Study on alkylation of benzene with ethylene over β-zeolite catalyst to ethylbenzene by in situ IR

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Abstract

The alkylation of benzene with ethylene over β-zeolite catalyst was studied using in situ IR method at 393, 433 and 473 K. Benzene (or ethylbenzene) and ethylene were injected into in situ IR cell either sequentially or in reverse order. The evolution of IR spectra was observed and recorded.

The alkylation mechanism inferred is as follows: adsorbed ethylene on weaker acidic site may react with adsorbed benzene or ethylbenzene on strong acidic sites. These substances are adsorbed competitively at the same kind of sites. Ethylene adsorbed becomes carbenium, a substance which has strong interaction with acidic sites, on the other hand, benzene and ethylbenzene adsorbed molecularly have weak interaction, in the form of hydrogen bonding, with acidic OH. If an activated ethylene molecule has too few adsorbed benzene molecules around to react to alkylation, this ethylene molecule can react with other ethylene through alkenyl carbenium ion to form an oligomer, a substance considered to be a precursor of coke. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The alkylation of benzene with ethylene to ethylbenzene (EB) is widely used in the petrochemical industry. (Ethylbenzene is the intermediate for styrene production.) In the petrochemical industry, the conventional processes of benzene alkylation are usually catalyzed by $AlCl_3$.

Use of catalysts such as $AlCl_3$ has caused increasing number of problems concerning handling, safety, corrosion, and waste disposal [1]. An immense effort has been put into developing alternative catalyst systems. The $AlCl_3$-based processes have been progressively substituted with zeolite-based processes. Since 1976, the medium-pore zeolite ZSM-5 has been in use in the Mobil-Badger process for the vapor-phase alkylation of benzene with ethylene, and it is operated at relatively high temperature (623–723 K) [2].

Then a new process was developed by UOP/Lummus/Monsanto/Unocal/Chemical Research Licensing [3]. Catalyst used in this new process is based on a Y-type zeolite and this new process is operated at much lower temperatures (~533 K) and higher pressure (>3.5 MPa). Under this circumstance feedstock is in liquid phase.

Good performance of β-zeolite was also reported for the benzene alkylation in liquid phase [1,4,5]. Recently a new vapor–liquid-phase process was developed by our laboratory [6,7]. This β-zeolite catalyst (FX-02) is proved to be an active and selective catalyst for alkylation of benzene with ethylene. FX-02

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can be used with polymer-grade ethylene [6], as well as ethylene from FCC unit off-gas with concentrations as low as 10–20 vol.% [7]. FX-02 operates at lower temperature (413–453 K) and lower pressure (1.0–2.0 MPa). The alkylation of benzene with propylene over β-zeolite were studied by in situ IR [8–10].

We have not seen any publication with detailed data on the spectroscopic characterization of ethylbenzene formation over β-zeolite catalyst. This paper reports the results of in situ IR spectroscopic studies obtained for adsorption (and reaction) of ethylene, benzene and ethylbenzene on β-zeolite catalyst and the evolution of surface species at 393, 433 and 473 K.

2. Experimental

β-zeolite catalyst ($SiO_2/Al_2O_3 = 28$) was supplied by our laboratory. Infrared spectra have been recorded on a Perkin-Elmer 1750 Fourier Transform Infrared Spectrometer with a resolution of $1\,cm^{-1}$. Self-supporting wafers of $9\,mg\,cm^{-2}$ thickness were pressed from the zeolite powder.

The wafers were then placed into a sample holder inside a stainless steel in situ IR flow-reactor cell (supplied by Tsing Hua University) with KBr windows, and pretreated for 90 min at 493 K in nitrogen. After cooling down to the desired temperature, the adsorbates/reactants were introduced in pulse and the IR spectra were recorded. The adsorbates/reactants used were benzene (purity > 99.98%), ethylbenzene (purity = 99.83%), diethylbenzene (purity = 98.9%) and ethylene (purity > 99.95%).

Two types of experiments were carried out. (a) Step 1: without catalyst wafer in the cell, we have recorded respective IR spectra of the following substances in the form of gas—ethylene, benzene, ethylbenzene and diethylbenzene. Step 2: with catalyst wafer in the cell, we have loaded the above substances as adsorbates. IR spectrum of each substance was observed and recorded. (b) Benzene or ethylbenzene and ethylene were injected sequentially or in reverse order into the in situ IR cell at 393–473 K and the evolution of IR spectra was obtained.

The procedures of experiments (b) were: Step 1: inject 134 μmol of adsorbate 1, perform nitrogen purging for 5 min; Step 2: inject 134 μmol of adsorbate 2, perform nitrogen purging for 5 min; Step 3: inject

134 μmol of adsorbate 2, perform nitrogen purging 5 min; Step 4: perform nitrogen purging 40 min. There were four modes on experiments (b). In mode 1, adsorbate 1 was benzene and adsorbate 2 was ethylene; in mode 2, adsorbate 1 was ethylene and adsorbate 2 was benzene; in mode 3, adsorbate 1 was ethylbenzene and adsorbate 2 was ethylene; in mode 4, adsorbate 1 was ethylene and adsorbate 2 was ethylbenzene.

3. Results and discussion

3.1. Ethylene and aromatics adsorption

Fig. 1 shows the respective spectra of the following substances in the form of gas: ethylene, benzene, ethylbenzene and diethylbenzene, without catalyst wafer in the in situ IR cell. Fig. 2 shows the spectra of those substances loaded on β-zeolite catalyst at 393 K, after subtracting the background spectrum of the zeolite. The spectra data and their assignment of gas phase and adsorbed species on the zeolite are listed in Tables 1 and 2, respectively.

3.1.1. Ethylene adsorption

The spectrum of ethylene adsorbed on β-zeolite shows the bands at about 2958 and $2930\,cm^{-1}$ assigned to CH_3- and $-CH_2-$ asymmetric stretching vibrations, respectively, a band at $2873\,cm^{-1}$ attributed to CH_3- symmetric vibration; the bands of the CH_3- and $-CH_2-$ deformation modes are observed at $1381\,cm^{-1}$ (Refer Figs. 1 and 2).

Negative bands in 3740 and $3605\,cm^{-1}$ reveal that acidic OH groups of β-zeolite is reduced. It is considered that the band at $3605\,cm^{-1}$ is from strongly acidic bridging hydroxyl groups, and that at $3740\,cm^{-1}$ is assigned to the terminal SiOH groups stretching vibration [11,12]. Xiao et al. [12] assigned a partial $3740\,cm^{-1}$ species to stronger acidic properties. Therefore, it can be deduced that ethylene is readily adsorbed at the active sites and reacts immediately by consuming the acidic OH group and partially changes into C^+-C, a very active substance and intermediate for further reaction. The band at $1501\,cm^{-1}$ is attributed to the C–C–C vibration of the allelic portion of alkenyl carbenium ions. This phenomenon suggests that not only alkyl but also alkenyl-type carbenium ions may be formed in secondary reactions
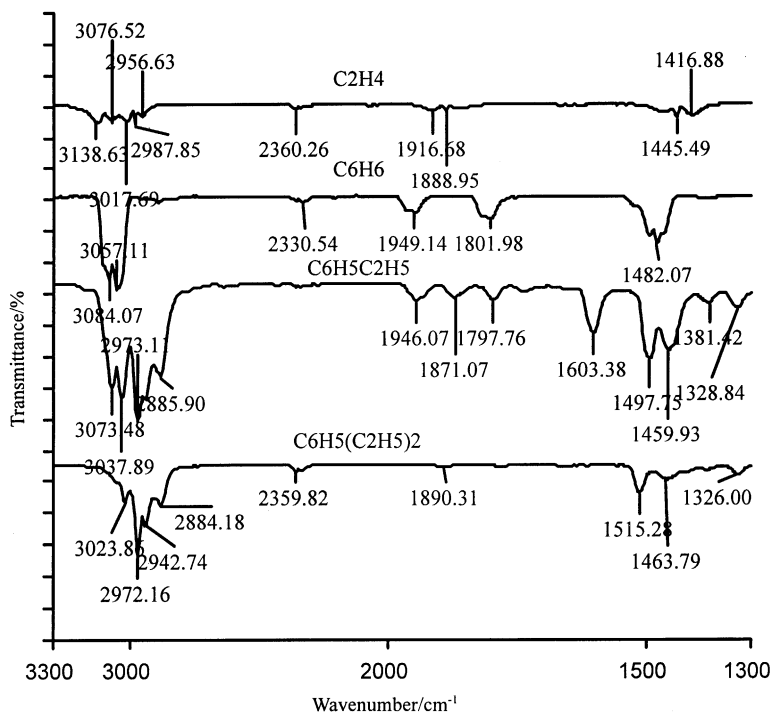
Fig. 1. IR spectra of ethylene, benzene, ethylbenzene and diethylbenzene.

that parallel the main transformation [13]. The above phenomenon is similar to the phenomena observed by Laniecki and Karge [14] for ethylene adsorbed on dealuminated mordenite and Kazanskii and coworkers [15] on HZSM-5 zeolite.

3.1.2. Aromatics adsorption

In contrast with ethylene, although aromatics (benzene, ethylbenzene and diethylbenzene) do adsorb on the acidic groups (negative band in $3740 \, cm^{-1}$) too, there is no band observed at $1501 \, cm^{-1}$. Moreover, the number of bands of the adsorbed benzene decreases so that there is only one band at $1479 \, cm^{-1}$ in $1600–1400 \, cm^{-1}$ region attributed to stretching vibration of benzene nuclei. Aromatics are considered to be molecularly adsorbed on β-zeolite and benzene nuclei are fixed by hydrogen bond between acidic OH groups of zeolite and themselves.

Furthermore, by comparing Tables 1 and 2, we see that the IR bands of aromatics adsorbed shifted to lower wave numbers. The bands in the range $3300–2800 \, cm^{-1}$ are assigned to the C–H stretching vibration and those in the range $1600–1450 \, cm^{-1}$ are assigned to C–C stretching vibration. As it is well known that hydrogen bond can cause the frequency reduction of stretching vibration.

3.2. Characteristic bands

As mentioned above, each of ethylene, benzene, ethylbenzene and diethylbenzene can be adsorbed on β-zeolite catalyst at the temperature range 393–473 K. The spectrum of each substance remains almost unchanged from initial adsorption state if scanning is done immediately after adsorption. Hence, in the IR spectra of adsorbates on β-zeolite catalyst, the characteristic bands 1600, 1495, 1452 and $1381 \, cm^{-1}$ appearing in the reaction system of benzene with ethylene are assigned to ethylbenzene, and the characteristic band $1512 \, cm^{-1}$ is assigned to diethylbenzene, while the characteristic bands above $3000 \, cm^{-1}$ disappeared.
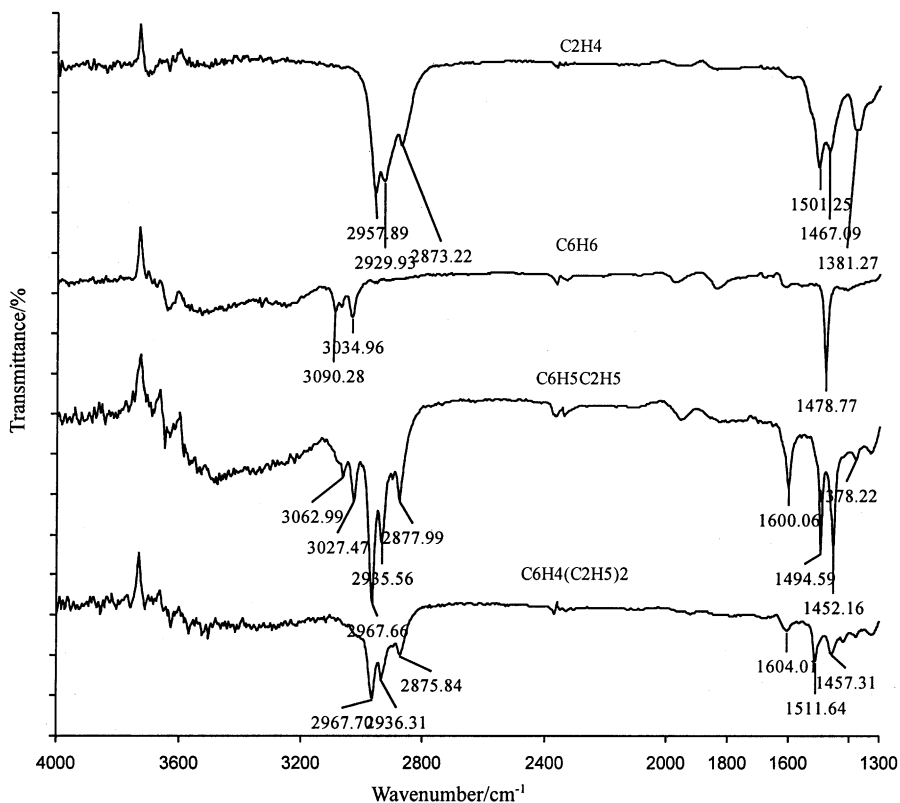
Fig. 2. IR spectra of ethylene, benzene, ethylbenzene and diethylbenzene adsorbed on β-zeolite catalyst.

Table 1
Band positions of species in gas phase

Substances	Groups	ν_{C-H} (cm^{-1})	ν_{C-C} (cm^{-1})	δ_{C-H} (cm^{-1})
Ethylene		3139, 3076, 3018		
Benzene		3057	1482	
Ethylbenzene	Benzene nucleus	3073, 3038	1603, 1498, 1460	1381
	$-C_2H_5$	2973, 2886		
Diethylbenzene	Benzene nucleus	3023	1515, 1464	1326
	$-C_2H_5$	2972, 2943, 2884		

Table 2
Band positions of species adsorbed on β-zeolite at 393 K

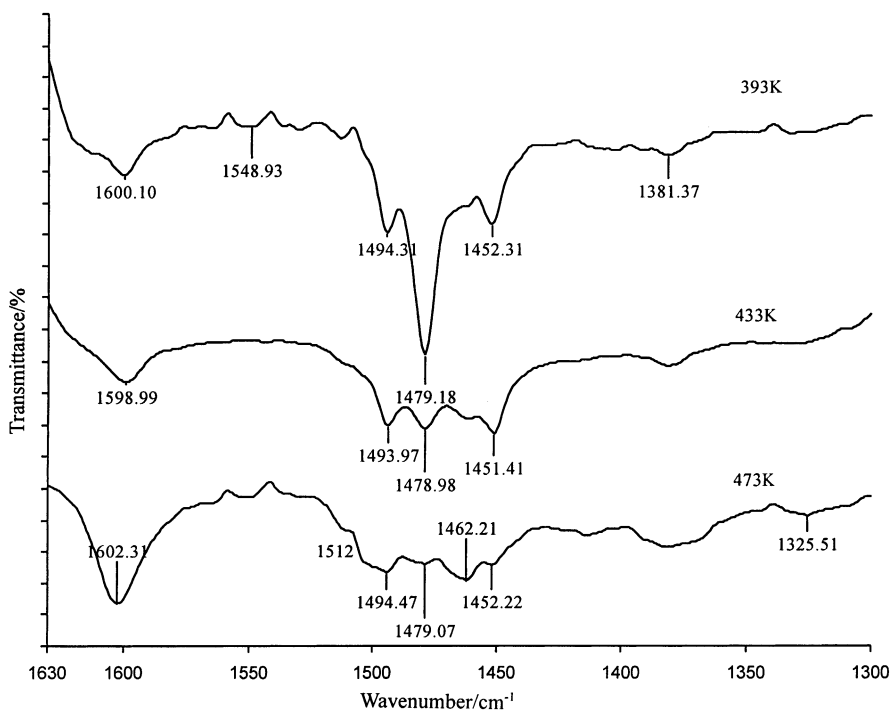| Substances	Groups	ν_{C-H} (cm^{-1})	ν_{C-C} (cm^{-1})	δ_{C-H} (cm^{-1})
Ethylene		2958, 2930, 2873		1381
Benzene		3035	1479	
Ethylbenzene	Benzene nucleus	3063, 3027	1600, 1495, 1452	1381
	$-C_2H_5$	2968, 2876		
Diethylbenzene	Benzene nucleus	Disappeared	1604, 1512, 1457	
	$-C_2H_5$	2967, 2936, 2876		

Fig. 3. IR spectra of in situ reaction of adsorbed benzene with ethylene at 393, 433 and 473 K of step 4.

3.3. Reaction of benzene with ethylene

As to mode 1, i.e., injecting benzene followed by ethylene, both ethylbenzene and minor diethylbenzene were formed in step 3 at 393 K, ethylbenzene were formed in step 2 at 433 K, and both ethylbenzene and diethylbenzene were formed in step 2 at 473 K. Fig. 3 shows spectra of step 4 at 393, 433 and 473 K, respectively. It is seen that, as the temperature is raised, the intensity of the ethylbenzene band at $1600\,cm^{-1}$ increases, and the characteristic band of diethylbenzene at $1512\,cm^{-1}$ appears obviously at 473 K. The process of alkylation is considered to take place in the following way. After benzene is adsorbed on acidic sites of β-zeolite, the molecules of ethylene must be adsorbed on the same kind of sites first, then they change into C^+–C. C^+–C then reacts with adsorbed benzene to form ethylbenzene. As the temperature rises, the number of both desorbed benzene molecules and activated molecules of ethylene increases, as a result, more intermolecular reactions occur. By comparison with alkylation of benzene with

propylene, a lot of isopropylbenzene is formed even at 393 K. This shows that the molecule of ethylene is more difficult to be activated than that of propylene.

As to mode 2, the spectra of injecting ethylene followed by benzene are shown in Fig. 4. Although the band at $1479\,cm^{-1}$ assigned to adsorbed benzene can be observed, no characteristic band at $1600\,cm^{-1}$ assigned to ethylbenzene appears at 393 K, a minor amount of ethylbenzene forms at 433 K, and little diethylbenzene appears before 473 K. Above observation shows that benzene adsorbed molecularly and weakly cannot be activated unless it adsorbs on strong acidic sites, and that adsorbed ethylene only reacts with benzene adsorbed on the same kind of sites (acidic OH groups). Adsorbed ethylene can react neither with benzene in the form of gas nor with those adsorbed on weak sites. Therefore, there is a competitive adsorption between ethylene and benzene. Ethylene adsorbed first changes into C^+–C that has strong interaction with acidic OH groups, as mentioned earlier in this paper. At lower temperature (393 K), the mobility of ethylene is so poor
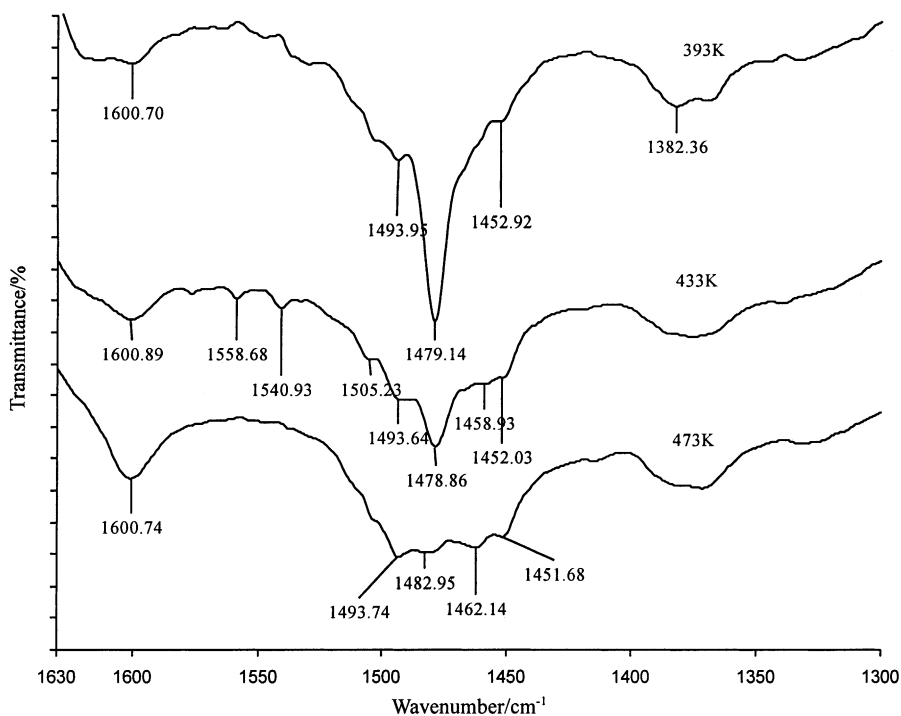
Fig. 4. IR spectra of in situ reaction of adsorbed ethylene with benzene at 393, 433 and 473 K of step 4.

that benzene with weak interaction with acidic OH in the form of hydrogen bond is hardly adsorbed. As the temperature is raised, the migration of ethylene increases, benzene can be adsorbed and be activated; then the reaction takes place.

In addition, the bands between 1505 and 1540 cm^{-1} at higher temperature (433 K) before injecting benzene should be due to the reaction between adsorbed ethylene molecules, i.e., the reaction of activated ethylene converting to alkenyl carbenium ion C–C–C [13]. As the temperature is raised to 473K, the above bands disappear. The band, which is attributed to –CH$_2$– and appears at 1462 cm^{-1}, is the evidence of the formation of oligomers. The observation is in accordance with a similar trend observed for the measurement of coke formation via ethylene reaction over HZSM-5 at 475 K [16]. This observation can also be evidenced circumstantially by experiments conducted from vapor-liquid-phase alkylation reactor. During those experiments, catalyst lifetime decreased obviously if the ratio of benzene to ethylene is reduced

from 6–8 to 2–3. If the catalyst cannot be moistened sufficiently by benzene, deactivation of catalyst will take place immediately.

At this point, we can have the following deduction: activated ethylene can react either with activated benzene or another ethylene molecule. If each activated ethylene molecule has too few adsorbed benzene molecules around to react to alkylation, this activated ethylene can react with another ethylene through alkenyl carbenium ion to form oligomer, a substance considered a precursor of coke.

3.4. Reaction of ethylbenzene with ethylene

As to mode 3, i.e., injecting ethylbenzene followed by ethylene, the band at 1512 cm^{-1} assigned to diethylbenzene was not observed at 393 K as shown in Fig. 5. However, in mode 1, i.e., injecting benzene substituting for ethylbenzene followed by ethylene, alkylation can take place in a small amount. Experiments show that ethylbenzene has stronger adsorption
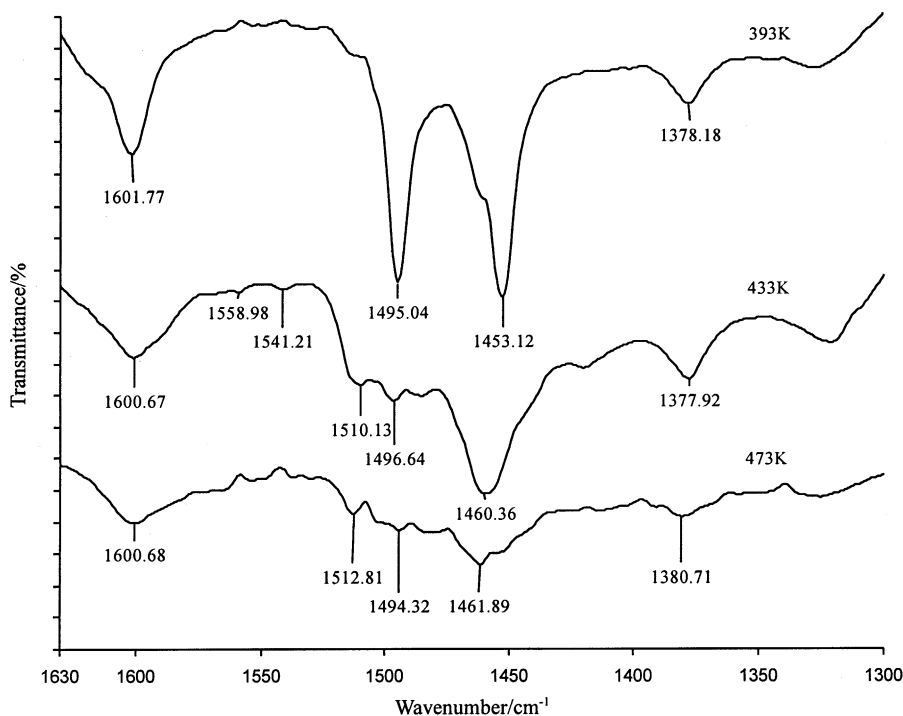
Fig. 5. IR spectra of in situ reaction of adsorbed ethylbenzene with ethylene at 393, 433 and 473 K of step 4.

on catalyst than benzene. Also it is a little more difficult for ethylene to replace adsorbed ethylbenzene than replaced adsorbed benzene. The reaction results at 433 and 473 K shown in Fig. 5 are similar to those of mode 1. At 433 K, decrease of adsorption capacity of ethylbenzene has caused increased adsorption of ethylene. Therefore, alkylation reaction occurred easily and the band at $1512 \, cm^{-1}$ appears. At 473 K, the reaction takes place at step 2, the first pulse of ethylene.

Similar to the reaction systems of benzene with ethylene and benzene with propylene, the reaction of adsorbed ethylbenzene with ethylene is more difficult than that of isopropylbenzene with propylene, however, the reaction of adsorbed ethylbenzene can be speeded up by raising temperature. That is due to the higher activation energy of ethylene adsorption to form C^+–C than propylene. The experiments in a vapor–liquid-phase alkylation reactor at the same conditions (413 K, benzene/olefin: 6) shows that the selectivity of ethylbenzene (97.5%) was higher than that of isopropylbenzene (91.5%).

Similar to mode 2, the reaction took place up to 473 K in mode 4 that is injecting ethylene followed by ethylbenzene as shown in Fig. 6. This can be explained by the strong adsorption of ethylene. At 473 K, the appearance of the bands at $1461 \, cm^{-1}$ and the disappearance of that at $1506–1558 \, cm^{-1}$, which exists at 393 K, indicates through alkenyl carbenium ions the forming of oligomer, the precursor of coke [16].

3.5. Reaction mechanism of benzene with ethylene

Based on the above discussion, the alkylation mechanism has been inferred as follows: benzene adsorbs molecularly and only those which adsorb on strong acidic sites can be activated. Adsorbed ethylene can react neither with benzene in the form of gas nor with benzene adsorbed on weak acidic sites. In mode 1, benzene contacts β-zeolite first, occupies the strong sites and is activated sufficiently; then injected ethylene adsorbs on the same sites but with a little weaker acidity or ethylene can replace some adsorbed benzene, and reaction can readily occur. While in
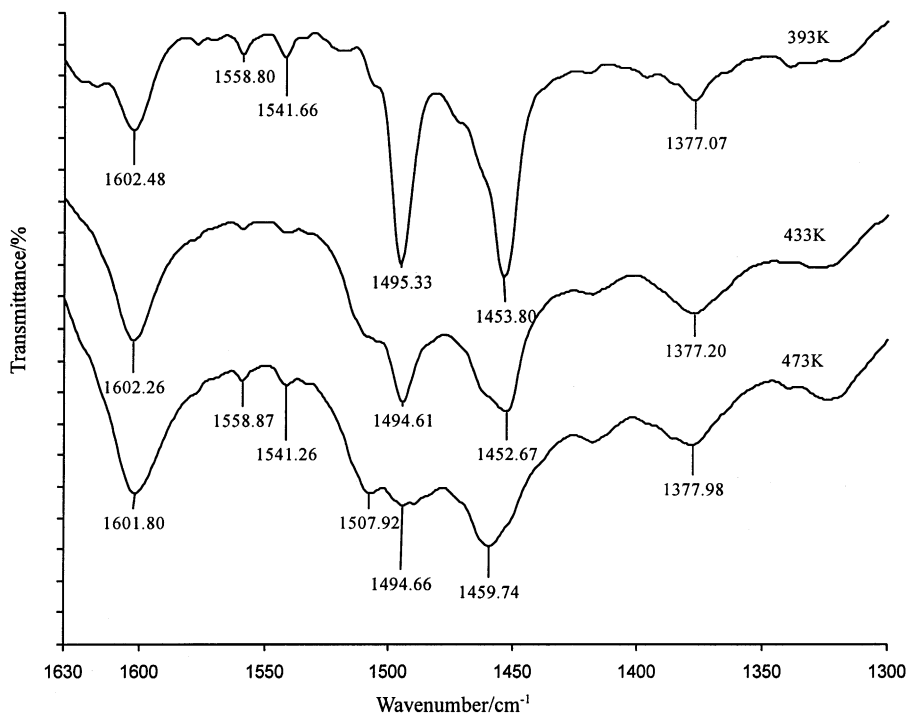
Fig. 6. IR spectra of in situ reaction of adsorbed ethylene with ethylbenzene at 393, 433 and 473 K of step 4.

mode 2, ethylene adsorbs on β-zeolite and changes into C^+–C that has strong interaction with acidic OH groups. At lower temperature (393–433 K), the migration capacity of adsorbed ethylene is poor, hence benzene that has weak interaction with acidic OH in the form of hydrogen bond cannot easily replace adsorbed ethylene. Benzene cannot be activated effectively on relative weak sites. In such case alkylation reaction cannot take place. As temperature is raised, the migration of ethylene increases, benzene can adsorb on strong sites partially and the reaction readily occurs. Therefore, there are competitive adsorptions between ethylene and benzene. The deduction above is in agreement with Sabatier's principle.

The molecule of ethylene is more difficult to be activated than that of propylene. If an activated ethylene molecule has too few adsorbed benzene molecules around to react to alkylation, it can react with another ethylene through alkenyl carbenium ion to form oligomer, a substance considered to be a precursor of coke.

The alkylation of ethylbenzene with ethylene is similar to that of benzene with ethylene, only the former has stronger adsorption. In comparison with the reaction of cumene with propylene, it is more difficult for the reaction of ethylbenzene with ethylene to take place at the same temperature.

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