Shape-selective disproportionation of ethylbenzene to *para*-diethylbenzene over ZSM-5 modified by chemical liquid deposition and MgO

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Abstract

Zeolite ZSM-5, for catalyzing shape-selective disproportionation of ethylbenzene (EB) to produce *para*-diethylbenzene (*p*-DEB), was modified by chemical liquid deposition of silica (SiO_2-CLD), chemical vapor deposition of silica (SiO_2-CVD), loading MgO and SiO_2-CLD and loading MgO. The results show that ZSM-5 modified by SiO_2-CLD (SiO_2-CLD/ZSM-5) has better catalytic performance than ZSM-5 modified by SiO_2-CVD (SiO_2-CVD/ZSM-5) due to passivation of partial acidic sites in channels of SiO_2-CVD/ZSM-5. When SiO_2-CLD/ZSM-5 is further modified by a loading of 0.50 wt% MgO to ZSM-5, it decreases both in acidic amount and in acidic strength, and its catalytic activity decreases slightly. But, the residual acidic sites on the external surface of SiO_2-CLD/ZSM-5 are well eliminated. As a result, MgO modification improves *para*-diethylbenzene selectivity (*p*-DEB to DEB) up to 98.6% with appreciable EB conversion of 28.1%, and it greatly reduces the side reaction of EB dealkylation. Besides, ZSM-5 modified by SiO_2-CLD and MgO (SiO_2-CLD and MgO/ZSM-5) shows a good stability due to proper modification of its acidity and structure.
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1. Introduction

para-Diethylbenzene is a kind of highly value-added aromatics. It is used as a desorbent in adsorptive separation process, such as UOP Para-ex and IFP eluxyl [1–3]. Besides, it is an important monomer for production of copolymers, such as ion-exchange resin and viscosity modifiers of lubricant oil. Because three *p*-DEB, *m*-DEB and *o*-DEB isomers are very similar in physical properties, usual distillation process cannot solve their separation. Although *p*-DEB was obtained from the mixed isomers by adsorptive separation, this process is energy consuming and very costly [4]. Besides, ethylation of benzene with ethanol was carried out over large pore aluminophosphate molecular sieves, but there is 17% yield of the mixed DEB without *p*-DEB selectivity [5]. In recent years, two processes have been developed for production of *p*-DEB, i.e., EB alkylation with ethanol or ethylene and shape-selective EB disproportionation [6]. Compared with EB alkylation, shape-selective EB disproportionation is the simpler process with less cost for the installation and longer lifetime of the catalyst.

EB disproportionation were investigated over a variety of zeolites, such as mordenite, USY, Beta, MCM-22, ZSM-5, etc. [7–9]. Although zeolites show a good catalytic stability for this reaction, an equilibrium composition of DEB isomers was given over most of zeolites, and the low *p*-DEB selectivity appears over ZSM-5 with large crystal sizes [9,10]. It is considered that the catalytic mechanism of shape-selective EB disproportionation is the same as that of the shape-selective disproportionation of toluene, i.e., shape-selectivity for diffusion difference among *p*-DEB, *m*-DEB and *o*-DEB isomers [11]. To improve *p*-DEB selectivity, the acidity and structure of zeolite is necessary to be modified. On one hand, modification passivates the acidic sites on the external surface of ZSM-5 for eliminating secondary isomerization of *p*-DEB. On the other hand, modification reduces opening sizes of ZSM-5 for distinguishing diffusivities among *p*-DEB, *m*-DEB and *o*-DEB. However, this modification may more or less affect the active sites in zeolite channels. So, it is highly desirable that the high selectivity can be achieved with a maximum reactivity by the proper modification.

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SiO_2-CVD with tetraethyl-orthosilicate (TEOS) is a usual method for improving shape-selectivity of zeolite. SiO_2-CVD/ZSM-5 showed high *p*-DEB selectivity more than 95% [6,12,13]. During CVD modification, TEOS first adsorbs on the external acidic sites of ZSM-5, and then decomposes into silica. As a result, the depositing silica covers the acidic sites on the external surface and reduces opening sizes of channels. Therefore, the modified ZSM-5 shows a great predomination of *p*-DEB diffusion, without the secondary isomerization of *p*-DEB on the external surface. Based on the above SiO_2-CVD, shape-selective EB disproportionation to produce *p*-DEB was commercialized with 96% *p*-DEB selectivity in 1990 [7].

In addition, modification by loading MgO or phosphate, used to prepare zeolite catalysts for alkylation of EB with ethylene or ethanol, might improve *p*-DEB selectivity over ZSM-5 during EB disproportionation [14,15]. But it was not as effective as SiO_2-CVD for obtaining high catalytic activity. However, modification with MgO can decrease the formation of non-aromatic hydrocarbon and benzene over ZSM-5, by reducing the side reaction of DEB dealkylation.

When the same ZSM-5 catalyst modified by SiO_2-CVD was used for catalyzing toluene disproportionation and EB disproportionation, respectively, *p*-DEB selectivity was higher than *p*-xylene selectivity due to the greater difference of diffusion among three DEB isomers [14,16,17]. In preparation of the commercial catalyst for the shape-selective disproportionation of toluene to *para*-xylene, the pre-coking method has been replaced by SiO_2-CLD [18]. Compared with CVD, CLD may be more easily transferred to an industrial preparation in large scale, such as SiO_2-CLD modification of ZSM-5 with polysiloxane in MTPX process [19].

In this work, SiO_2-CLD for ZSM-5 modification was firstly compared with SiO_2-CVD. Modification of SiO_2-CLD combining with loading MgO was developed to prepare ZSM-5 catalyst for shape-selective EB disproportionation. Mechanism of the above modification was studied by infrared spectroscopy (IR), probe-molecule adsorption, temperature programmed desorption (NH_3-TPD), physical adsorption and constraint index (CI).

2. Experimental

2.1. Preparation of modified ZSM-5 catalyst

ZSM-5 with Si/Al 15 was hydrothermally synthesized according to the reported method [20]. The as-synthesized ZSM-5 was exchanged with NH_4NO_3 solution at 363 K. Then, NH_4-form ZSM-5 was mixed with solution of polyphenylmethylsiloxane (PPMS) in hexane, at 12 wt% PPMS to ZSM-5, and then stirred for 4 h at the room temperature. After the above-impregnated ZSM-5 was dried at 393 K, it was calcined by heating to 823 K at a rate of 2 K/min and holding at this temperature for 2 h. After the above procedure was repeated three times, the SiO_2-CLD modified ZSM-5 (SiO_2-CLD/ZSM-5) was obtained. As a reference, the SiO_2-CVD modified ZSM-5 (SiO_2-CVD/ZSM-5) was prepared with TEOS

from NH_4-form ZSM-5 according to the reported procedure [21]. In order to get the same amount of depositing silica in SiO_2-CVD as that in SiO_2-CLD, SiO_2-CVD conditions were adjusted properly.

The above SiO_2-CLD/ZSM-5 was mixed with 50/50 (w/w) ethanol–water solution of $Mg(CH_3COO)_2$, at the ratio of 0.5 wt% MgO to ZSM-5, and then stirred for 1 h at the room temperature. After the above-impregnated sample was dried at 393 K and calcined at 823 K for 2 h, the SiO_2-CLD and MgO modified ZSM-5 (SiO_2-CLD and MgO/ZSM-5) was obtained. Alone MgO modified ZSM-5 (MgO/ZSM-5) was also prepared at the ratio of 0.50 wt% MgO to ZSM-5 from NH_4-form ZSM-5 according to the above procedure.

2.2. Characterization

2.2.1. IR spectroscopy

Pyridine (Py) or 2,6-di-*tert*-butylpyridine (DTBPy) absorbed infrared spectrum was, respectively, conducted at 473 K, with Pekin-Elmer 2000 FT-IR spectrometry and a self-supported wafer of sample.

2.2.2. Physical adsorption

N_2 adsorption was carried out using physical adsorption instrument (Digitsorb-2600, USA). After a sample was first evacuated in pretreatment at 623 K for 2 h, its surface area and pore distribution was determined by N_2 adsorption at 77 K. The mesoporous volume and microporous volume were calculated by Horvath–Kawazoe method.

2.2.3. Temperature-programmed desorption of ammonia

NH_3-TPD was determined using Altmira-100 Characterization System (Zeolton, USA). The sample was first treated in the flow of helium at 823 K for 1 h, and then cooled down to 393 K. The adsorption of NH_3 was performed with the flow of 10% NH_3/He at 393 K. The desorption was conducted between 393 and 973 K at a heating rate of 12 K/min.

2.2.4. Constraint index

The constraint index of zeolite was determined with a fixed-bed micro-reactor and hexane/3-methylpetane of 1/1 as the mixed reactants, according to the reported procedure [22].

2.3. Catalytic reaction

The catalytic reaction of EB disproportionation was, respectively, carried out over the parent ZSM-5, SiO_2-CLD/ZSM-5, SiO_2-CVD/ZSM-5, MgO/ZSM-5 and SiO_2-CLD and MgO/ZSM-5. The reaction was conducted in the fixed-bed reactor with WHSV 4 h^{-1} and 2.0 Mpa hydrogen flow (the molar ratio of hydrogen/EB 3.0) at 673 K. The products were determined by on-line gas chromatography with 50 m–0.32 mm i.d. FFAP capillary column and FID.
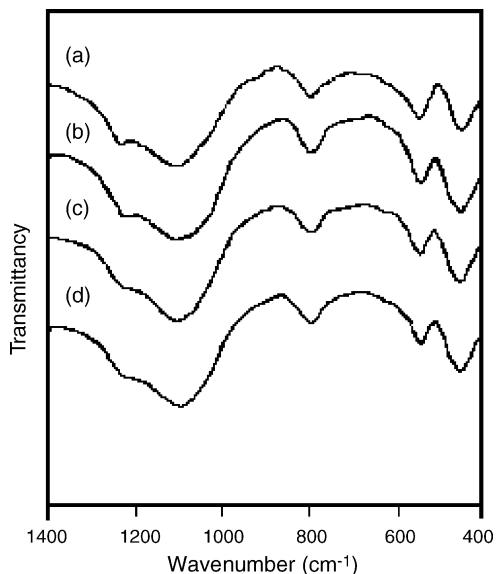
Fig. 1. IR spectra of ZSM-5 framework: (a) SiO$_2$-CLD and MgO/ZSM-5, (b) SiO$_2$-CLD/ZSM-5, (c) SiO$_2$-CVD/ZSM-5 and (d) Parent ZSM-5.

3. Results and discussion

3.1. Physicochemical properties

In order to understand the modification mechanism, it is necessary to clarify how zeolite properties change in modification. Characteristic IR spectra between 400 and 1400 cm^{-1} show that the framework structure of ZSM-5 remains unchanged in SiO$_2$-CLD, SiO$_2$-CLD and MgO or SiO$_2$-CVD modification, seen in Fig. 1. So, silica deposition over ZSM-5 has no influence on Si–O–Si and Si–O–Al structures of ZSM-5 framework under the modification conditions used in this work.

Constraint index (CI) is an effective method to determinate pore structure of zeolite, based on cracking reaction of probe molecules. The textural properties of ZSM-5 before or after modification were characterized by CI determination and N$_2$ physical adsorption, seen in Table 1. All modified ZSM-5 obviously decreases in surface area, especially in meso-

porous volume, but their microporous volumes drop down slightly. The results indicate that silica mainly deposits on the external surface of ZSM-5 in SiO$_2$-CLD with polysiloxane or SiO$_2$-CVD with TESO. However, compared with SiO$_2$-CVD, SiO$_2$-CLD retains larger surface area and microporous volume under the approximate amount of silica depositing over ZSM-5.

Generally, it is considered that TESO cannot enter ZSM-5 channels in SiO$_2$-CVD process, not interfering the acidic sites in channels. But, the decreased number of the acidic sites is more than that of the acidic sites on the external surface. In order to clarify the process of SiO$_2$-CVD with TESO, the products that exit from TESO decomposition during calcination treatment in SiO$_2$-CVD, were determined by GC-MS in this work. The results in Table 2 reveal that partial decomposed products, such as (HO)$_2$Si(OCH$_2$CH$_3$)$_2$ and (HO)$_3$SiOCH$_2$CH$_3$, can enter channels of ZSM-5, passviating some acidic sites in channels. Usually, the above specification has not been noticed in the previous studies of SiO$_2$-CVD. In contrast, ZSM-5 channels are hardly influenced by PPMS polysiloxane (including siliceous products from PPMS decomposition) as their molecular sizes are more than opening sizes of ZSM-5 channels [23]. In most cases of SiO$_2$-CVD, this influence on the acidic sites in channels is not severe in SiO$_2$-CVD, and silica deposition mainly takes places on the external surface of ZSM-5.

It is seen in Table 1 that alone modification, with 0.50 wt% MgO loading over ZSM-5, is not enough to cause an appreciable change of its textural properties. Besides, the highest CI of SiO$_2$-CLD and MgO/ZSM-5 shows that SiO$_2$-CLD and MgO modification is very effective for reduction of opening sizes and elimination of the active sites on the external surface.

3.2. Acidic properties

Modification for acidity of ZSM-5 is a main aspect for improving its shape-selectivity. NH$_3$-TPD results in Fig. 2 and Table 3 show that each modified ZSM-5 has two peaks of NH$_3$ desorption, corresponding to strong acidic sites and weak acidic sites, respectively. Comparatively, SiO$_2$-CLD/ZSM-5 or SiO$_2$-

Table 1
The characterization of physical adsorption of zeolites

Samples	Loading amount (wt%)	Surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	CI value
Parent ZSM-5		412	0.15	0.041	6.1
SiO$_2$-CVD/ZSM-5	8.6	358	0.13	0.025	8.4
SiO$_2$-CLD/ZSM-5	8.7	381	0.14	0.023	8.6
MgO/ZSM-5	0.5	397	0.14	0.032	7.0
SiO$_2$-CLD and MgO/ZSM-5	9.2	373	0.13	0.020	9.9

Table 2
Siliceous species from decomposition of TESO and PPMS on ZSM-5 determined by PGC-MS

Compounds	[a]Products from decomposition of polysiloxane compounds
TEOS Si-(OCH$_2$CH$_3$)$_4$	HOSi(OCH$_2$CH$_3$)$_3$, (HO)$_2$Si(OCH$_2$CH$_3$)$_2$, (HO)$_3$SiOCH$_2$CH$_3$, O-(SiOH(OCH$_2$CH$_3$)$_2$)$_2$
PPMS –(CH$_3$/C$_6$H$_5$SiCH$_3$-O)$_n$–	HOPhSi(Me)$_2$, (Me)$_3$SiPh, (Me)$_3$Si–O–Si(Me)$_2$Ph, D$_3$, D$_4$, D$_5$, D$_6$

[a] –D$_3$, –D$_4$, –D$_5$ or –D$_6$ is a cycle-form ogliomer of –(XSiCH$_3$–O)$_n$– (X = CH$_3$ or Ph; n = 3, 4, 5 or 6)
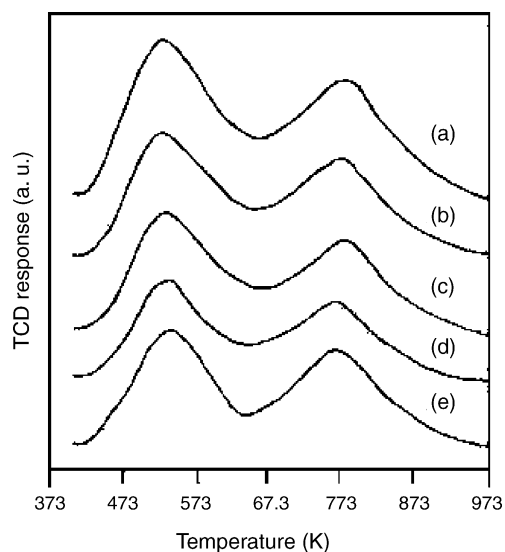
Fig. 2. The NH$_3$-TPD patterns of ZSM-5: (a) parent ZSM-5, (b) SiO$_2$-CLD/ZSM-5, (c) SiO$_2$-CVD/ZSM-5, (d) SiO$_2$-CLD and MgO/ZSM-5 and (e) MgO/ZSM-5.

CVD/ZSM-5 is less than that of parent ZSM-5 in acidic amount, but similar to that of parent ZSM-5 in the distribution of acidic strength. The above fact indicates that the elimination of the acidic sites mainly depends on the positions of acidic sites over ZSM-5 in silica deposition, not on their properties. However, MgO/ZSM-5 or SiO$_2$-CLD and MgO/ZSM-5 decreases both in acidic amount and in acidic strength. Unlike silica deposition, MgO modification may be prior to neutralize the strong acidic sites of ZSM-5, especially for the strong acidic sites on the external surface.

Py-IR characterization in Fig. 3 shows that SiO$_2$-CLD or SiO$_2$-CVD modification results in Bronsted acidic sites and Lewis acidic sites decreasing simultaneously, due to the coverage of acidic sites with depositing silica. On the other hand, the ratio of Bronsted acidic sites to Lewis acidic sites decreases after SiO$_2$-CLD or SiO$_2$-CVD modification, which results from a little dealumination of ZSM-5 framework in calcination treatment. In the dealumination of zeolite, Bronsted acidic sites decrease, forming new Lewis acidic sites [24]. However, MgO modification causes the decrease of Bronsted acidic sites, due to the interaction between Bronsted acidic sites with base MgO. It is also seen that Py-IR results are well in agreement with NH$_3$-TPD characterization.

Compared with adsorption of pyridine both on external surface and in channels of zeolite, the adsorption of 2,6-di-*tert*-
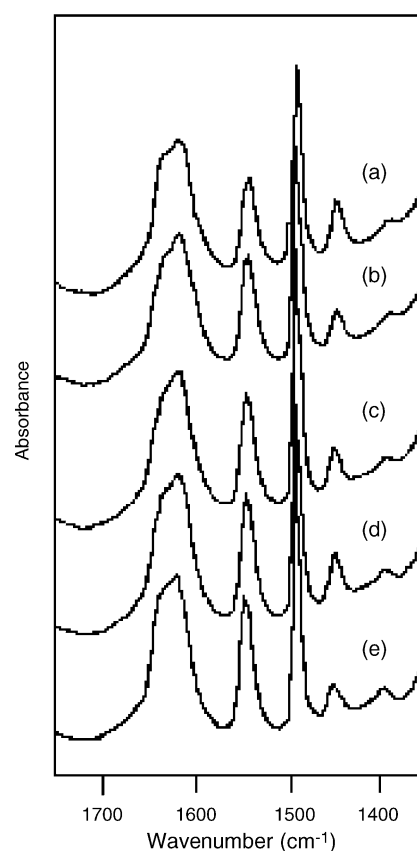

Fig. 3. Py-IR spectra of ZSM-5: (a) SiO$_2$-CLD and MgO/ZSM-5, (b) SiO$_2$-CVD/ZSM-5, (c) SiO$_2$-CLD/ZSM-5, (d) MgO/ZSM-5 and (e) parent ZSM-5.

butylpyridine occurs only on the external surface due to its large molecular size. So, it can quantitatively monitor the external acidic sites of zeolite according to absorbance at 3370 cm^{-1} [25]. It is shown in Fig. 4 that the external acidic sites are less over SiO$_2$-CLD and MgO/ZSM-5 than over SiO$_2$-CLD/ZSM-5. Alone modification by loading 0.50 wt% MgO can eliminate about half of the external acidic sites of ZSM-5. It may be considered that the external acidic sites of ZSM-5 are apt to be passivated in MgO modification. As a result, the further MgO modification can eliminate the residual acidic sites on the external surface of SiO$_2$-CLD/ZSM-5. On the other hand, MgO modification lightly decreases the total acidic sites of ZSM-5, but the influence of this reduction on catalytic activity is acceptable in view of the improvement for overall catalytic properties.

In addition, the residual external acidic sites of SiO$_2$-CVD/ZSM-5 is almost equal to that of SiO$_2$-CLD/ZSM-5, but

Table 3
Results of NH$_3$-TPD characterization of samples

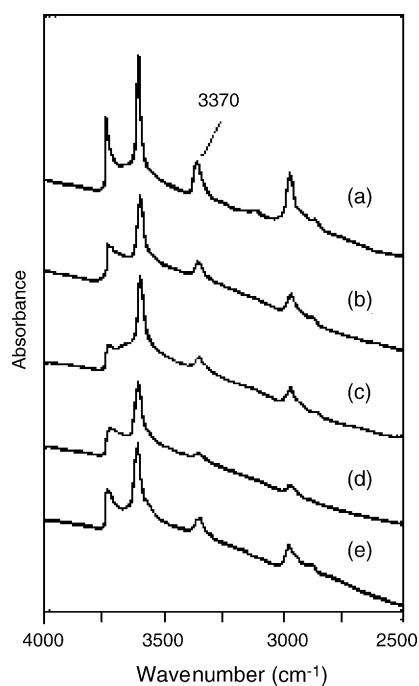| Samples	Weak acidic sites		Strong acidic sites	
	Peak temperature (K)	Desorbed NH$_3$ (mmol/g)	Peak temperature (K)	Desorbed NH$_3$ (mmol/g)
Parent ZSM-5	533	0.68	782	0.74
SiO$_2$-CLD/ZSM-5	534	0.52	781	0.59
SiO$_2$-CVD/ZSM-5	532	0.51	779	0.54
SiO$_2$-CLD and MgO/ZSM-5	535	0.48	767	0.51
MgO/ZSM-5	535	0.59	770	0.61

Fig. 4. DTBPy-IR spectra of ZSM-5: (a) parent ZSM-5, (b) SiO$_2$-CVD/ZSM-5, (c) SiO$_2$-CLD/ZSM-5, (d) SiO$_2$-CLD and MgO/ZSM-5 and (e) MgO/ZSM-5.

the SiO$_2$-CVD/ZSM-5 loses a few of acidic sites in channels according to the calculation from Py-IR and DTBPy-IR results, using the method reported [26]. This is because the siliceous products formed from PPMS decomposition are too large in molecular size to enter pores and to passivate the acidic sites in channels. Whereas, the partial products from TESO decomposition may enter pores of ZSM-5, inactivating some acidic sites in channels. During selective alkylation and disproportionation of EB in the presence of xylene over ZSM-5 modified with TESO, 92–95% p-DEB selectivity was obtained, but 14–11% EB conversion is not satisfied [27,28].

3.3. EB disproportionation over modified ZSM-5

In addition to the commercial usage to produce p-DEB, EB disproportionation to benzene and DEB has been widely used as the test reaction for characterizing the acidity and structure of zeolites [29–31]. On the other hand, there is more and less side reaction of EB dealkylation to benzene and ethane under the reaction medium of hydrogen. The ratio of benzene to DEB (B/DEB ratio) is corresponding to reactivity of dealkylation,

equal to 1.00 under no dealkylation. According to the results of NH$_3$-TPD and Py-IR characterization, it is found that the catalytic activity for EB disproportionation is approximately proportional to the number of Bronsted acid sites of zeolite. Similarly, it has been reported that toluene disproportionation is catalyzed mainly by Bronsted acid [32]. From the study of EB isomerization over bifunctional Pt/Al$_2$O$_3$-NaHMOR catalyst, the reactivity of EB disproportionation, as the side reaction, was proportional to the number of Bronsted acid sites. Moreover, the reactivity of EB dealkylation directly relates to the strength of acidic sites, and the strong acidity promotes EB dealkylation [33–35].

The experimental results in Table 4 indicate that SiO$_2$-CLD and MgO/ZSM-5 shows lightly lower EB conversion compared to SiO$_2$-CLD/ZSM-5 and SiO$_2$-CVD/ZSM-5. But, it has higher selectivity of p-DEB and lower B/DEB ratio, i.e., the low dealkylation reactivity. Besides, SiO$_2$-CLD/ZSM-5 has higher EB conversion than SiO$_2$-CVD/ZSM-5 under the approximate p-DEB selectivity. This fact also indicates that there is some difference between SiO$_2$-CLD and SiO$_2$-CVD. This has been revealed by the above-mentioned characterization for the structure and acidity of the modified ZSM-5. As a result, SiO$_2$-CLD/ZSM-5 is of better catalytic performance for EB shape-selective disproportionation than SiO$_2$-CVD/ZSM-5. This is well in agreement with the result obtained in toluene disproportionation [36].

On the other hand, MgO/ZSM-5 shows the low reactivity of EB dealkylation as MgO modification greatly decreases the acidic strength of ZSM-5. It may be considered that the acidic sites, needed for catalyzing EB disproportionation (i.e., transalkylation between two EB molecules), are relatively weaker than those for catalyzing EB dealkylation. Therefore, the dealkylation reaction is mainly contributed to the portion of strong acidic sites over zeolites. MgO modification may preferentially neutralize some strong Bronsted acidic sites, which greatly decrease dealkylation reactivity.

Moreover, MgO modification may effectively eliminate the residual acidic sites on the external surface of SiO$_2$-CLD/ZSM-5, which cannot be completely passivated by SiO$_2$-CLD as the steric restriction prevents siliceous modifiers from reaching these acidic sites. According to the previous report, the secondary isomerization over the external acidic sites is faster than disproportionation reaction over three orders of magnitude [37]. Fig. 5 shows that the amount of MgO loading over ZSM-5 directly relates to catalytic activity and selectivity. p-DEB selectivity increases with MgO loading over ZSM-5, and then tends to stability. Besides, EB conversion and EB dealkylation both

Table 4
Results of EB disproportionation to p-DEB over zeolites

Samples	EB conversion (%)	p-DEB/DEB (%)	DEB/benzene (molar/molar)	[a]Non-aromatics (wt%)	[b]Relative p-DEB yield (%)
Parent ZSM-5	42.3	27.8	0.75	4.49	36.7
SiO$_2$-CVD/ZSM-5	29.6	96.4	0.70	4.56	86.4
SiO$_2$-CLD/ZSM-5	31.3	96.2	0.71	4.54	91.6
MgO/ZSM-5	34.4	30.3	0.93	1.64	38.1
SiO$_2$-CLD and MgO/ZSM-5	28.1	98.6	0.91	1.58	100.0

[a] Total amount of alkane and alkene in products.

[b] The normalized data relative to 100.0% of SiO$_2$-CLD and MgO/ZSM-5 catalyst.
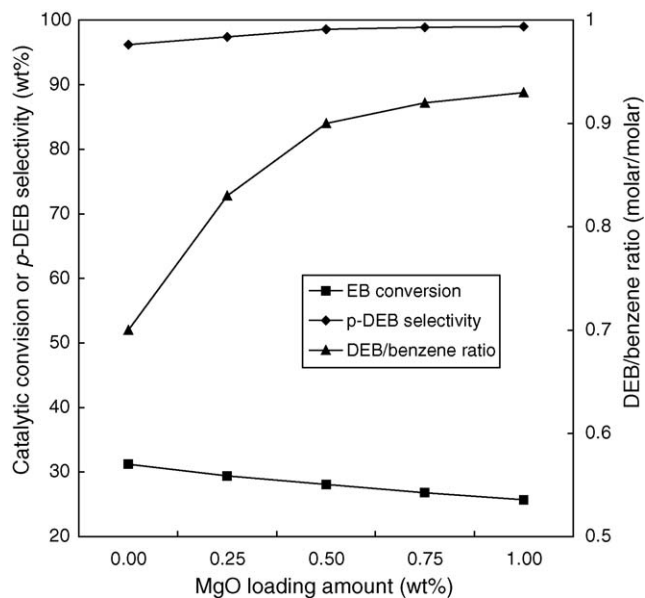
Fig. 5. Catalytic activity, selectivity and DEB/benzene ratio of SiO$_2$-CLD and MgO/ZSM-5 and MgO loading amount.

Fig. 6. Catalytic activity of SiO$_2$-CLD and MgO/ZSM-5 and ZSM-5 with time-on-stream.

reduces with increasing MgO loading. This is a consequence of the fact that the number and strength of acidic sites decreases with increasing MgO loading over ZSM-5.

Taking both catalytic activity and *p*-DEB selectivity into consideration, a loading of about 0.50 wt% MgO over ZSM-5 is suitable for the further modification of SiO$_2$-CLD/ZSM-5. Therefore, the following MgO modification of SiO$_2$-CLD/ZSM-5 improves its *p*-DEB selectivity, and MgO modification ought to be controlled properly as well.

On the other hand, the obvious *p*-DEB selectivity has been shown neither over the parent ZSM-5 nor over MgO/ZSM-5 as the opening sizes of the channels of parent ZSM-5 or MgO/ZSM-5 are not small enough to distinguish diffusion difference between *p*-DEB with *o*-DEB and *m*-DEB.

In conclusion, SiO$_2$-CLD/ZSM-5 has better catalytic performance than SiO$_2$-CVD/ZSM-5. Although the further MgO modification lightly decreases EB conversion of SiO$_2$-CLD/ZSM-5, it may improve its *p*-DEB selectivity, greatly reducing the side reaction of EB dealkylation. So, SiO$_2$-CLD and MgO/ZSM-5 may be considered as a promising catalyst for EB disproportionation.

3.4. Catalytic performance for EB disproportionation with time on-stream

The results depicted in Fig. 6 show that the EB conversion decreases with increasing reaction time over parent ZSM-5, but it almost keeps stable over SiO$_2$-CLD and MgO/ZSM-5. Comparatively, the deactivation of parent SM-5 is much more severe than that of SiO$_2$-CLD and MgO/ZSM-5. On the other hand, it is seen in Fig. 7 that *p*-DEB selectivity of SiO$_2$-CLD and MgO/ZSM-5 remains almost stable and increases slightly with increasing reaction time. Whereas, *p*-DEB selectivity of parent ZSM-5 first shows thermodynamic equilibrium, and then increases lightly. This process is similar to the coking modifi-
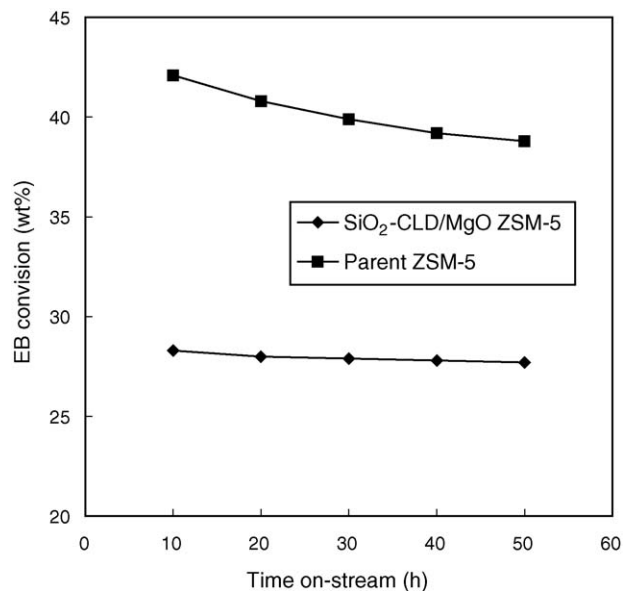
cation of ZSM-5, which might be used for improving *p*-xylene selectivity in toluene disproportionation [16].

TGA determination in Table 5 shows that coking is more severe over parent ZSM-5 than over SiO$_2$-CLD and MgO/ZSM-5. Compared with the fresh catalyst, the surface area and total pore volume slightly decreases with coking in the reaction. But, the microporous volumes almost remain unchanged. Above results indicate that coking mainly takes place near the pore mouth and on the external surface of ZSM-5. As a result, *p*-DEB selectivity of SiO$_2$-CLD and MgO/ZSM-5 slightly increases with coking. As for parent ZSM-5, *p*-DEB selectivity does not appear until the pore opening reduces to a certain size, which is small enough to distinguish diffusion difference among three DEB isomers. Besides, the relative stronger acidity of unmodified ZSM-5 is easy to result in the formation of coke. This phenomenon has been revealed in the previous report [38]. Therefore, SiO$_2$-CLD and MgO/ZSM-5 shows much better sta-
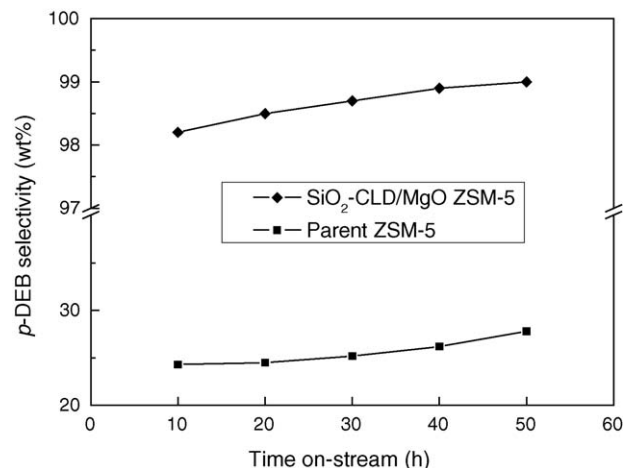

Fig. 7. Catalytic selectivity of SiO$_2$-CLD and MgO/ZSM-5 and ZSM-5 with time-on-stream.

Table 5
The characterization of physicochemical properties of used zeolite catalysts

Samples	Coke content (wt%)	Surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	CI value
Parent ZSM-5	4.5	382	0.13	0.028	7.1
SiO_2-CLD and MgO/ZSM-5	3.1	361	0.12	0.017	11.2

bility than the parent ZSM-5 thank to the effective modification of the strong Bronsted acidic sites and the elimination of the external acidic sites.

4. Conclusions

In contrast, SiO_2-CLD/ZSM-5 retains more acidic sites, as the siliceous products, formed from PPMS decomposition in SiO_2-CLD, are too large in molecular size to enter channels of ZSM-5, not affecting the acidic sites in channels. Whereas, SiO_2-CVD/ZSM-5 loses more acidic sites, because partial products from TESO decomposition in SiO_2-CVD may enter channels of ZSM-5, such as $(HO)_2Si(OCH_2CH_3)_2$ and $(HO)_3SiOCH_2CH_3$, passivating some acidic sites in channels. So, SiO_2-CLD/ZSM-5 shows higher catalytic activity for shape-selective EB disproportion than SiO_2-CVD/ZSM-5 under the approximate *p*-DEB selectivity.

The following MgO modification for SiO_2-CLD/ZSM-5 reduces both acidic amount and acidic strength, but it greatly eliminates the residual acidic sites on the external surface. Although SiO_2-CLD/ZSM-5 lightly decreases by about 2% EB conversion in MgO modification, SiO_2-CLD and MgO/ZSM-5 shows high EB conversion of 28.1%. In particular, MgO modification improves *p*-DEB selectivity of SiO_2-CLD/ZSM-5 up to 98.6%, greatly reducing the side reaction of EB dealkylation with the molar ratio of 0.91 DEB to benzene. Besides, SiO_2-CLD and MgO/ZSM-5 shows a good stability due to proper modification of acidic and structural properties. Considering EB conversion, *p*-DEB selectivity and EB dealkylation, SiO_2-CLD and MgO/ZSM-5 turns out to be a promising catalyst for shape-selective EB disproportionation to *p*-DEB.

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