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Methane Aromatization over Cobalt and Gallium -Impregnated HZSM-5 Catalysts

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Abstract The influence of the catalyst acidity, the ratio of cobalt in the catalyst on the conversion of methane and the stability were evaluated using a fixed-bed microreactor at atmospheric pressure and at a flow rate of 1500 mL/g h (GHSV 600 h^{-1}). The reaction was conducted at 973 K and 1023 K over gallium and cobalt -impregnated HZSM-5 catalysts. The 2%Ga–2% Co/HZSM-5 catalyst exhibited remarkable stability with no significant deactivation for 100 h on stream, and yielded a maximum conversion of methane to benzene equal to 9.9%. These catalysts were thoroughly characterized using XRD, N_2 adsorption measurements, TPD of NH_3 and FT-IR. The acidity changes 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 aromatization reaction, while the superfluous strong Bronsted acid sites, which can be decreased by adding Ga and Co, are shown to be related with the aromatic carbonaceous deposits on the catalysts. After adding Ga and Co the strength of Lewis acid sites of the catalyst increased. But the total amount of the acidity on the catalyst decreased.

Keywords Methane · Cobalt · Gallium · HZSM-5 · Aromatization

1 Introduction

It is more important to develop production of aromatic hydrocarbon by the exploitation of new raw material and technology along with the augment of demanded amount for aromatic hydrocarbon. Zeolite catalyst shows high activity for the aromatization of hydrocarbon. The production of aromatic hydrocarbon from low molecular weight alkyl hydrocarbon has developed rapidly since the Cyclar technics for the aromatization of alkyl hydrocarbon has been used. V. Kanazirev, who was the first researcher discussed the acidic and catalytic characters of Ga modified HZSM-5 zeolites [1]. Hereafter, the character of the catalyst has been researched and improved, so the productivity of aromatic hydrocarbon has increased and scope of raw material has been extended. Natural gas (mostly methane) reserves are abundant throughout the world and are becoming a promising energy source due to the increasing prices of oil. Recently, a major limitation to the utilization of the resource is the high price to transport the natural gas to the desired location. Therefore, one of the current challenges of the petrochemical industry is to develop more economical processes of directly upgrading vast worldwide reserves of natural gas at its source to higher valued liquid fuels and petrochemical intermediates. A worldwide investigation has been conducted to attempt to convert methane directly to chemicals and fuels [2, 3]. Normally there are two approaches for the direct selective conversion of methane, namely oxidative and nonoxidative transformations [4]. For both the processes, the scission of a C–H bond is the first step that a methane transformation reaction

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encounters. Due to its perfect symmetry, methane has the most stable C–H bonds when compared with its homologues such as ethane and propane; thus, the activation of the C–H bond of methane needs a weaker C–H bond of the product with respect to that of the methane results in relatively higher temperature. However, the high temperature used aggravates a selective reaction, i.e. for oxidative reactions, difficulty in efficiently controlling the degree of oxidation, whereas for other reactions, such as non-oxidative aromatization, suppression of the coke formation during the reaction remains a major problem. Methane dehydrogenation and aromatization over Mn/HZSM-5 in the absence of an oxidant was investigated. Mn/HZSM-5 was prepared by impregnation of HZSM-5 with manganese acetate tetrahydrate solution; Mn_3O_4 formed was the precursor of active phase for methane activation. The induction period over Mn/HZSM-5 catalyst before aromatic products appear was long at 700 °C [5]. Methane dehydrogenation and aromatization over Mn/HZSM-5 in the absence of an oxidant was investigated. Mn_3O_4 formed was the precursor of active phase for methane activation [6]. Thermogravimetric (TG) analysis confirms that glow discharge plasma treatment has a remarkable influence on coke formation during the non-oxidative aromatization of methane over a Mo–Fe/HZSM-5 catalyst. The plasma treatment favors formation of active carbon species for methane aromatization. CH_4 conversion is 6.9% and the yield of aromatics is 6.3% over 4 wt% Mn/HZSM-5 catalyst at 1073 K [6]. Parallel improved catalytic behaviors were obtained as for the reaction conducted at 1023 K where the yields of aromatics on dealuminated catalyst after 420 min on stream is about 32% higher than that of parent Mo/HZSM-5(P) (8.7% via 6.6%) [7], and the conversion of methane is 10.9%. Low-temperature oxygen-free methane aromatization was carried out over Ru–Mo/HZSM-5 in a catalytic membrane reactor [8]. The 0.5%Ru-3%Mo/HZSM-5 catalyst showed highly selectivity toward benzene production. The catalyst exhibited remarkable stability with no significant deactivation for 24 h on stream. A maximum conversion of methane to benzene equals to 3.8%, i.e., 73% of the thermodynamic equilibrium conversion (5.2%). Under similar conditions, the maximum conversion to benzene attained in CMR mode was 9%. Co/HZSM-5 catalysts with Co/Al ratios of 0.09–0.22 were prepared by aqueous exchange. Turnover rates for propane conversion to propene and to C_6–C_8 aromatics on these catalysts are about 10-fold higher than on H-ZSM-5 [9]. However, research work on methane aromatization over Co–Ga/HZSM-5 catalysts has never been conducted. In this work, methane aromatization over Co and Ga-modified HZSM-5 in the absence of an oxidant was studied to determine whether an active and stable catalyst can be obtained. To elucidate the nature of the active phase on the Co–Ga/HZSM-5 catalyst the catalyst was characterized by the X-ray diffraction (XRD), N_2 adsorption measurements, temperature programmed desorption (TPD) of NH_3, and FT-IR studies. These results are presented in this paper.

2 Experimental

2.1 Catalyst Preparation

The nonimpregnated HZSM-5 catalyst was prepared according to the procedure reported by Chen et al. [10]. The cobalt and gallium-impregnated HZSM-5 catalysts (Co–Ga/HZSM-5) were obtained by wet impregnation techniques using aqueous solutions of cobalt and gallium nitrates (analytical grade and obtained from Guangzhou Chemical reagent Company, Guangzhou, China) as the precursor. The impregnation step was carried out for 24 h. After this step, the catalysts were dried overnight at 100 °C, then calcined at 520 °C for 6 h in a muffle furnace. Altogether, six Co–Ga/HZSM-5 catalysts which contented $0\sim3\%$ (*w*) cobalt and 2% gallium were prepared. The resulting cobalt and gallium -impregnated HZSM-5 catalysts were designated as K0 (HZSM-5), K1 (0.5% Co-2% Ga/HZSM-5), K2 (1% Co-2%Ga/HZSM-5), K3 (1.5% Co-2% Ga/HZSM-5.), K4 (2% Co-2%Ga/HZSM-5) and K5 (3% Co-2%Ga/HZSM-5), respectively.

2.2 Catalytic Evaluation

Methane aromatization reactions were carried out in a continuous flow reactor system equipped with a quartz tube (10 mm id) 1.5 mL of catalyst pellets of 40–60 mesh was packed in the reactor. The feed gas mixture of 97.5% CH_4 with 2.5% argon was introduced into the reactor at a rate of 1500 mL/g h (GHSV 600 h^{-1}). The reaction was conducted at 973 K and 1023 K under a total pressure of 0.1 MPa. The tail gas out of the reactor was detected on-line by a six-way valve connected with two sets of gas chromatographs. The conversion of methane and the selectivity to products including ethylene, ethane, benzene, toluene, naphthalene, CO, and CO_2 were calculated by a method similar to that reported by Liu et al. [11]. Details can be found elsewhere [12].

2.3 Catalyst Characterization

2.3.1 Physical Property Characterization

(1) N_2 Adsorption Measurements The surface area and pore volume of all of the catalysts were determined using a micromeritics adsorption equipment (Model ASAP 2000) which was equipped with a micropore analysis program using nitrogen (99.995% purity; obtained from Bixiou Gas

LTD, Shanghai, China) as the analysis gas. Prior to analysis, each catalyst was evacuated at 300 °C at a vacuum of 0.54 K Pa for 10 h. HZSM-5 based catalysts contains mostly micropores, thus, the surface areas measured were the micropore surface areas. Therefore, the Dubinin-Astakhov program was used in evaluating the micropore surface areas.

(*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 gallium concentration. The XRD measurements were made with a Phillips diffractometer using Cu Kα (0.15418 nm) radiation in the scanning angle (2θ) range of 5–50° at a scanning speed of 2 deg/min.

2.3.2 *Chemical Property Characterization*

The chemical property characterization techniques were employed principally for the determination of the acidity of the catalysts which are described below.

(*1*) *Temperature Programmed Desorption of Ammonia* In order to determine the acid strengths and distributions on the catalysts NH_3-TPD was performed. Prior to adsorption, 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 973 K for 0.5 h. At 323 K pure NH_3 was adsorbed until saturation, then the catalyst was flushed with N_2 at the same temperature for 1 h. TPD measurements were conducted from 323 K to 1023 K at a heating rate of 15 K/min, using N_2 as the carrier gas. The amount of desorbed ammonia was detected by a thermal conductive detector.

(*2*) *FT-IR Measurements* The FT-IR technique was employed to identify the nature of acid sites present on the catalyst. The IR measurements were made on powdered catalyst samples using a Biorad Infrared Spectrometer (Model FTS 40, Digilab Division). 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 150 °C for 1 h in the same flow system which 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

Table 1 shows the methane conversion, benzene yield, and the distribution of various products of Co–Ga/HZSM-5 after 450 min at 973 K and 0.1 MPa on stream. It is clear that the conversion of CH_4 remained almost stable (about 12%) for HZSM-5(K0), 05%Co-2%Ga/HZSM-5(K1), 1%Co-2%Ga/HZSM-5(K2), 1.5%Co-2%Ga/HZSM-5(K3), 2%Co-2%Ga/HZSM-5(K4) and (3%Co-2%Ga/HZSM-5(K5) catalysts. On the contrary, a dramatic increase of benzene yield is observed with the increase of cobalt. Compared with HZSM-5(K0), the benzene yield from the methane aromatization catalyzed by impregnated catalysts gradually reaches a plateau at 2%Co-2%Ga/ HZSM-5(K4), raised by about 1/2, i.e., from 6.3% to 9.9%. .With methane conversion being similar, an increase in benzene yield means that the product distribution of this reaction changed. It is interesting to note that the enhancement of benzene selectivity after adding cobalt and gallium comes from the strong suppression of coke formation (the selectivity toward naphthalene almost remains constant).

3.2 Catalyst Characterization

(*1*) *Powder XRD Measurements* The XRD patterns of the nonimpregnated HZSM-5 and 2%Co-2%Ga/HZSM-5 (Fig. 1) did not show any appreciable change in the place of the peaks which implied that, up to 2% cobalt concentration, there was no loss of crystallinity in the catalysts due to cobalt and gallium impregnation. Also, no new XRD lines were observed in the cobalt and gallium-impregnated catalysts although the intensity of the diffraction become little weaker. After modification by Co, the corresponding patterns display only the characteristic peaks of HZSM, and no CoO crystallite patterns could be observed even for a Co loading as high as 2%. This indicates that CoO is highly dispersed on the HZSM-5 surface and/or in its channels.

(*2*) *N_2 Adsorption Measurements* The micropore surface areas of the cobalt- gallium-impregnated and non-impregnated HZSM-5 catalysts are given in Table 2 which used as a function of cobalt and gallium concentration. It is seen that the micropore surface area decreased slowly with the increase of cobalt and gallium concentration in the catalyst. As was mentioned earlier, HZSM-5 catalyst contains mostly micropores, also, it is known that the micropore surface area in HZSM-5 is a measure of the surface area in the inner channel. Thus, the decrease in micropore surface area with the increase of cobalt and gallium concentration may be due to pore blockage of the micropores of the impregnated catalysts (most likely in the form of CoO and Ga_2O_3). Pore blockage is also supported by the decrease in pore volume with the increase of cobalt and gallium concentration (see Table 2). 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.

Table 1 Catalytic performance of Co–Ga/HZSM-5 catalysts[a]

Catalyst	Methane conversion (%)	Selectivity/%						Yields of aromatics (%)
		Benzene	Toluene	Naphthalene	$C2^{2-}$	$C2^{0}$	Coke	
K0	11.6	45.1	2.5	6.2	4.2	1.1	39.1	6.3
K1	11.7	50.2	2.1	6.8	4.1	1.4	34.2	7.0
K2	11.9	55.6	2.5	7.0	4.3	1.5	27.9	7.7
K3	12.1	65.7	2.9	7.2	4.7	1.6	16.2	9.3
K4	12.8	66.5	3.0	7.3	4.8	1.6	15.7	9.9
K5	12.8	66.5	3.1	7.2	4.8	1.6	15.7	9.9

[a] Time on stream, 450 min; reaction temperature, 973 K; reaction pressure, 0. 1 MPa; GHSV = 600 h^{-1}

$C2^{2-}$: ethylene; $C2^{0}$: ethane

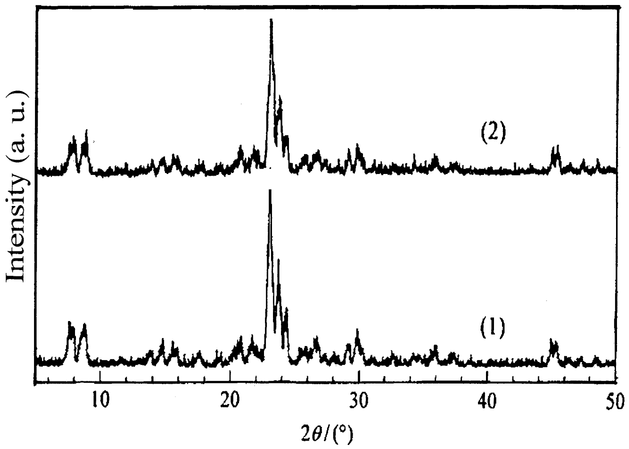

Fig. 1 XRD spectra of ZSM-5 catalyst (1)HZSM-5; (2)2%Co, 2%Ga HZSM-5

Acid site density can be used to represent the concentration of the acid sites present on the surface area 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 depended on the accessible acid sites present on the catalyst. In this work, the acid site density of each catalyst was calculated as adsorbed amount of NH_3 per unit micropore surface of the catalysts as follows:

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

where

μ = adsorbed amount of NH_3 per unit micropore surface area, mmol/ (m^2 of catalyst micropore surface area)
α = adsorbed amount of NH_3 (mmol/g)

The results from the five catalysts are given in Table 2. It is seen from the table that the acid site density decreased as the concentration of cobalt in the catalysts increased.

(*3*) *TPD of NH_3* Figure 2 is the TPD spectra of the catalyst (K0, K1, K2, K3, K4 and K5) The figure showed that the nonimpregnated HZSM-5 catalyst (K0) as well as the impregnated HZSM-5 catalysts containing 2%gallium and different content of cobalt (i.e., K1, K2, K3, K4 and K5) exhibited two well-resolved TPD peaks designated as the low-temperature peak (l) and the high-temperature peak (h). Hidalgo et al. [13] suggests that if the NH_3 TPD peak temperature is greater than 350 °C, then this peak represents strong acid sites (i.e., h peak), whereas peaks with temperatures less than 350 °C represent weak acid sites (i.e., l peaks). Thus, the existence of TPD peaks at 220–250 °C and 520 °C for nonimpregnated and impregnated HZSM-5 catalysts signifies the presence of both the weak and strong acid sites on the catalysts. It is well-known that, for weak acid site, an increase in the peak temperature represents an increase in the strength of the acid site.

Table 2 Characteristics of Co and Ga impregnated and nonimpregnated HZSM-5 catalysts

Catalyst	Catalyst identity	Catalyst micropore surface area (m^2/g)	Adsorbed amount (10^{-3}m mol/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%Ga/HZSM-5	K1	385	6.69	0.149	0.0173
1%Co-2% Ga/HZSM-5	K2	378	6.45	0.145	0.0171
1.5%Co + 2% Ga/HZSM-5	K3	370	6.16	0.138	0.0166
2%Co, + 2% Zn/HZSM-5	K4	365	5.85	0.132	0.0162
3%Co-2% Ga/HZSM-5	K5	360	5.80	0.130	0.0161

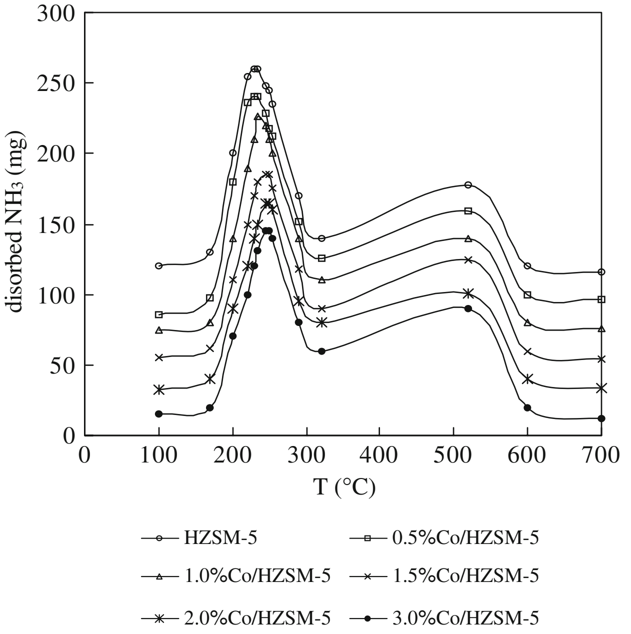

Fig. 2 TPD spectra of the catalysts contained different amount of cobalt (Content of Ga is 2%)

Therefore the progressive shift to higher peak temperatures for l peak implies that there was an increase in the strengths of the L acid sites with the increase of cobalt and gallium concentration in the catalysts (see Fig. 2)

Figure 3 showed TPD graphs of the catalyst from different react time. As seen in Fig. 5, with the react time extended, the acidity of the strong site decreased quickly, but the change of the acidity in low acidic site is not conspicuous. It owes to which a majority of strong acidic sites have been covered with cokes, while the low acidic site is not easy to produce coke. After adding cobalt and gallium, the strength of the low acidic site increased, so the activity of the catalyst increased. The surface of the catalyst is uneasy to produce coke because the strength of the strong acidic site decreased with the addition of Co and Ga. It resulted in an increase of the stability of the catalyst. The experiment result showed that the 2%Ga-2%Co/HZSM-5 catalyst exhibited remarkable stability with no significant deactivation for 100 h on stream (see Fig. 4).

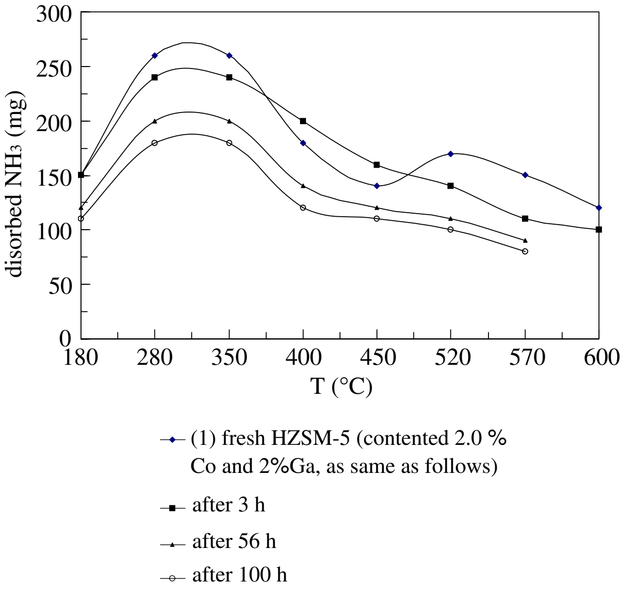

Fig. 3 TPD spectra of the catalyst from different reaction time (973 K, GHSV = 600 h^{-1})

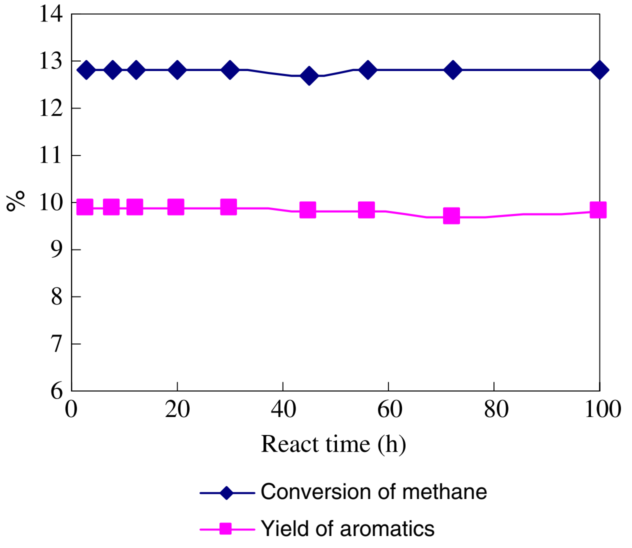

Fig. 4 Activity of the 2%Co- 2%Ga/HZSM-5 catalyst in different react time at 973 K, GHSV 600 h^{-1}

(4) FT-IR Studies In addition to determining the strength and total number of acid sites the TPD of NH_3 has been used, it was also necessary to determine the types of acid sites (i.e., whether Lewis or Bronsted acid sites) as well as their distribution on the surface of the catalyst which was used as a function of cobalt because the variation in the amounts of these various acid types has a tremendous effect on product distribution. As suggested by Vedrine et al. [12] the 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 from fresh and pyridine adsorbed samples showing these two regions are presented in Figs. 5 and 6, respectively, for catalysts K0, K1, K2, K3, and K4. In Fig. 5, the band at 3668 cm^{-1} is the characteristic of a terminal hydroxyl group (OH) (i.e., adsorbed water), while the bands at 3740 cm^{-1} 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. [12], the terminal Si–OH and the acidic hydroxyl Al–OH groups are particularly important because of their ability to generate

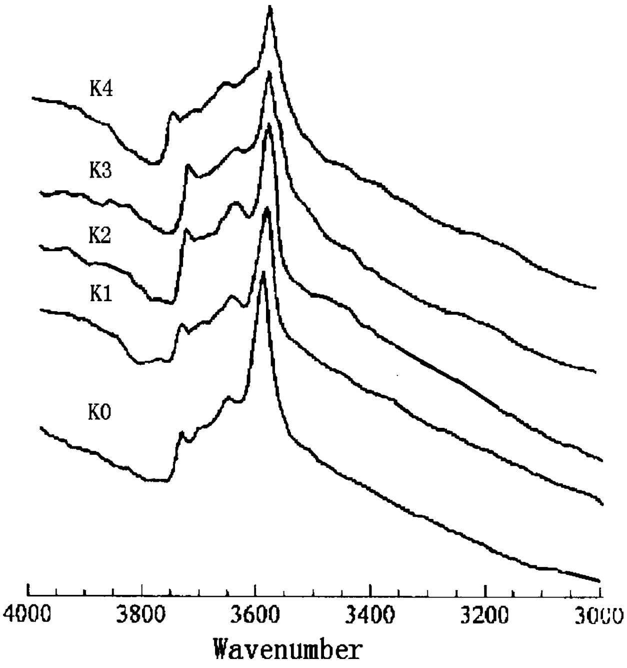

Fig. 5 IR spectra of HZSM-5 and Co–Ga-impregnated HZSM-5 catalysts in the hydroxyl region (K0, HZSM-5; K1, 0.5% Co-2%Ga/HZSM-5; K2, 1% Co-2%Ga/HZSM-5; K3, 1.5%Co-2%Ga /HZSM-5; K4, 2%Co-2%Ga/HZSM-5)

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 cobalt and gallium concentrations. From Fig. 5, it is seen that these three bands are very prominent for the nonimpregnated and impregnated HZSM-5 catalysts. Likewise, there is no evident influence as cobalt and gallium impregnated in the catalyst.

The IR spectra in the pyridine region (1410–1575 cm^{-1}) for HZSM-5 (K0), 0.5% Co-2% Ga/HZSM-5 (K1), 1% Co- 2% Ga/HZSM-5 (K2), 1.5% Co-2% Ga/HZSM-5 (K3), 2%Co-2%Ga/HZSM-5 (K4) are presented in Fig. 6. HZSM-5 catalysts exhibited bands at frequencies of 1545 and 1455 cm^{-1}. According to Rahman et al. [14], Borade and Clearfield [15], the band at 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. On the other hand, the band at 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}. Figure 6 showed that as cobalt and gallium concentration in the catalyst increased the intensity of the band at 1545 cm^{-1} (Bronsted acid sites) and 1635 cm^{-1} decreased. On the other hand, an increase in the cobalt and gallium concentration resulted in an increase of the intensity of the band at 1455 cm^{-1} and 1616 cm^{-1} (which was attributed to the formation of Lewis acid sites), which were stronger than those present in nonimpregnated HZSM-5 catalyst.

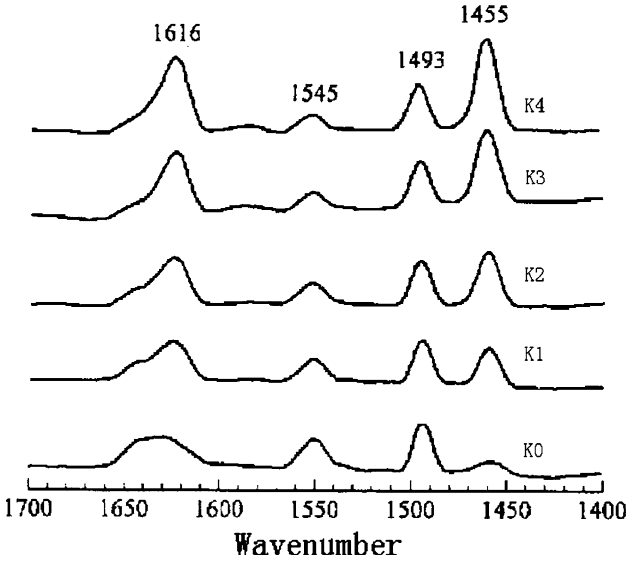

Fig. 6 IR spectra of HZSM-5 and Co–Ga impregnated HZSM-5 catalysts in the pyridine region (K0, HZSM-5; K1, 0.5% Co-2%Ga/HZSM-5; K2, 1% Co- 2%Ga/HZSM-5; K3, 1.5%Co-2% Ga/HZSM-5; K4, 2%Co-2%Ga/HZSM-5)

4 Conclusion

A remarkable improvement on the catalytic performance of 2%Ge/HZSM-5 catalysts for methane aromatization reaction is reached by adding 2% cobalt It leads to the reduction of both the amount and the strength of Bronsted acid sites of the catalyst. While these superfluous Bronsted acid sites are proven to be useless for the intermediate aromatization of methane aromatization, they actually facilitated the holding of coking precursors for a longer time on the surface, which allows for the further polymerization of these precursors, thus largely increasing the aromatic type carbonaceous deposition. Removal of these unnecessary Bronsted acid sites by adding cobalt leads to an efficient and effective suppression of the aromatic coke in the current reaction, and an increase of the strength of Lewis acid sites of 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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