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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Catalytic conversion of methyl chloride to lower olefins over modified H-ZSM-34

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ABSTRACT

Among several typical zeolites, H-ZSM-34 was found to be an efficient catalyst for the conversion of methyl chloride to lower olefins, i.e., ethylene, propylene, and butenes. Treatment of H-ZSM-34 with a $\text{Na}_2\text{H}_2\text{EDTA}$ (EDTA = ethylenediaminetetraacetate) aqueous solution followed by ion exchange and calcination enhanced the catalytic performance significantly. The selectivity to lower olefins increased significantly for certain $\text{Na}_2\text{H}_2\text{EDTA}$ aqueous solution concentrations; when the H-ZSM-34 catalyst was treated with a 0.1 mol/L $\text{Na}_2\text{H}_2\text{EDTA}$ solution, the selectivity and yield of $\text{C}_2\text{--C}_4$ olefins reached 82% and 61%, respectively, at 673 K and a CH_3Cl partial pressure of 9.2 kPa. The modification of H-ZSM-34 with Ce ions improved $\text{C}_2\text{--C}_4$ olefin selectivity and yield. Catalyst characterization suggests that treatment with $\text{Na}_2\text{H}_2\text{EDTA}$ or modification by Ce decreases the acidity of H-ZSM-34. The weakened acidity of the treated or modified H-ZSM-34 may suppress the hydrogen transfer reaction and prevent lower olefins from further transformation to paraffins.

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1. Introduction

Lower olefins, in particular ethylene and propylene, are among the most important building-block chemicals. Ethylene and propylene are primarily produced from petroleum via steam cracking of naphtha. The demand for the lower olefins has grown rapidly in recent years. There is a strong incentive to develop non-petroleum routes for the production of lower olefins to reduce reliance on diminishing petroleum sources. The production of lower olefins via novel routes such as the dehydrogenation of lower paraffins [1] and the methanol-to-olefins (MTO) process [2,3] has attracted much attention.

Methane is the main constituent of natural gas, coal-bed gas,

shale gas, landfill gas, biogas, and methane hydrates. The transformation of abundant and affordable methane resources to key building-block chemicals such as lower olefins is one of the most important research goals in catalysis. Current technology for chemical use of methane involves high-temperature steam reforming to produce syngas and the subsequent conversion to methanol, followed by methanol transformation to chemicals (e.g., propylene and ethylene). However, steam reforming of methane is an energy- and cost-intensive process [4]. Many studies have been devoted to the direct transformation of methane to chemicals such as methanol, formaldehyde, and ethylene, but yields of desired products are low [4–9]. The development of novel catalytic routes for the trans-

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formation of methane to building-block chemicals is of high significance from a practical and fundamental point of view.

Recently, we reported a two-step route for the conversion of methane to lower olefins, particularly C_3H_6 , via CH_3Cl or CH_3Br [10].

The HCl or HBr generated in the second step can be used directly in the first step, and the net reaction is the oxidative dehydrogenation of methane to lower olefins, i.e., Eq. (3).

The key to realizing this novel two-step route is to develop efficient catalysts for both steps. Some catalysts such as Ru/SiO_2 [11], Rh/SiO_2 [12], $FePO_4/SiO_2$ [13], $LaOCl$ [14–16], and CeO_2 [10] have been studied for use in Step 1, i.e., the oxidative chlorination or bromination of methane to CH_3Cl or CH_3Br by HCl or HBr in the presence of O_2 . This work is devoted to studying catalysts for Step 2.

Some studies have investigated catalysts for the conversion of methyl halides to light olefins. H-SAPO-34 is an efficient catalyst for the MTO process [2,3,17–19]. Because of the chemical similarities between methyl halides and methanol, H-SAPO-34 has been employed mainly as a catalyst for the formation of light olefins in methyl halide conversion [20–25]. We have demonstrated that H-ZSM-5 is a highly efficient catalyst for the conversion of methyl halides (CH_3Cl and CH_3Br) to C_2 – C_4 olefins, particularly C_3H_6 , after modification such as by NH_4F treatment [10,26].

In addition to SAPO-34 and H-ZSM-5, H-ZSM-34 is also a promising catalyst for the formation of lower olefins. ZSM-34 zeolite, which is an intergrowth of erionite and offretite, has an open micropore size of ~ 0.50 nm [27,28]. The pore size for ZSM-34 is between that for SAPO-34 (0.38–0.42 nm) and ZSM-5 (0.52–0.56 nm). Several research groups have reported that H-ZSM-34 exhibits unique product selectivities for the conversion of methanol to olefins [29–31]. In this paper, for the first time, we report on the catalytic behavior of H-ZSM-34 for the conversion of CH_3Cl to lower olefins, which is key in the two-step production of lower olefins from methane [10]. The modification of H-ZSM-34 to enhance its catalytic performance and the key factors determining the catalytic behavior will also be discussed.

2. Experimental

2.1. Catalyst preparation

Zeolites including H-ZSM-5, SAPO-34, SAPO-11, H- β , H-MOR, and HY were purchased from Nankai University Catalyst Co. Na-ZSM-34 was synthesized using an organic template-free procedure reported by Xiao and co-workers [28]. In brief, 3.5 g $NaAlO_2$, 7 g NaOH, 22 g KOH, and 67.5 g aqueous silica gel (40%) were stirred and aged at room temperature for 72 h and produced a clear solution denoted as L seed. NaOH (5.54 g) and fumed silica (28.85 g) were added to 83 mL water and stirred for 5 h. $Al_2(SO_4)_3 \cdot 18H_2O$ (2.71 g) and the L seed (13.5 mL) were introduced into the mixture, followed by further stirring for 13

h. The mixture was transferred into an autoclave to crystallize at 393 K for 7 d. The product was collected by filtration, washing, and drying followed by calcination at 823 K in air for 5 h to obtain Na-ZSM-34. H-form ZSM-34 zeolite was prepared by the ion exchange of Na-ZSM-34 using NH_4NO_3 aqueous solution. Typically, 1.0 g powdered Na-ZSM-34 was added to 50 mL NH_4NO_3 aqueous solution (1.0 mol/L) and the suspension was stirred at 353 K for 3 h. After filtration and washing, the sample was dried at 373 K. This ion-exchange procedure was repeated three times, and the product was calcined at 823 K in air for 6 h to obtain H-ZSM-34.

The procedure for treating H-ZSM-5 with Na_2H_2EDTA (EDTA = ethylenediaminetetraacetate) is as follows. Typically, powdered H-ZSM-34 (2.0 g) was immersed into an aqueous solution of Na_2H_2EDTA (100 mL, 0–0.3 mol/L) and the suspension refluxed at 373 K. The solid product was recovered by filtration, washing with deionized water, and drying at 373 K. Ion exchange of the Na^+ in the treated zeolite with NH_4^+ was performed by adding the treated zeolite into an aqueous NH_4NO_3 solution (50 mL, 1.0 mol/L), followed by washing and drying at 373 K. The ion exchange was repeated three times. Na_2H_2EDTA -treated H-ZSM-34 was obtained after calcination at 823 K in air for 6 h, and the sample was denoted H-ZSM-34-EDTA or H-ZSM-34-EDTA- x , where x is the concentration of Na_2H_2EDTA .

Rare earth metal ion-modified H-ZSM-34 samples were also synthesized using a procedure similar to that for the synthesis of parent H-ZSM-34, with the introduction of rare earth metal salts into the mixture of NaOH, fumed silica, and $Al_2(SO_4)_3 \cdot 18H_2O$ before hydrothermal synthesis for Na-ZSM-34. The sample obtained was denoted RE-H-ZSM-34 (RE represents a rare earth metal). The molar ratio of RE to Al in this series of samples was controlled at 0.080.

2.2. Catalyst characterization

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed with an Agilent ICP-MS 4500 to measure catalyst composition. Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'pert Pro diffractometer with $Cu K\alpha$ radiation (40 kV, 30 mA). Ar physisorption was used to gain information about the pore structure of catalysts and was performed at 87 K on a Micromeritics ASAP-2010M instrument. The pore size distribution in the microporous region was evaluated by the Horváth-Kawazoe (HK) method.

NH_3 temperature-programmed desorption (NH_3 -TPD) was performed on a Micromeritics AutoChem 2920 II instrument to measure the acidity. Typically, the sample loaded in a quartz reactor was pretreated with high-purity He gas at 673 K for 1 h. After cooling to 373 K, NH_3 adsorption was performed by switching the He flow to a 10% NH_3 /He gas flow and maintained at 373 K for 1 h. The gas phase or weakly adsorbed NH_3 molecules were purged by high-purity He at the same temperature. NH_3 -TPD was performed in the He flow by raising the temperature to 1073 K at 10 K/min. The desorbed NH_3 molecules were detected by a ThermoStar GSD 301 T2 mass spectrometer with signal of $m/e = 16$.

Pyridine-adsorbed Fourier transform infrared (FT-IR) measurements were performed with a Nicolet Avatar instrument equipped with an MCT detector with 4 cm^{-1} resolution. Typically, the sample (10 mg) was pressed into a self-supported wafer and placed in an in situ FT-IR cell. After pretreatment under vacuum at 673 K for 30 min, the sample was cooled to 473 K. Pyridine was adsorbed at 473 K onto the sample for a sufficient length of time. FT-IR spectra were recorded after gaseous or weakly adsorbed pyridine molecules were removed by evacuation at 473 K.

^{27}Al magic-angle spinning nuclear magnetic resonance (^{27}Al MAS NMR) was used to investigate the coordination environment of Al. Measurements were carried out on a Varian Infinity Plus AS400 spectrometer (Varian Inc.) operated at 104.26 MHz frequency, 0.5 μs pulse width, 50 G radiofrequency field strength, 0.5 s pulse delay, and 7 kHz spinning rate and with 85 000 scans.

2.3. Catalytic reaction

The catalytic conversion of CH_3Cl was carried out on a fixed-bed tubular quartz reactor operated at atmospheric pressure. The catalyst loaded in the reactor was pretreated in a N_2 (purity > 99.999%) gas flow at 673 K for 1 h before reaction. The reaction was started by introducing CH_3Cl (purity > 99.99%) diluted with N_2 . All products were analyzed using an on-line gas chromatograph equipped with TCD and FID detectors. An RT-PLOTQ column was used to separate the CH_3Cl and carbon-containing products including CH_4 , C_2 – C_4 paraffins (C_2H_6 , C_3H_8 , and C_4H_{10}), and C_2 – C_4 olefins (C_2H_4 , C_3H_6 , and C_4H_8). A Porapak Q column was used to separate N_2 and CH_3Cl . The amount of CH_3Cl formed was calculated using N_2 as an internal standard with a TCD detector. The amount of hydrocarbon product was quantified with an FID detector. The hydrocarbon product selectivity was calculated from the amount of hydrocarbon product (mol) divided by the total amount of the CH_3Cl (mol) converted on a carbon basis. The C_{5+} hydrocarbons were typically condensed in an alkali cold-trap that was employed to capture HCl, and thus were not detected by the RT-PLOTQ column. The selectivity to C_{5+} hydrocarbons was estimated by a normalization method, i.e., by subtraction of the selectivity to C_1 – C_4 hydrocarbons from 100%, and was typically

less than 10% for the ZSM-34-based catalysts. In some cases, we removed the cold-trap and analyzed the C_{5+} hydrocarbons with the PLOTQ column and an FID detector. C_5H_{10} , C_5H_{12} , C_6H_{12} , C_6H_{14} , C_7H_{14} , C_7H_{16} , and benzene were identified as the main components of the C_{5+} hydrocarbons, and the total selectivity calculated from the amounts of these hydrocarbons (mol) was approximately 5%–10%. This also suggests that the normalization method is applicable to the calculation of selectivity to C_{5+} hydrocarbons. The carbon balance was calculated from the amount of product (mol) divided by the total amount of CH_3Cl converted (mol). The carbon deposition was detected and became significant at long reaction times (for example, ≥ 3 h for H-ZSM-34-based catalysts). The main components of the carbon deposited were various aromatics such as benzene, naphthalene, and their derivatives. Without considering carbon deposition, the carbon balance was typically better than 90% for all catalysts at a shorter reaction time (1 or 2 h).

3. Results and discussion

3.1. Catalytic performance of several typical zeolites

Table 1 shows the catalytic performance of several typical H-form zeolites for the conversion of CH_3Cl at 673 K. H-ZSM-5, H-ZSM-34, and H-SAPO-34 displayed the highest CH_3Cl conversions. The yield of lower (C_2 – C_4) olefins was larger than 35% over these three zeolite catalysts. The conversion of CH_3Cl was lower than 30%, and the yield of lower olefins was lower than 20% over other zeolites, although some (H- β , H-MCM-22, and H-MOR) exhibited comparable or higher selectivities to lower olefins. Among the three active catalysts, i.e., H-ZSM-5, H-ZSM-34, and H-SAPO-34, H-SAPO-34 was the most selective for the formation of lower olefins, but its CH_3Cl conversion was the lowest. Compared with H-ZSM-5, H-ZSM-34 provided a higher selectivity to C_2 – C_4 olefins although its conversion was lower. A comparison of catalytic performance between H-ZSM-34 (5.0) and H-Y (4.8) with similar Si/Al ratio showed that H-ZSM-34 had a higher CH_3Cl conversion and C_2 – C_4 olefin selectivity, and its yield of C_2 – C_4 olefins was the highest. To the best of our knowledge, to date there has been no report on the conversion of methyl halides to lower olefins using H-ZSM-34. Thus, we have focussed on H-ZSM-34 for the conversion of

Table 1
Catalytic performance of several typical zeolites for the conversion of CH_3Cl .

Catalyst ^a	Conversion (%)	Selectivity ^b (%)						Yield (%)		
		CH_4	C_2H_4	C_3H_6	C_4H_8	C_{2-4}^0	C_{5+}	C_2H_4	C_3H_6	C_4H_8
H-ZSM-5 (100)	89	1.4	18	16	5.6	37	22	16	15	5.2
H-ZSM-34 (3.3)	72	3.5	29	21	7.7	31	7.8	21	15	5.6
H-ZSM-34 (5.0)	67	4.3	31	23	10	26	5.1	21	16	6.9
H-SAPO-34	50	1.1	46	32	0.5	19	0.9	23	16	0.3
H-SAPO-11	<1	—	—	—	—	—	—	—	—	—
H- β (50)	26	0.4	20	31	20	16	12	5.3	8.3	5.2
H-MCM-22 (30)	16	1.5	10	37	28	12	12	1.6	5.7	4.3
H-MOR (12)	8.7	1.9	23	26	25	7.8	16	2.0	2.3	2.2
H-Y (4.8)	24	0.5	12	17	19	20	30	2.9	4.1	4.6

Reaction condition: catalyst 0.30 g, $p(\text{CH}_3\text{Cl}) = 3.3\text{ kPa}$, $p(\text{N}_2) = 98.0\text{ kPa}$, $F = 15.5\text{ mL/min}$, 673 K, 2 h.

^a Si/Al ratio in parentheses.

^b C_{2-4}^0 and C_{5+} denote C_2 – C_4 paraffins and hydrocarbons with carbon numbers ≥ 5 , respectively.

CH₃Cl.

3.2. Effect of modification on catalytic behavior of H-ZSM-34

Although H-ZSM-34 catalyzed the conversion of CH₃Cl to lower olefins with relatively better yields than other typical zeolites, the selectivity to the undesirable C₂–C₄ paraffin products (C₂–C₄⁰) was still relatively high. The conversion of CH₃Cl over H-ZSM-34 was also lower than that over H-ZSM-5 (Table 1). The change in reaction conditions by increasing the amount of catalyst and the CH₃Cl partial pressure increases CH₃Cl conversion to > 90% at 673 K and a time on stream of 1 h, but the selectivity to C₂–C₄ paraffins also increases (Table 2). Thus, modification of the H-ZSM-34 to decrease selectivity to C₂–C₄ paraffins and increase that to lower olefins is a key research target.

We found that the treatment of H-ZSM-34 in an aqueous solution of Na₂H₂EDTA followed by ion exchange with NH₄⁺ and calcination was an effective means to improve the selectivity to lower olefins. Na₂H₂EDTA concentration influences catalytic behavior (Table 2). Under both reaction conditions, increasing Na₂H₂EDTA concentration decreased CH₃Cl conversion but increased selectivity to lower olefins, particularly C₃H₆ and C₄H₈, significantly. The selectivity to C₂–C₄ paraffins decreased significantly. The selectivity to C₅⁺ hydrocarbons also decreased slightly. When the Na₂H₂EDTA concentration reached 0.1

mol/L, the selectivities to C₃H₆ and C₄H₈ at 673 K were approximately twice those over H-ZSM-34 without treatment. The selectivity and yield of C₂–C₄ olefins were 82% and 61%, respectively, over the H-ZSM-34-EDTA-0.1M. A further increase in Na₂H₂EDTA concentration from 0.1 to 0.3 mol/L led to a slight increase in selectivity to C₃H₆ and C₄H₈, but CH₃Cl conversion decreased, resulting in a lower yield of lower olefins. Thus, an appropriate concentration of Na₂H₂EDTA is required for the treatment of H-ZSM-34 to obtain the highest yield of lower olefins.

Modification of H-ZSM-34 with rare earth metal ions also improved the catalytic performance of H-ZSM-34. The introduction of rare earth metal ions into H-ZSM-34 can increase the selectivity to lower olefins (see Table 3), particularly of C₃H₆, and decrease that to C₂–C₄ paraffins under both reaction conditions. For instance, the presence of La, Ce, Eu, and Y in H-ZSM-34 increased the selectivity for C₃H₆ to > 40%, which was twice that over H-ZSM-34 without modification. However, significant decreases in CH₃Cl conversion were observed over catalysts modified by La, Eu, and Y. Among the RE-H-ZSM-34 catalysts, Ce-H-ZSM-34 provided the best yield of lower olefins at 673 K (Table 3).

To gain insight into the effect of Na₂H₂EDTA treatment and Ce modification on reaction pathways, we compared the catalytic behaviour of H-ZSM-34, H-ZSM-34-EDTA-0.1, and Ce-H-ZSM-34 for CH₃Cl conversion with different contact times.

Table 2

Catalytic behavior of H-ZSM-34 samples treated with different concentrations of Na₂H₂EDTA aqueous solutions for conversion of CH₃Cl.

Na ₂ H ₂ EDTA concentration (mol/L)	Conversion (%)	Selectivity (%)						Yield (%)		
		CH ₄	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	C ₂ –C ₄ ⁰	C ₅ ⁺	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈
0 ^a	72	3.5	29	21	7.7	31	7.8	21	15	5.6
0.1 ^a	58	4.5	27	42	13	6.8	6.7	16	24	7.5
0.2 ^a	52	5.1	28	41	14	5.3	6.4	15	21	7.3
0.3 ^a	41	5.3	29	43	14	2.0	6.4	12	18	5.7
0 ^b	92	1.8	26	20	5.2	40	7.0	24	18	4.8
0.05 ^b	88	2.0	28	24	7.0	32	7.0	24	21	6.1
0.1 ^b	74	2.3	27	43	12	8.8	6.9	20	32	9.1
0.2 ^b	66	2.6	28	44	12	6.8	6.6	19	29	8.1
0.3 ^b	52	2.7	27	48	13	2.6	6.6	14	25	6.9

^a Reaction conditions: catalyst 0.30 g, $p(\text{CH}_3\text{Cl}) = 3.3$ kPa, $p(\text{N}_2) = 98.0$ kPa, $F = 15.5$ mL/min, 673 K, 2 h.

^b Reaction conditions: catalyst 0.70 g; $p(\text{CH}_3\text{Cl}) = 9.2$ kPa, $p(\text{N}_2) = 92.1$ kPa, $F = 11$ mL/min, 673 K, 1 h.

Table 3

Catalytic behavior of H-ZSM-34 samples modified with different rare earth metal ions for conversion of CH₃Cl.

Modifier ^a	Conversion (%)	Selectivity (%)						Yield (%)		
		CH ₄	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	C ₂ –C ₄ ⁰	C ₅ ⁺	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈
None ^b	72	3.5	29	21	7.7	31	7.8	21	15	5.6
La ^b	26	4.1	24	58	8.5	3.6	2.6	6.0	15	2.2
Ce ^b	62	5.4	31	43	7.3	9.1	3.8	19	27	4.5
Nd ^b	72	7.6	32	24	8.4	21	6.0	23	17	6.0
Sm ^b	63	5.8	28	37	11	14	4.7	18	23	6.8
None ^c	92	1.8	26	20	5.2	40	7.0	24	18	4.8
La ^c	33	2.1	21	55	15	4.6	2.3	7.1	18	5.1
Ce ^c	79	2.8	29	41	6.3	13	7.9	23	32	5.0
Nd ^c	91	3.9	29	25	5.7	31	5.4	17	22	5.1
Sm ^c	80	3.0	25	35	8.0	18	11	20	28	6.6
Eu ^c	40	3.5	28	45	14	7.2	2.3	11	18	5.4
Y ^c	49	3.2	31	44	11	8.1	2.7	15	22	5.4

^a Molar ratio of rare earth metal to Al was controlled at 0.08.

^b Reaction conditions: catalyst 0.30 g, $p(\text{CH}_3\text{Cl}) = 3.3$ kPa, $p(\text{N}_2) = 98.0$ kPa, $F = 15.5$ mL/min, 673 K, 2 h.

^c Reaction conditions: catalyst 0.70 g, $p(\text{CH}_3\text{Cl}) = 9.2$ kPa, $p(\text{N}_2) = 92.1$ kPa, $F = 11$ mL/min, 673 K, 1 h.

Fig. 1. Effect of contact time on catalytic behavior of H-ZSM-34 (1), H-ZSM-34-EDTA-0.1 (2), and Ce-H-ZSM-34 (3) for CH_3Cl conversion. (a) CH_3Cl conversion; (b) C_2H_4 selectivity; (c) C_3H_6 selectivity; (d) C_4H_8 selectivity; (e) $\text{C}_2\text{--C}_4$ paraffin selectivity; (f) C_{5+} hydrocarbon selectivity. Reaction conditions: $p(\text{CH}_3\text{Cl}) = 9.2 \text{ kPa}$, $p(\text{N}_2) = 92.1 \text{ kPa}$, $F = 11 \text{ mL/min}$, 673 K .

As shown in Fig. 1(a), the conversion of CH_3Cl increased almost linearly with contact time in the initial stage (shorter contact times) over the three catalysts. The H-ZSM-34-EDTA-0.1 and Ce-H-ZSM-34 catalysts showed slightly lower CH_3Cl conversions than H-ZSM-34 for the same contact time. For H-ZSM-34, with shorter contact times (i.e., initial reaction stage), lower olefins, i.e., C_2H_4 , C_3H_6 , and C_4H_8 , were formed as main products (Fig. 1(b–d)). An increase in contact time decreased the selectivity to lower olefins and increased that to $\text{C}_2\text{--C}_4$ paraffins (Fig. 1(e)) and C_{5+} hydrocarbons (Fig. 1(f)). These results suggest that, over H-ZSM-34, the lower olefins are the primary products, while the $\text{C}_2\text{--C}_4$ paraffins and C_{5+} hydrocarbons are secondary products formed from the lower olefins probably via hydrogen transfer and/or aromatization reactions. For the H-ZSM-34-EDTA-0.1 and Ce-H-ZSM-34 catalysts, the selectivity to lower olefins, particularly C_3H_6 , also decreased with increasing contact time, but this decrease was lower than that for H-ZSM-34 without treatment or modification (Fig. 1(c)). The increase in selectivity to $\text{C}_2\text{--C}_4$ paraffins with contact time became less significant after $\text{Na}_2\text{H}_2\text{EDTA}$ treatment or Ce modification (Fig. 1(e)). These observations suggest that $\text{Na}_2\text{H}_2\text{EDTA}$ treatment and Ce modification of H-ZSM-34 suppress the hydrogen transfer reaction significantly.

Rapid catalyst deactivation was observed during the conversion of methyl halides over zeolite catalysts because of coke deposition [10,20–26]. We also investigated the stability of the H-ZSM-34, H-ZSM-34-EDTA-0.1, and Ce-H-ZSM-34 catalysts during CH_3Cl conversion at 673 K . Although H-ZSM-34 without modification showed a relatively higher CH_3Cl conversion at a

time on stream of 1 h, rapid deactivation was observed (Fig. 2(a)). After 4 h, CH_3Cl conversion and lower olefin yield decreased significantly from 92% to 17% and from 47% to 13%, respectively. $\text{Na}_2\text{H}_2\text{EDTA}$ treatment and Ce modification could improve catalyst stability. Figure 2(b) and (c) show that the decrease in CH_3Cl conversion and the lower olefin yield become less rapid after $\text{Na}_2\text{H}_2\text{EDTA}$ treatment or Ce modification; the lower olefin yields of 49% and 47% could still be sustained after 4 h over the H-ZSM-34-EDTA-0.1 and Ce-H-ZSM-34 catalysts, respectively.

3.3. Characterization of modified H-ZSM-34 catalysts

Figure 3 shows the XRD patterns of the H-ZSM-34 catalysts treated with $\text{Na}_2\text{H}_2\text{EDTA}$ and modified with Ce ions. Diffraction peaks at $2\theta = 7.8^\circ, 11.9^\circ, 13.5^\circ, 20.6^\circ, 23.8^\circ, 25.0^\circ, 27.1^\circ, 28.5^\circ, 31.4^\circ, 33.6^\circ$, and 36.3° , which could be ascribed to crystalline ZSM-34 [28,31], were observed for the $\text{Na}_2\text{H}_2\text{EDTA}$ -treated H-ZSM-34. However, the intensity of the diffraction peaks attributed to H-ZSM-34 became weaker at the higher concentration of $\text{Na}_2\text{H}_2\text{EDTA}$ used for H-ZSM-34 treatment. This suggests that the crystalline structure of H-ZSM-34 can be sustained after $\text{Na}_2\text{H}_2\text{EDTA}$ treatment, but the crystallinity decreases when a higher concentration of $\text{Na}_2\text{H}_2\text{EDTA}$ is used. For the Ce-modified H-ZSM-34, the main diffraction peaks attributed to the crystalline H-ZSM-34 were observed, but these peak intensities were lower than those for the parent H-ZSM-34. This suggests that the introduction of Ce species during the hydrothermal stage affects zeolite crystallinity. No diffraction peaks

Fig. 2. Changes in catalytic performance with time on stream for CH₃Cl conversion over H-ZSM-34 (a), H-ZSM-34-EDTA-0.1 (b), and Ce-H-ZSM-34 (c). Reaction conditions: catalyst 0.70 g, $p(\text{CH}_3\text{Cl}) = 9.2$ kPa, $p(\text{N}_2) = 92.1$ kPa, $F = 11$ mL/min, 673 K.

assignable to Ce species could be detected, indicating that the Ce species might be well dispersed in the catalyst.

We measured the Al and Si contents in the H-ZSM-34 catalysts with Na₂H₂EDTA treatment and Ce modification. As shown in Table 4, the Si/Al molar ratio for H-ZSM-34 was 3.3. The Si/Al ratio increased in the H-ZSM-34-EDTA. When the Na₂H₂EDTA concentration for H-ZSM-34 treatment was increased from 0 to 0.1 and 0.3 mol/L, the Si/Al ratio increased from 3.3 to 4.8 and 5.9. The decrease in Al content after Na₂H₂EDTA treatment suggests the dealumination of H-ZSM-34 zeolite. The Ce-modified H-ZSM-34 (Ce-H-ZSM-34) catalyst

Fig. 3. XRD patterns for H-ZSM-34 samples treated with Na₂H₂EDTA and modified with cerium together with parent H-ZSM-34.

Table 4

Composition of H-ZSM-34 catalysts treated with Na₂H₂EDTA and modified with Ce.

Catalyst	Composition ^a (wt%)			Si/Al molar ratio	Ce/Al molar ratio
	Al	Si	Ce		
H-ZSM-34	9.9	31	—	3.3	—
H-ZSM-34-EDTA-0.1	7.4	34	—	4.8	—
H-ZSM-34-EDTA-0.3	6.3	37	—	5.9	—
Ce-H-ZSM-34	8.7	38	3.1	3.7	0.068

^a Measured by ICP.

possesses a slightly higher Si/Al ratio (3.8) than the H-ZSM-34 without modification. Meanwhile, the Ce/Al ratio was 0.068 for the Ce-H-ZSM-34 catalyst and the value was close to 0.08, which was used in the synthesis gel, suggesting that Ce modification did not change the Al content in H-ZSM-34 significantly and most of the Ce ions could be incorporated into the catalyst.

Figure 4 shows the Ar adsorption-desorption isotherms and corresponding pore diameter distributions for our catalysts. All samples exhibit type-I isotherms, which are typical for microporous zeolites. Pore diameter distributions derived from the isotherms by the HK method show that our H-ZSM-34 without any treatment or modification possesses micropores ~0.5 nm in size, which are typical for H-ZSM-34. After

Fig. 4. Ar adsorption-desorption isotherms (a) and pore diameter distribution (b) of H-ZSM-34 samples derived from Ar physisorption isotherms by the HK method.

Fig. 5. NH_3 -TPD profiles for H-ZSM-34 samples treated with $\text{Na}_2\text{H}_2\text{EDTA}$ and modified with Ce together with parent H-ZSM-34.

$\text{Na}_2\text{H}_2\text{EDTA}$ treatment, pore diameter distributions become slightly broadened. This may result from dealumination from the H-ZSM-34 framework. For the Ce-modified sample (Ce-HZSM-34), the pore distribution was similar to that for H-ZSM-34. Thus, the pore structure for the Ce-HZSM-34 resembles that for HZSM-34.

Figure 5 shows the NH_3 -TPD profiles for H-ZSM-34, H-ZSM-34-EDTA, and Ce-H-ZSM-34. Two distinct NH_3 desorption peaks at ~ 473 and ~ 723 K were observed over H-ZSM-34, which could be attributed to the NH_3 molecules adsorbed on weak and strong acid sites, respectively. After treatment with $\text{Na}_2\text{H}_2\text{EDTA}$, the NH_3 desorption peak intensity, particularly the higher-temperature peak, decreased significantly. The position of the higher-temperature peak shifted to lower temperatures. Thus, $\text{Na}_2\text{H}_2\text{EDTA}$ treatment decreased both the strength and density of the H-ZSM-34 acid sites. Based on this information and the ICP results (Table 4), we propose that dealumination by $\text{Na}_2\text{H}_2\text{EDTA}$ treatment causes the decrease in H-ZSM-34 acidity. Similarly, the strength and density of H-ZSM-34 acid sites also decreased because of Ce modification (Fig. 5). Since the Si/Al ratio in the Ce-H-ZSM-34 is similar to that in

H-ZSM-34 (Table 4), we speculate that the weaker Ce-H-ZSM-34 acidity results from the Ce ions existing in the cationic-exchanging position to replace some of the protons.

To gain further information about the acid sites, we performed FT-IR studies on adsorbed pyridine for H-ZSM-34, $\text{Na}_2\text{H}_2\text{EDTA}$ -treated H-ZSM-34, and Ce-modified H-ZSM-34 samples. As shown in Fig. 6, three IR bands at 1542, 1487, and 1450 cm^{-1} were observed for H-ZSM-34. The IR bands at 1542 and 1450 cm^{-1} could be attributed to the Brönsted and Lewis acid sites, respectively, while the band at 1487 cm^{-1} could originate from both the Brönsted and Lewis acid sites [32]. For the H-ZSM-34-EDTA and Ce-H-ZSM-34 samples, the intensities of the IR bands belonging to both the Brönsted and Lewis acid sites decrease compared with those for H-ZSM-34. This demonstrates that the $\text{Na}_2\text{H}_2\text{EDTA}$ treatment and Ce modification could decrease densities of both the Brönsted and Lewis acid sites.

^{27}Al MAS NMR is an effective technique for gaining information on the coordination state of Al species. Generally, Al species in four-, five- and six-coordination environments exhibit signals at $\delta = 55\text{--}60$, ~ 30 , and ~ 0 , respectively [33]. To obtain insight into the coordination of Al in our catalysts, Fig. 7 gives ^{27}Al MAS NMR spectra of H-ZSM-34, H-ZSM-34-EDTA, and Ce-H-ZSM-34 catalysts. H-ZSM-34 without any treatment or modification showed a signal at $\delta = \sim 60$, which could be assigned to the tetrahedral Al in the framework of H-ZSM-34. No signals at $\delta = 30$ and 0 were observed, indicating the absence of five- and six-coordinated Al species in H-ZSM-34. After treatment with $\text{Na}_2\text{H}_2\text{EDTA}$, a weak signal at $\delta = 0$ appeared, and this signal became stronger with increasing $\text{Na}_2\text{H}_2\text{EDTA}$ concentration. This indicates that octahedrally coordinated Al species, i.e., extra-framework Al species, formed during $\text{Na}_2\text{H}_2\text{EDTA}$ treatment. This is in agreement with our speculation that $\text{Na}_2\text{H}_2\text{EDTA}$ treatment leads to dealumination. For Ce-modified H-ZSM-34, a broad signal at $\delta = 0$ was also observed, suggesting the appearance of an extra-framework Al in this sample. At the same time, the signal at $\delta = 60$ became broader. These observations imply that several different types of Al species may exist in the Ce-H-ZSM-34.

Fig. 6. FT-IR spectra of adsorbed pyridine for H-ZSM-34 samples treated with $\text{Na}_2\text{H}_2\text{EDTA}$ and modified with Ce together with parent H-ZSM-34.

Fig. 7. ^{27}Al MAS NMR spectra of H-ZSM-34 samples treated with $\text{Na}_2\text{H}_2\text{EDTA}$ and modified with Ce together with parent H-ZSM-34.

Fig. 8. GC-MS analyses of methylbenzene intermediates trapped in several catalysts after 2 h under conditions in Fig. 2. (1) H-ZSM-34; (2) H-ZSM-34-EDTA-0.1; (3) Ce-H-ZSM-34. C_2Cl_6 was used as internal standard for quantification of methylbenzenes. MB: methylbenzene.

3.4. Possible reaction mechanism

Many studies have contributed to understanding the reaction mechanism for the conversion of MTO. The “hydrocarbon pool” mechanism is a widely accepted mechanism [3,18]. It is proposed that methylbenzenes with different numbers of methyl substituents and the corresponding carbenium ions function as active intermediates or their stable forms or precursors in the “hydrocarbon pool” in the working catalyst for the production of lower olefins. A similar “hydrocarbon pool” mechanism has also been proposed for the conversion of methyl halides to lower olefins over H-SAPO-34 and H-ZSM-5 [21,26].

We analyzed the hydrocarbon compounds trapped in our used catalysts according to the method proposed by Bjørger et al. [34]. After 2 h, the catalyst was dissolved in HF solution and the organic compounds extracted by CH_2Cl_2 for GC-MS analysis. As shown in Fig. 8, methylbenzenes with different methyl substituents were observed for H-ZSM-34, H-ZSM-34-EDTA, and Ce-H-ZSM-34 catalysts, suggesting that these methylbenzenes were the main organic compounds existing in the “hydrocarbon pool” over our catalysts. Figure 9 shows the distribution of methylbenzenes calculated from Fig. 8 for H-ZSM-34, H-ZSM-34-EDTA-0.1, and Ce-H-ZSM-34 catalysts. Compared with H-ZSM-34, the fraction of tetra-, penta-, and hexa-methylbenzenes in the “hydrocarbon pool” increases over the H-ZSM-34-EDTA-0.1, and Ce-H-ZSM-34 catalysts.

From the results obtained, we speculate that during the conversion of CH_3Cl , lower olefins may form from methylbenzene intermediates existing in the “hydrocarbon pool” as in the

Fig. 9. Distribution of methylbenzene intermediates trapped in H-ZSM-34, H-ZSM-34-EDTA-0.1, and Ce-H-ZSM-34 catalysts after 2 h under conditions of Fig. 2.

MTO process. From our results with varying contact time, we suggest that the lower olefins, i.e., C_2H_4 , C_3H_6 , and C_4H_8 , are formed as the primary products (Fig. 1). It is proposed that the conversion of CH_3Cl over the H-ZSM-34-based catalysts proceeds according to the reaction mechanism in Scheme 1. We speculate that the formation of lower olefins from the methylbenzene intermediates may resemble that in the MTO process [3,18]. It has been reported that mono-, di-, and tri-methylbenzenes may be responsible for the formation of C_2H_4 , whereas tetra-, penta-, and hexa-methylbenzenes may be responsible for the formation of C_3H_6 and C_4H_8 in the MTO process [3,18]. Thus, we tentatively suggest that the increase in fraction of tetra-, penta-, and hexa-methylbenzenes for catalysts with EDTA treatment or Ce modification may contribute to the increase in ratio of C_3H_6 to C_2H_4 in the final product. Further studies are required to understand the detailed reaction mechanism for the formation of C_2H_4 and C_3H_6 in the conversion of CH_3Cl .

It is proposed that the main byproducts, i.e., C_2 – C_4 paraffins and C_5+ hydrocarbons, form from the lower olefins via hydrogen transfer and/or aromatization reactions. For example, C_2H_6 , C_3H_8 , and C_4H_{10} could be formed from C_2H_4 , C_3H_6 , and C_4H_8 via inter-molecular hydrogen transfer reactions. Generally, a high density of stronger acid sites is required for hydrogen transfer and aromatization reactions [35,36]. Our results indicate that Na_2H_2EDTA treatment and Ce modification decrease the density of acid sites, particularly the density of the stronger Brønsted acidity of H-ZSM-34 (Figs. 5 and 6). This may suppress the further conversion of lower olefins over the H-ZSM-34-EDTA and Ce-H-ZSM-34 catalysts, thereby decreasing

Scheme 1. Proposed reaction mechanism for conversion of CH_3Cl over H-ZSM-34-based catalysts.

ing the selectivity to C₂–C₄ paraffins and C₅⁺ hydrocarbons (Fig. 1). However, the conversion of CH₃Cl decreases significantly over a catalyst with lower acidity such as H-ZSM-34-EDTA-0.3 (Table 2 and Fig. 5). This suggests that an appropriate acidity is required to obtain a higher selectivity to lower olefins and higher activity for CH₃Cl conversion over the H-ZSM-34-based catalyst.

4. Conclusions

H-ZSM-34 exhibited a higher yield to lower olefins (i.e., C₂H₄, C₃H₆, and C₄H₈) in the conversion of CH₃Cl than several other typical zeolites including H-ZSM-5, H-SAPO-34, H-SAPO-11, H-β, HY, H-MCM-22, and H-MOR. We demonstrated that the treatment of H-ZSM-34 with Na₂H₂EDTA aqueous solution followed by ion exchange and calcination enhanced the selectivity and yield to lower olefins significantly. Na₂H₂EDTA concentration is an important factor influencing catalytic behavior. At a Na₂H₂EDTA concentration of 0.1 mol/L, the yield of lower olefins reached 61% with a CH₃Cl conversion of 74% at 673 K and CH₃Cl partial pressure of 9.2 kPa. Modification with rare earth metal ions is also an efficient means to promote the selectivity to lower olefins. Over the Ce-H-ZSM-34 catalyst, the selectivity to C₃H₆ is twice that without any modification, and a lower olefin yield of 60% was obtained. Characterization indicates that the acidity of H-ZSM-34, particularly the stronger Brönsted acidity, decreases by treatment with Na₂H₂EDTA or modification with Ce ions. We propose that the decrease in stronger acidity may suppress the hydrogen transfer and aromatization reactions, which leads to the transformation of primary lower olefin products into C₂–C₄ paraffins and C₅⁺ hydrocarbons and thus increases the selectivity to lower olefins.

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Graphical Abstract

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Catalytic conversion of methyl chloride to lower olefins over modified H-ZSM-34

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H-ZSM-34 was an efficient catalyst for the conversion of methyl chloride to lower olefins. The treatment of H-ZSM-34 with Na₂H₂EDTA or modification with Ce further enhanced the lower olefin yield to 60%–61%.

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改性H-ZSM-34上氯甲烷催化转化制低碳烯烃

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摘要: 比较了几种典型的沸石分子筛在氯甲烷转化制乙烯、丙烯和丁烯等低碳烯烃反应中的催化性能, 发现H-ZSM-34具有较佳的催化活性和选择性. 经乙二胺四乙酸二钠($\text{Na}_2\text{H}_2\text{EDTA}$)水溶液处理, 并经离子交换及焙烧后, H-ZSM-34上氯甲烷转化制低碳烯烃的催化性能显著改善. 当 $\text{Na}_2\text{H}_2\text{EDTA}$ 浓度为0.1 mol/L, 反应温度为673 K, CH_3Cl 分压9.2 kPa时, $\text{C}_2\text{--C}_4$ 烯烃选择性和收率分别达82%和61%. 研究还发现, Ce修饰H-ZSM-34催化剂同样可改善氯甲烷制低碳烯烃的选择性和收率. 表征结果表明, $\text{Na}_2\text{H}_2\text{EDTA}$ 处理和Ce修饰均降低了H-ZSM-34的酸性. 酸性的降低可抑制低碳烯烃的氢转移反应, 继而避免了其进一步转化为低碳烷烃.

关键词: 氯甲烷; 低碳烯烃; H-ZSM-34; 乙二胺四乙酸二钠处理; 铈修饰; 酸性

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