

Aromatization of methane by using propane as co-reactant over cobalt and zinc-impregnated HZSM-5 catalysts

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Abstract

The activities of the cobalt and zinc-impregnated HZSM-5 catalysts to the non-oxidative conversion of propane (C₃) and methane (C₁) into aromatic hydrocarbons were evaluated using a fixed-bed microreactor. C₁ conversion reached 36.7% and the selectivity of aromatic products reached above 88.7% at atmospheric pressure, weight (hourly) space velocity (WHSV) 1.6 g h⁻¹/(g cat)⁻¹ and 873 K. The influence of the acidity and the ratio of cobalt in the catalyst on the conversion of methane and propane was evaluated. C₁ incorporation was conclusively confirmed by the mass spectral analyses of aromatic products produced in a run with ¹³CH₄ which shows a significant ¹³C enrichment in the C₆H₆⁺, C₇H₈⁺ and C₈H₁₀⁺ fragments. The methane activation could result from its hydrogen-transfer reaction with alkenes. These catalysts were thoroughly characterized using XRD, N₂ adsorption measurements, TPD of NH₃, and FT-IR. The results showed that the activation of methane in low temperature was due to existence of propane. The acidic changes and micropore area of the catalyst severely affected aromatization, and resulted in drastic modifications in product distribution. From this work, we found that only a small fraction of tetrahedral framework aluminum, which corresponds to the Bronsted acid sites, is sufficient to accomplish the aromatization of the intermediates in methane and propane aromatic reaction, while the superfluous strong Bronsted acid sites, which can be decreased by adding Co and Zn, are showed to be related with the aromatic carbonaceous deposits on the catalysts. The density of acidic site and the strength of strong acid decreased when the concentration of Co and Zn in the catalyst increased. Therefore, a much higher benzene yield and a longer durability of the catalysts are obtained when compared with the conventional HZSM-5 catalysts.

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1. Introduction

Natural gas (mostly methane) reserves are abundant throughout the world and are becoming a promising energy source due to the increasing prices of oil. The utilization of methane as a raw material is important to maintain a safe and reliable energy and chemical supplies in the future. A major limitation to the utilization of the resource is the high price to transport the natural gas to the desired location. Recently, a worldwide investigation has been conducted to attempt to convert methane directly to chemicals and fuels [1–6]. However, because of the difficulty in the activation of stable C–H bonds in the CH₄ molecule, methane conversion directly to more useful chemicals and fuels remains a challenge [7]. Further improve-

ments in the catalysts are being performed worldwide. Many studies have also been conducted simultaneously to exploit other non-conventional conversion technologies. The conversion of methane to benzene in the absence of oxygen has been investigated over different TMI/H-ZSM-5 zeolites (with TMI=Mo, Fe, V, W, and Cr) as a function of the preparation and treatment method, the metal ion loading, and the zeolite acidity. Optimum catalytic performance was obtained [8] for Co-pre-reduced 2–4 wt.% TMI/H-ZSM-5 zeolites, and their activities decreased in the order: Mo > W > Fe > V > Cr. Co/H-ZSM5 materials which increase propane conversion and the productivity of aromatics have been previously prepared via aqueous [9,10] and solid-state exchange methods [11]. It catalyzes the H₂ formation rates by combinative desorption. We have reported the technology of the aromatization for C_{3–4} alkyl hydrocarbon with the catalysis of Zn–Ga modified zeolite catalyst [12]. Choudhary and Kinage reported an approach for obtaining high rates of conversion of methane to higher

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hydrocarbons, without formation of carbon oxides and at much lower temperatures (400–600 °C) which involves non-oxidative activation of methane by hydrogen-transfer reactions between methane and alkene over H–Ga–Al–MFI zeolite [13]. Naccache et al. investigated the conversion of a mixture of methane and ethylene at low and high temperatures [14]. In this work, the effects of the degree of acid site dilution of HZSM-5 catalysts on the yields of aromatic hydrocarbons from methane and propane hydrocarbons conversion has been discussed. We have also evaluated the optimum catalyst characteristics and reaction operating variables required for maximum production of aromatic from methane and propane. This work involved the preparation of cobalt and zinc-impregnated HZSM-5 catalysts. It also involved the thorough characterization of these catalysts using techniques such as X-ray diffraction (XRD), N₂ adsorption measurements, temperature programmed desorption (TPD) of NH₃ and FT-IR studies, in order to obtain a better understanding of the relationship between catalyst performance and catalyst characteristics. The results have been used to elucidate the reaction pathway for aromatization over cobalt and zinc-impregnated HZSM-5 catalysts. These results are presented in this paper.

2. Experimental

2.1. Catalyst preparation

The cobalt and zinc-impregnated HZSM-5 catalysts (Co–Zn/HZSM-5) used in this work were obtained by incorporating cobalt and zinc into HZSM-5 catalyst. The non-impregnated HZSM-5 catalyst was prepared according to the procedure reported by Chen et al. [15]. HZSM-5 with a Si/Al mole ratio of 15 was used as the parent zeolite. Altogether, six Co–Zn HZSM-5 catalysts of 2% zinc and cobalt concentrations in the range 0–2.5 wt.% were prepared. Cobalt and zinc were incorporated into the HZSM-5 catalyst by wet impregnation techniques using aqueous solutions of cobalt and zinc nitrates (analytical grade and obtained from Guangzhou Chemical reagent Company, Guangzhou, China) as the precursor. This impregnation step was carried out for 24 h. After this step, the catalysts were dried overnight at 373 K and then calcined at 693 K for 6 h in a muffle furnace. The resulting cobalt and zinc-impregnated HZSM-5 catalysts were designated as K0 (0 wt.% cobalt and 0 wt.% zinc, respectively), K1 (0.5 wt.% cobalt and 2 wt.% zinc, respectively), K2 (1 wt.% cobalt and 2 wt.% zinc, respectively), K3 (1.5 wt.% cobalt and 2 wt.% zinc, respectively), K4 (2 wt.% cobalt and 2 wt.% zinc, respectively) and K5 (2.5 wt.% cobalt and 2% zinc, respectively).

2.2. Catalyst performance studies equipment

The performance of the Zn and Co-impregnated and non-impregnated HZSM-5 catalysts was studied in a stainless steel (SS 316) fixed-bed (down flow) microreactor SR22 (11.5 mm i.d. and 400 mm overall length) microprocessor-based autotuning PID temperature controller (Shimaden Co. Ltd., Tokyo, Japan) using a K-type thermocouple. The furnace temperature was controlled by a series of heating elements placed on the side of the

furnace. A separate thermocouple was used to monitor the temperature of the catalyst bed. This arrangement was capable of ensuring an accuracy of temperature (1 °C for the catalyst bed).

2.3. Conversion of methane and propane

The test runs were performed for each catalyst at atmospheric pressure and reaction temperature in the range 723–893 K and weight (hourly) space velocity (WHSV) ranging from 0.8 to 2.0 g h⁻¹/(g cat)⁻¹. The reactant gas (methane/propane molar ratio of 1.0, contains 10% (v) argon) was obtained from Shanghai Bixiou Gas Company (Shanghai, China) every experimental run required 2 g of the catalyst (2.5 mm of diameter). A typical test run was conducted as follows: a plug of quartz glass wool (about 0.5 g), which was used as screen as well as support for the catalyst, was placed on a stainless steel grid positioned centrally within the reactor. The catalyst was then loaded on the glass wool. The catalyst bed was heated to the desired reaction temperature in flowing argon gas. When this temperature was reached, the argon flow was stopped and the feed was pumped into the reactor at the desired methane and propane space velocity. The product mixture leaving the reactor was condensed in a water-cooled heat exchanger, followed by an ice-cooled condenser to separate gaseous and liquid products for separate analysis. The gaseous products were collected over saturated brine, while the liquid products were collected in a glass trap positioned after the condenser.

2.4. Procedures of reaction products analysis and calculation

The gaseous products were analyzed by an on-line Varian CP-3800 gas chromatograph, with a flameionization detector (FID) using an OV-101 column, and a thermal conductivity detector (TCD) using a Hayesep-D column. The temperature of the column was raised from 293 to 473 K. Prior to calculate conversion of methane and propane, calculate total flow rate at outlet from concentration of argon. The liquid products were analyzed by liquid chromatograph (Prominence LC20AT, Shimadzu, Japan). The date was calculated after the normalization of carbon balance (the amount of deposited carbon was needed to normalized):

the conversion of methane (%)

$$= \frac{(\text{methane in the feed (mol)} - \text{methane in the product (mol)}) + \text{methane produced from propane (mol)}}{\text{methane in the feed (mol)}} \times 100$$

When: methane produced from propane is produced under the same condition without methane in the feed.

2.5. Determination for carbonaceous deposition and C-13 labelling investigation

Thermal gravimetric analysis (TG) was processed with PE-TGA-Type instrument (P.E. Company, USA). After the reaction,

take 20 mg sample, pretreat it 30 min with argon in 673 K and decrease the temperature to 313 K, then increase the temperature from 313 to 1023 K at the rate of 10 K/min and 30 ml/min of the oxygen. The change in weight was used as the carbonaceous deposition on the catalyst. It was converted into the carbonaceous deposition in the interzone of analysis sample and taken it to the normalized calculation of the carbon balance.

The conversion of mixtures of propane and methane of various composition was attempted over cobalt and gallium-modified HZSM-5 under the conditions at which the carbon balance and/or methane consumption could be accurately measured. Because cobalt and gallium-modified HZSM-5, similar to that used by Choudhary and Kinage [13], is subject to deactivation, the square pulse technique was used.

^{13}C -enriched methane (99.5% atom in ^{13}C) was used without further treatment under the same experimental conditions. All the products were collected in a cold trap. The products obtained with ^{13}C methane were analyzed by gas chromatography/mass spectrometry (GC/MS) at the AMI-2000-GC (Dycor System, USA). The products were transferred to a 1 L metallic container kept at 60 °C and were introduced into the spectrometer via a molecular leak. The resolution of the spectrometer was adjusted to within 5000, thus enabling the separation of two very close masses of two distinct entities. For example, this resolution enabled the separation of $^{13}\text{CH}_3 = 16:027$ u from $^{12}\text{CH}_4 = 16.031$ u. In addition, the latter can be safely discriminated from $^{16}\text{O} = 15:995$ u. Furthermore, the water OH fragment (OH = 17:003 u) can be unambiguously separated from $^{13}\text{CH}_4 = 17:035$ u.

2.6. Catalyst characterization

2.6.1. N_2 adsorption measurements [16]

The surface area, pore volume, pore size, and pore size distribution of all of the catalysts were determined using a micromeritics adsorption equipment (Model ASAP 2000) which was equipped with a micropore analysis program using N_2 (Bixiou Gas Ltd., Shanghai, China) as the analysis gas. Prior to analysis, each catalyst was evacuated at 573 K at a vacuum of 0.54 kPa for 10 h. The surface area was evaluated using BET method and the Dubinin–Astakhov program was used in evaluating the micropore surface areas, while the Horvath–Kawazoe equation was used to estimate the median pore sizes of both HZSM-5 and Co–Zn HZSM-5 catalysts.

2.6.2. Powder X-ray diffraction measurements

Powder XRD measurements were performed to identify component phases as well as to determine the degree of crystallinity of the catalysts as a function of cobalt and zinc concentration. The XRD measurements were made with a Phillips diffractometer using $\text{Fe K}\alpha$ radiation in the scanning angle (2θ) range of 10–90° at a scanning speed of 2°/min.

2.6.3. Temperature programmed desorption of ammonia

TPD analysis was performed in order to determine the acid strengths and distributions on the catalysts. NH_3 –TPD experiment: the sample (0.14 g) was dried in a flowing N_2 (99.995%

purity; obtained from Shanghai Bixiou Gas Ltd., Shanghai, China, 60 ml/min) at 873 K for 0.5 h prior to adsorption. Pure NH_3 was adsorbed until saturation took place at 323 K, then the catalyst was flushed with N_2 at the same temperature for 1 h. TPD measurements were conducted from 323 to 1023 K at a heating rate of 15 K/min with N_2 as the carrier gas. The amount of desorbed ammonia was detected by a thermal conductivity detector.

2.6.4. FT-IR measurements

The FT-IR technique was employed to identify the nature of acid sites present on the catalyst samples. The IR measurements were made on powdered catalyst samples using a Biorad Infrared Spectrometer (Model FTS 40, Digilab Division) in reflective mode. Two regions of the IR spectra were explored. These were the hydroxyl and pyridine regions. Consequently, fresh and pyridine chemisorbed catalyst samples were used to obtain the spectra for hydroxyl (3500–4000 cm^{-1}) and pyridine (1400–1650 cm^{-1}) regions, respectively. Pyridine chemisorbed samples were obtained by passing pyridine vapor over the catalysts at 423 K for 1 h in the same flow system that was used previously for NH_3 adsorption. After the pyridine adsorption, each sample was allowed to cool to room temperature and subsequently used for IR analysis.

3. Results and discussion

3.1. Activity of the catalyst

3.1.1. The effect of the content of cobalt on the activity of the catalyst

The results of methane (C1) aromatization in the presence of propane (C3) over different content of cobalt and 2% Zn/HZSM-5 catalysts are summarized in Table 1. As shown in Table 1, the effect of the content of cobalt on the conversion of methane and propane is obvious. The conversion of methane and the selectivity of aromatics increased with the increase of the content of cobalt. When the content of cobalt is 2.0% the conversion of methane was up to 36.7%. The conversion of methane and the selectivity for aromatic increased slowly when the content of cobalt is 2.5%. The selectivity of the product changed with the content of cobalt.

3.1.2. Methane activation in the absence or presence of propane over the catalyst

Table 2 shows methane activation in the absence or presence of propane over 2% Co–2% Zn/HZSM-5 (HZ1) and HZSM-5 (HZ) catalysts. The results showed that whatever catalyst cannot catalyze non-oxidative aromatization of methane at 873 K. But the aromatization of propane can proceed on the same conditions and the conversion of propane is about 73%. When the mixture of methane and propane was as the feed, the results of the reaction were not the simple addition of which methane or propane was as the feed of the aromatization. In this reaction the conversion of propane changes slowly, the conversion of methane is up to 36.7%, and the selectivity of aromatics is 88.7%. In Table 2 the conver-

Table 1

The results of methane aromatization in the presence of propane over $x\%$ Co + 2% Zn HZSM-5 ($x=0, 0.5, 1.0, 1.5, 2.0, 2.5$) catalysts^a

Co content in catalyst, x	Conversion (%)					Selectivity (%)					
	CH ₄	C ₃ H ₈	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₆ ^b	C ₇ ^b	C ₈ ^b	C ₉ ^{+c}	C _x ^d	AH ^e
0	30.8	75.6	4.3	2.5	6.7	28.0	25.9	23.7	7.4	1.4	85.0
0.5	32.6	77.5	4.2	2.0	8.4	27.5	26.7	13.5	16.5	1.2	84.2
1.0	33.7	78.0	3.5	1.6	7.0	27.2	24.6	12.6	22.4	1.1	86.8
1.5	34.6	79.6	3.5	1.5	6.1	27.5	23.5	11.8	25.1	1.0	87.9
2.0	36.7	79.7	3.3	1.4	5.8	28.5	20.3	19.5	20.4	0.8	88.7
2.5	36.9	79.8	3.2	1.5	5.5	28.6	20.3	19.6	20.5	0.8	89.0

^a Feed: C₁ + C₃ + argon, WHSV = 1.6 g h⁻¹/(g cat)⁻¹; T = 873 K; t = 90 min; partial pressure of methane, P_{C1} = 0.045 MPa; partial pressure of propane, P_{C3} = 0.045 MPa; the conversion of methane is calculated following (2.4).

^b Aromatics.

^c Number of C ≥ 9 aromatics.

^d Coke on the catalyst.

^e Total aromatics.

sion of methane is -14.5% when the absence of propane over HZ. This means that there was a net formation of methane.

It is generally reported that the activation of methane occurs on active species of the catalyst forming ethylene as primary product C₂H₄ being converted benzene over acid sites of the zeolite [17–19]. In other work it was shown by contrast that acetylene was the primary product of the reaction of methane over Mo/HZSM-5 [20]. Choudhary and Kinage [13] investigated the reaction of methane in the exist of long-chain alkane or long-chain alkene. They proved that methane can be activated in low temperature because the migration of hydrogen between methane and alkene. When the mixture of methane and propane was as the reagent propane is easier to be activated than methane. Propane was likely to dehydrogenate to become alkene. The methane being activated via the migration of hydrogen occurred between methane and alkene or predecessor of alkene. Naccache et al. confirmed that the absence of methane activation and methane carbon cannot be inserted into olefin aromatization products on the conversion of various mixtures of propene and methane or ethene and methane over Hgallo aluminosilicate (MFI) zeolite under the reported conditions by the use of C¹³-labelled methane [14].

3.1.3. The influence of the methane/propane ratio on the activity of Co–Zn/HZSM-5

Table 3 shows the activity of 2% Co–2% Zn/HZSM-5 from different methane/propane ratio at 873 K in the aromatization of methane and propane. The results showed that when the methane/propane molar ratio is equal to or over 0.4/1 the conversion of propane is great than the conversion of propane when without methane. In fact, the conversion of methane and propane did not change in line. Generally, when the conversion of methane decreased the conversion of propane increased. It proved that there were a competition and co-activation between methane and propane in the reaction. Although the selectivity of aromatics is over 80%, the relative product of C₆H₆ to C₇H₈ changed with the change of $n(C_1)/n(C_3)$ which can be seen from the distribution of the product. When the methane/propane molar ratio is equal to 1 the selectivity of C₆H₆ is great than which of C₇H₈ and the selectivity of naphthalene is get up to 20.4%. Otherwise when the methane/propane molar ratio is less than 1 the selectivity of C₆H₆ is less than which of C₇H₈. The selectivity of C₈H₁₀ decreased with the increase of the methane/propane molar ratio. These results showed that methane participated in the process to produce aromatics. Furthermore, because the process of

Table 2

Methane activation in the absence or presence of propane over 2% Co + 2% Zn HZSM-5 (HZ1) and HZSM-5 (HZ) catalysts^a

Feed	Cat.	Conversion (%)		Product selectivity on the total carbon (%)									
		CH ₄	C ₃ H ₆	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	C ₆ H ₆	C ₇ H ₈	C ₆ H ₁₀	C ₉ ^{+b}	Total aromatic	C _x ^c
CH ₄ ^d	HZ1	0.0	–										
	HZ	0.0	–										
C ₁ + C ₃ ^e	HZ1	36.7	79.7		3.3	1.4	5.8	28.5	20.3	19.5	20.4	88.7	0.8
	HZ	-14.5	17.6	40.6	1.0	38.2	0.0	15.6	4.4	0.0	0.0	20.0	0.2
C ₃ H ₈ ^f	HZ1	–	73.5	2.6	2.6	5.6	7.6	25.4	30.6	15.7	10.3	81.7	0.9
	HZ		56.8	39.2	1.6	39.5	0.0	15.2	4.5	0.0	0.0	19.7	2.1

^a The other conditions are the same as in Table 1, time on stream: 90 min.

^b Number of C ≥ 9 aromatics.

^c Coke on the catalyst.

^d Partial pressure of methane is 0.045 MPa.

^e $n(C_1)/n(C_3) = 1.0$, partial pressure of methane is 0.045 MPa; partial pressure of propane is 0.045 MPa.

^f Partial pressure of propane is 0.045 MPa.

Table 3
Influence of $n(C1)/n(C3)$ ratio on C1 and C3 conversion over 2% Co–2% Zn/HZSM-5^a

$n(C1)/n(C3)$	Conversion (%)		Products selectivity (%)										
	C1	C3	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀	C ₉ ^{+b}	C ₁₀ H ₈	AH ^c	C _x ^d	$n(C_6)/n(C_7)$ ^e
0.4	26.2	70.1	2.3	1.5	3.2	24.2	29.5	28.4	0.04	8.6	90.7	0.7	0.82
0.6	27.3	81.0	2.4	1.8	3.8	28.5	32.5	21.7	0.03	6.8	89.5	0.8	0.88
0.8	31.6	80.2	2.6	1.6	4.1	29.8	32.1	20.0	0.02	7.9	89.8	0.8	0.93
1.0	36.7	79.7	3.3	1.4	5.8	28.5	20.3	19.5	0.02	20.4	88.7	0.8	1.40

^a The conditions are the same as in Table 1.

^b Number of C \geq 9 aromatics (except naphthalene).

^c Total aromatics.

^d Coke on the catalyst.

^e $n(C_6H_6)/n(C_7H_8)$; C₁₀H₈: naphthalene.

Table 4
The results of methane aromatization in the presence of propane over 2% Co–2% Zn/HZSM-5 catalysts at different time on stream

Time on stream (h)	Conv. (%)		Product selectivity on the total carbon (%)									
	CH ₄	C ₃ H ₆	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	C ₆ H ₆	C ₇ H ₈	C ₆ H ₁₀	C ₉ ^{+a}	C ₁₀ ^b	AH ^c	C _x ^d
1.5	36.7	79.7	3.3	1.4	5.8	28.5	20.3	19.5	0.02	20.4	88.7	0.8
3.0	36.7	71.7	1.5	4.1	4.9	28.5	20.3	19.4	0.02	20.3	88.7	0.8
12.0	36.7	72.1	1.6	3.9	4.9	28.7	20.5	19.5	0.01	20.0	88.8	0.8
36.0	36.5	71.7	1.4	4.0	5.1	28.5	20.3	19.5	0.02	20.2	88.7	0.8
84.0	35.5	71.5	1.8	4.0	6.3	27.6	20.4	18.8	0.01	19.9	86.8	1.1
120.0	35.2	71.5	2.2	3.9	6.7	26.4	20.6	18.7	0.02	20.1	86.0	1.2

Feed: C₁ + C₃ + argon; WHSV = 1.6 g h⁻¹/(g cat)⁻¹; T = 873 K; partial pressure of methane, P_{C1} = 0.045 MPa; partial pressure of propane, P_{C3} = 0.045 MPa; the conversion of methane is calculated following (2.4).

^a Number of C \geq 9 aromatics (except naphthalene).

^b Naphthalene.

^c Total aromatics.

^d Coke on the catalyst.

methane to participate to produce aromatics is complex methane either could enter into aromatic ring or could enter into side chain. The idiographic mechanism needs to be made farther investigation.

3.1.4. The activity of the catalyst at different time on stream

Table 4 shows the activity of HZSM-5 which contains 2% Co and 2% Zn at 873 K for the aromatization of methane and propane at different time on stream. On the whole, as a function of time on stream the naphthalene concentration did not change significantly. The conversion of methane and propane decreased slowly with the time on stream extended. Similarly the selectivity of aromatics did not change evidently.

3.2. The result from C-13 labelling investigation

The C-13 labelling investigation has been used under the same conditions to testify methane to be activated and to incorporate into the aromatization products. Table 5 lists the results for C₆H₆, C₇H₈ and C₈H₁₀. It can be seen in Table 5 that in the un-labelled CH₄ and C₃H₈ reaction the area of the MC ion of C₆H₆⁺ ($m/e = 78$) is great by comparing with those of the areas ($m/e = 79, 80$). The area of $m/e = 78$ is 16 times more than the area of $m/e = 79, 80$. Otherwise, in the reaction of ¹³CH₄ and C₃H₈ the area of $m/e = 78$ is much smaller than those of $m/e = 79, 80$. The area of $m/e = 79$ is 430 times as which of $m/e = 78$. In the un-labelled CH₄ and C₃H₈ reaction the area of the MC ion of C₇H₈⁺ ($m/e = 91$) is almost double by comparing with which

Table 5
Mass spectra data for aromatic product from ¹³CH₄ and un-labelled CH₄ aromatization in the presence of propane over 2% Co–2% Zn/HZSM-5

¹³ CH ₄ ⁺ C ₃ H ₈						CH ₄ ⁺ C ₃ H ₈					
C ₆ H ₆ ⁺		C ₇ H ₈ ⁺		C ₈ H ₁₀ ⁺		C ₆ H ₆ ⁺		C ₇ H ₈ ⁺		C ₈ H ₁₀ ⁺	
m/e	10 ⁵ Abundance	m/e	10 ⁵ Abundance	m/e	10 ⁵ Abundance	m/e	10 ⁵ Abundance	m/e	10 ⁵ Abundance	m/e	10 ⁵ Abundance
78	0.0100	91	0.1100	106	0.0182	78	6.4900	91	3.1900	106	0.1870
79	4.3100	92	2.2900	107	0.1790	79	0.4100	92	1.7100	107	0.0200
80	0.3200	93	1.3100	108	0.0020	80	0.0150	93	0.1300	108	–

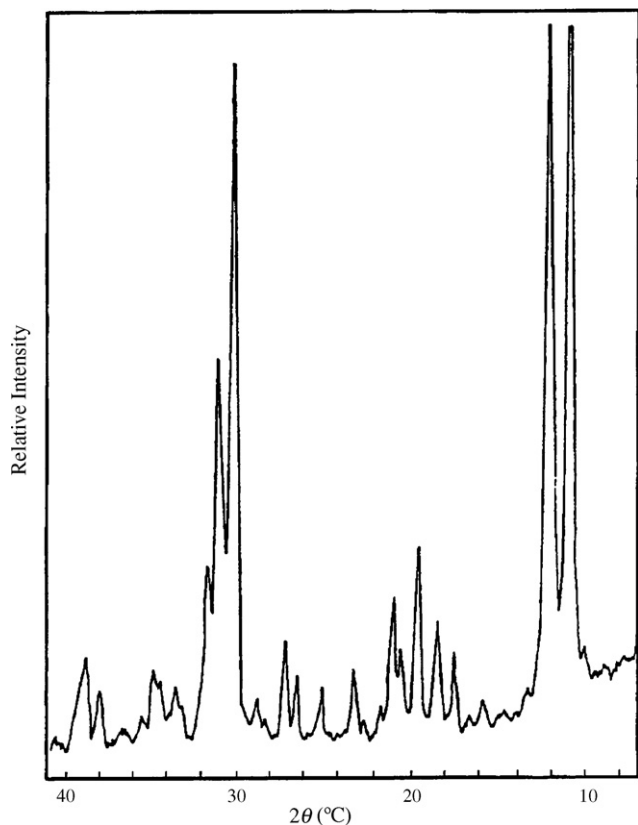


Fig. 1. XRD spectra of ZSM-5 catalyst.

of the areas ($m/e = 92$). In the reaction of $^{13}\text{CH}_4$ and C_3H_8 the areas of $m/e = 92, 93$ are much greater than which of $m/e = 91$. In the un-labelled CH_4 and C_3H_8 reaction the area of the MC ion of $\text{C}_8\text{H}_{10}^+$ ($m/e = 106$) is almost 10 times as the area of $m/e = 107$. But, in the reaction of $^{13}\text{CH}_4$ and C_3H_8 the area of $m/e = 107$ is 10 times as which of $m/e = 106$. These results showed that there was significant incorporation of ^{13}C into the aromatization reaction products and methane is actually incorporated into the aromatics products.

3.3. Catalyst characterization

3.3.1. Powder XRD measurements

The XRD pattern of the non-impregnated HZSM-5 catalyst (K0) is shown in Fig. 1 and is consistent with those reported in the literature [21,22]. The XRD patterns for the Co and Zn-impregnated catalysts did not show any appreciable change from that given in Fig. 1, implying that, up to 2 wt.% Co and 2 wt.% Zn concentration, respectively, there was no loss of crystallinity by the catalysts due to Co and Zn impregnation. Also, no new XRD lines were observed in the Co and Zn-impregnated catalysts.

3.3.2. N_2 adsorption measurements

The micropore surface areas of the Co and Zn-impregnated and non-impregnated HZSM-5 catalysts are given in Table 6 as a functions of cobalt and zinc concentration. It is seen that the micropore surface area decreased slowly with the increase of Co and Zn concentration in the catalyst. Also, it is known

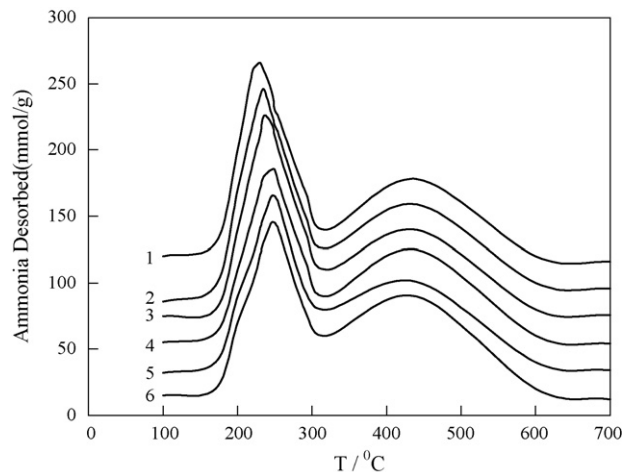


Fig. 2. TPD spectra of the catalysts contained different amount of Co (content of Zn is 2%). (1) HZSM-5, (2) 0.5% Co + 2% Zn HZSM-5, (3) 1% Co + 2% Zn HZSM-5, (4) 1.5% Co + 2% Zn HZSM-5, (5) 2% Co + 2% Zn HZSM-5 and (6) 2.5% Co + 2% Zn HZSM-5.

that the micropore surface area in HZSM-5 is a measure of the inner channel surface area of the micropores. Thus, the decrease in micropore surface area with the increase of Co and Zn concentration may be due to pore blockage of the micropores of the impregnated catalysts by cobalt and zinc (most likely in the form of CoO and ZnO). Pore blockage is also supported by the decrease in micropore volume with increasing Co and Zn concentration (see Table 6). These results were used in conjunction with results obtained from TPD of NH_3 to evaluate the acid site densities of the respective catalysts. This is discussed below.

3.3.3. TPD of NH_3

The TPD- NH_3 spectra for the five catalysts (K0, K1, K2, K3 and K4) are given in Fig. 2. The figure shows that the non-impregnated HZSM-5 catalyst (i.e., K0 containing 0 wt.% Co and 0 wt.% Zn) as well as the impregnated HZSM-5 catalysts containing 2% Zn and 0.5–2.5 wt.% Co, respectively (i.e., K1, K2, K3, and K4) exhibited two well-resolved TPD peaks designated as the low-temperature peak (l) and the high-temperature peak (h). The literature [23] suggests that if the NH_3 -TPD peak temperature is greater than 623 K, then this peak represents strong acid sites (i.e., h peak), whereas peaks with temperatures less than 623 K represent weak acid sites (i.e., l peaks). Thus, the existence of TPD peaks at 493–523 and 673–793 K for non-impregnated and impregnated HZSM-5 catalysts signify the presence of both the weak and strong acid sites on the catalysts. Therefore, the progressive shift to lower peak temperatures for h peak implies that there was a decrease in the strengths of the strong acid sites when the concentration of cobalt in the catalyst increased.

Acid site density can be used to represent the concentration of the acid sites present on the surface of the catalyst which is accessible to the reactants. Acid site density on the basis of surface area becomes important because catalytic cracking reactions are essentially a surface phenomenon which depends on the accessible acid sites presented on the catalyst. In this work, acid site density of each catalyst was calculated as the ratio of

Table 6
Characteristics of Co and Zn impregnated and non-impregnated HZSM-5 catalysts

Catalyst	Catalyst identity	Catalyst micropore surface area (m ² /g)	Adsorbed amount (10 ⁻³ mmol/g)	Micropore volume (cm ³ /g)	Acid density 10 ⁻³ mmol/(m ² of catalyst surface area)
HZSM-5	K0	395	6.96	0.156	0.0176
0.5% Co + 2% Zn HZSM-5	K1	386	6.70	0.150	0.0174
1% Co + 2% Zn HZSM-5	K2	372	6.34	0.142	0.0170
1.5% Co + 2% Zn HZSM-5	K3	370	6.16	0.138	0.0166
2% Co + 2% Zn HZSM-5	K4	360	5.80	0.130	0.0161
2.5% Co + 2% Zn HZSM-5	K5	358	5.76	0.129	0.0161

the total adsorbed amount of NH₃ to the micropore surface area (i.e., inner channel area of the pores) of the catalysts as follows [16]:

$$\mu = \frac{\alpha}{(\text{micropore surface area/g of catalyst})} \quad (1)$$

where μ is the adsorbed amount of NH₃ per unit micropore surface area, mmol/(m² of catalyst micropore surface area) and α is the adsorbed amount of NH₃, mmol/g.

The results for the five catalysts are given in Table 6. It is seen from the table that both the acid site density and micropore area decreased as the cobalt concentration in the catalysts increased. Thus, it can be concluded that the incorporation of cobalt and zinc into HZSM-5 catalyst the concentration of the acid sites decreased. The reaction results showed (Table 1) that the productivity of aromatics increased and the coke on the catalyst decreased with the increase of the content of cobalt, after added Co and Zn the strength of the strong acid becoming weak and the decrease of micropore area resulted in the decrease of the coke on the catalyst and the increase of the activity. Certainly, the conversion does not entirely lie on the strength of the acid site. An alternative interpretation of the role of the transition metal oxides is that they directly participate in the reaction which needs to be investigated further.

Fig. 3 shows TPD graphs of the catalyst after reacted different time. As seen in Fig. 3, with the reaction time extended, the number of the strong acid sites decreased quickly, but the

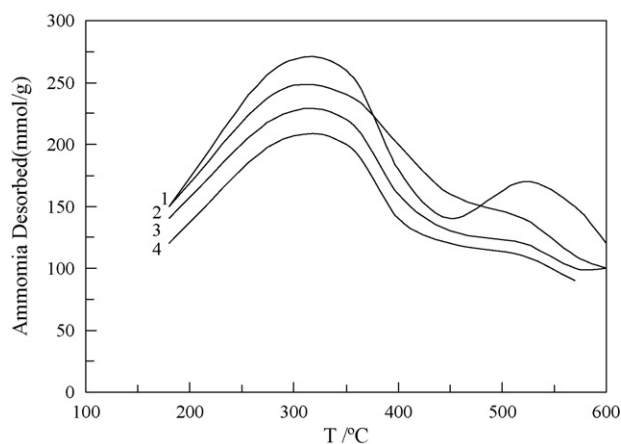


Fig. 3. TPD spectra of the catalyst from different reaction time (feed: C1 + C3 + argon; WHSV = 1.6 g h⁻¹/(g cat)⁻¹, T = 873 K; at atmospheric pressure). (1) Fresh catalyst, (2) after 36 h, (3) after 48 h and (4) after 120 h.

decrease of the number of the weak acidic sites is not conspicuous. It owes to a majority of strong acidic sites have been covered with surface cokes because the stronger the strength of the acidity is, the more easy the coke is produced. But the weak acidic sites are not easy to produce coke. After adding Co and Zn the strength of the strong acid decreased, so the carbonaceous is uneasy to deposit on the surface of the catalyst. It may be the cause of which the catalyst showed high stabilization (see Table 4).

3.3.4. FT-IR studies

In addition to determining the strength and total number of acid sites using the TPD of NH₃, it was also necessary to determine the types of acid site present (i.e., whether Lewis or Bronsted acid sites) as well as their distribution on the catalyst surface as a function of Co and Zn concentration. According to the literature, the variation in the amounts of these various acid types has a tremendous effect on product distribution. As suggested by Vedrine et al. [24] information regarding the types of acid sites present on the catalysts was obtained from the IR spectra of the samples in the pyridine region (frequency in the range 1425–1575 cm⁻¹) as well as in the hydroxyl stretching range (frequency in the range 3500–4000 cm⁻¹).

The IR spectra of fresh and pyridine adsorbed samples showing these two regions are presented in Figs. 4 and 5, respectively, for catalysts K0, K1, K2, K3, and K4. In Fig. 4, the band at 3668 cm⁻¹ is characteristic of a terminal hydroxyl group (OH) (i.e., adsorbed water), while the bands at 3740 and 3610 cm⁻¹ are assigned to the lattice terminal Si–OH groups and acidic hydroxyl Al–OH groups, respectively. According to Vedrine et al. [24], the terminal Si–OH and the acidic hydroxyl Al–OH groups are particularly important because of their ability to generate Bronsted acid sites which are known to be essential for all cracking reactions. It is therefore desirable to determine how these bands are distributed in the catalyst as a function of Co and Zn concentrations. In Fig. 4, it is seen that these three bands are very prominent for the non-impregnated and impregnated HZSM-5 catalysts. Likewise, there is no evident influence as Co and Zn impregnated.

The IR spectra of the catalysts (HZSM-5 (K0), 0.5% Co + 2% Zn HZSM-5 (K1), 1% Co + 2% Zn HZSM-5 (K2), 1.5% Co + 2% Zn HZSM-5 (K3), and 2% Co + 2% Zn HZSM-5 (K4)) in the region of pyridine absorbing (1410–1575 cm⁻¹) are presented, respectively in Fig. 5. It can be seen from the figure that HZSM-5 catalysts exhibited bands at frequencies of 1550 and 1460 cm⁻¹.

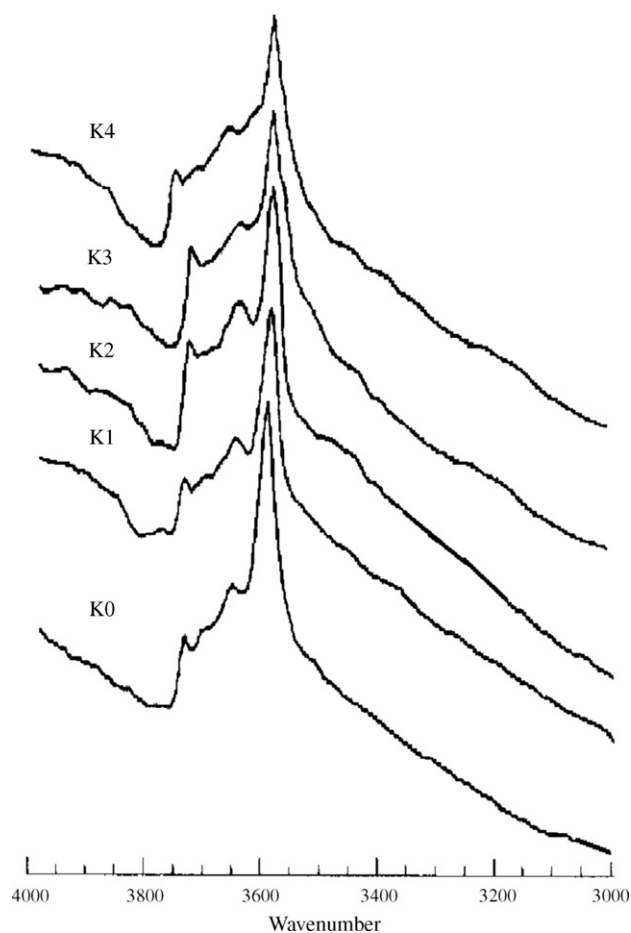


Fig. 4. IR spectra of HZSM-5 and Co, Zn-impregnated HZSM-5 catalysts in the hydroxyl region (K0, HZSM-5; K1, 0.5% Co+2% Zn HZSM-5; K2, 1% Co+2% Zn HZSM-5; K3, 1.5% Co+2% Zn HZSM-5; K4, 2% Co+2% Zn HZSM-5).

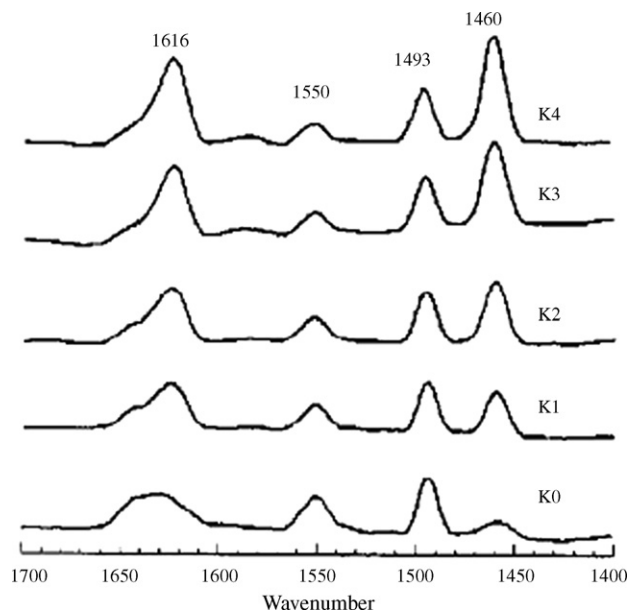


Fig. 5. IR spectra of HZSM-5 and Co and Zn-impregnated HZSM-5 catalysts in the pyridine region (K0, HZSM-5; K1, 0.5% Co+2% Zn HZSM-5; K2, 1% Co+2% Zn HZSM-5; K3, 1.5% Co+2% Zn HZSM-5; K4, 2%Co+2% Zn HZSM-5).

According to Rahman et al. [25], Borade and Clearfield [26], the band around the frequency of 1545 cm^{-1} represents the Bronsted acid sites, whereas the one at 1493 and 1635 cm^{-1} represent the presence of a mixture of both Bronsted and Lewis acid sites. The band around the frequency of 1455 cm^{-1} is characteristic of the Lewis acid sites. Impregnated HZSM-5 catalysts exhibited band at frequencies of 1616 cm^{-1} . The intensity of the band at 1550 cm^{-1} (Bronsted acid sites) decrease as the concentration of Co and Zn in the catalyst increased. Otherwise, when the concentration of Co and Zn in the catalyst increases the intensity of the band at 1460 and 1616 cm^{-1} increased. It was the formation of Lewis acid sites which were stronger than those presented in non-impregnated HZSM-5 catalyst.

4. Conclusion

The activation of methane in low temperature was due to the existence of propane. The incorporation of cobalt and zinc into HZSM-5 catalyst decreased both the strength of strong acid and the micropore area of the catalyst which results in the decrease of the coke on the catalyst. After adding Co and Zn an increase of the strength of Lewis acid sites in the catalyst. While the superfluous strong Bronsted acid sites decreased, which are showed to be related with the aromatic carbonaceous deposits on the catalyst. Therefore, a much higher benzene yield and a longer durability of the catalysts are obtained when compared with the conventional HZSM-5 catalysts.

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