contact time of the reactant with the catalyst. If the contact time is very short $(1/LHSV < 10^{-3})$ no conversion of DME takes place. By increasing the contact time $(1/LHSV \sim 10^{-1})$ the formation of especially small olefins becomes dominant (methanol-to-olefins process). Long contact times $(LHSV \sim 1)$ enhance the formation of paraffins and aromatic hydrocarbons (methanol-to-gasoline process).

The product distribution in methanol conversion reactions over silicon and germanium modified ZSM-5 zeolites were analyzed after 1, 2 and 3 hours from the beginning of the reaction. The catalytic activity dropped as a function of time due to the formation of coke precursors thus increasing the shape selectivity similarly as discussed below. The product composition after the reaction time of 1 hour is presented in Table 2. There were no significant changes in the

$$2\ CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3$$

paraffins
aromatics $\longleftarrow$ C₂-C₅ olefins
cycloparaffins
C₆⁺ olefins

Scheme 1.

Table 2
Conversion of methanol to hydrocarbons over HZSM-5 and outer surface modified ZSM-5 zeolites

| | Catalyst number [a] | | | | | |
	1	2	3	4	5	6
Conversion of methanol (%)	62.1	53.0	52.6	80.9	55.3	26.0
CH_3OH (%)	24.2	27.8	30.8	15.4	27.9	39.6
CH_3OCH_3 (%)	13.7	19.1	16.6	3.7	16.8	34.4
WHSV [b]	68.8	69.6	69.4	38.0	38.3	39.2
Hydrocarbons (%)						
Aliphatics	82.9	84.4	84.4	84.7	83.9	87.6
Aromatics	17.1	15.6	15.6	15.3	16.1	12.4
Linear	55.5	55.4	62.2	55.8	57.5	76.7
Branched	27.5	28.9	22.1	28.9	26.3	10.2
Olefins (%)						
C_2	14.4	17.3	21.5	13.1	19.6	30.6
C_3	17.9	19.9	21.8	20.7	19.3	31.6
C_4	5.3	6.6	6.8	6.2	5.7	7.8
C_2-C_4(total)	37.6	43.8	50.1	40.0	44.6	70.0
C_5-C_6 (total)	2.4	2.6	2.9	4.0	3.2	1.9
Paraffins (%)						
C_2	0.0	0.0	0.0	0.4	0.3	0.0
C_3	11.6	7.9	8.1	8.8	6.7	1.8
C_4	4.8	3.7	4.1	3.9	3.7	3.8
$i-C_4$	12.6	12.5	8.7	13.0	10.5	3.0
C_2-C_4 (total)	29.0	24.1	20.9	26.1	21.2	8.6
C_5	12.4	13.9	10.5	13.8	14.1	5.7

Reaction conditions: $T = 370°C$, $p = 1$ atm.
[a] Catalyst numbers: (1) HZSM-5, (2) Ge_1ZSM-5, (3) Si_1ZSM-5, (4) HZSM-5, (5) Ge_2ZSM-5, (6) Si_2ZSM-5.
[b] WHSV (g of methanol) h^{-1} (g of catalyst)$^{-1}$.

shape selectivity of germanium deposited catalysts compared with HZSM-5 although the modifications increased slightly the formation of small olefins and decreased the formation of small paraffins. However, more notable changes in the product distribution over silicon modified zeolites were observed. Increased shape selective properties of silane treated ZSM-5 were concluded from the enhanced formation selectivity of small olefins and linear aliphatic products as well as from the decreased amounts of aromatic and branched hydrocarbons compared with unmodified catalyst. However, the product distribution of Si_3ZSM-5 may not be absolutely comparable with the other samples due to a relative low conversion level. As discussed

above the reactions of silicon and germanium alkoxides with ZSM-5 affected mainly the outer surface acidity. Therefore the loss of catalytic activity of the modified zeolites is more probably due to the decreased diffusion rates of reactant molecules through the narrowed pore openings rather than to the loss of intracrystalline acidic centers in the zeolite framework. As mentioned in NMR results the partial destruction of the zeolite structure was observed to take place especially in the case of triply modified Si_3ZSM-5. The low activity and good selectivity of Si_3ZSM-5 may be explained by the formation of extra framework silicon or aluminium species which may be located in the zeolite channels thus forming diffusion barriers or even blocking some pores. Therefore the increased selectivity may be due to the steric hinderance experienced by bulky molecules in the pores.

4. Conclusions

In the present work we have studied the effect of modifications with silicon and germanium alkoxides on the acidic and catalytic properties of ZSM-5 zeolite. The modifications were carried out by using a chemical vapor deposition technique and the samples were characterized by IR and MAS NMR spectroscopy. Due to the large dimensions of the alkoxides the modifications took place mainly on the external surface and therefore no significant loss of acid sites was observed. The amount of chemisorbed pyridine decreased over triply silicon and germanium modified zeolites. The reduced chemisorption capability is supposed to be due to decreased pore dimensions thus affecting the diffusion rates of pyridine molecules. On the basis of ^{29}Si and ^{27}Al MAS NMR spectra the dealumination of the zeolite framework was observed to take place during the modifications. The partial destruction of framework was the most drastic in the case of triply silane treated ZSM-5 in which the loss of both structural aluminium and silicon was detected.

Cracking of 1,3-di-isopropyl benzene was used as a model reaction to characterize the external surface acidity before and after the modifications. The number of non-shape selective acid sites located on the outer surface decreased in both Si and Ge modifications but the passivation took place more effectively in silane depositions.

The effect of germanium and silane modifications on shape selectivity was studied in a methanol conversion reaction as well as in the cracking of n-hexane. The catalytic activity of modified zeolites, especially in the case of triply silane deposited ZSM-5, decreased in both reactions. The loss of activity was assumed to be due to diffusional effects or even to the blocking of the zeolite channels. Enhanced shape selective properties of Si and Ge deposited zeolites was observed especially in the conversion of methanol to hydrocarbons. The formation selectivity of aliphatic and linear hydrocarbons increased and the production of aromatic and branched products decreased over modified zeolites. Also the formation of small olefins C_2-C_4 was enhanced by the depositions in both reactions.

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