Modification of the ZSM-5 zeolite using Ga and Zn impregnated silica fibre for the conversion of *n*-butane into aromatic hydrocarbons

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The modification of ZSM-5 by metals is generally performed by methods such as ion-exchange, impregnation, chemical vapour deposition and physical mixing. In this work a silica fibre pre-impregnated with Ga and Zn has been used during the synthesis by which Ga-ZSM-5 and Zn-ZSM-5 zeolite catalysts were prepared. The synthesised zeolite catalysts were characterised by an X-ray powder diffractometer, a scanning electron microscope, an X-ray fluorescence spectrometer, a solid state NMR, an energy dispersive X-ray analyser and a sorptomatic 1900. The acidity of the catalysts was determined by temperature programmed desorption of ammonia. The reaction of *n*-butane to aromatic hydrocarbons was carried out over the H-ZSM-5, Ga-ZSM-5 and Zn-ZSM-5 catalysts and it was observed that these catalysts exhibited high catalytic activity in the conversion of *n*-butane and formation of aromatic hydrocarbons. The effect of temperature on the conversion of *n*-butane and formation of aromatic hydrocarbons was studied at 713, 743, 773 and 803 K with a space velocity (WHSV) of 2.5 h^{-1}. The effect of time on stream on the *n*-butane conversion and formation of aromatic hydrocarbons over the synthesised catalysts was investigated at 803 K for 4.5 h.

Keywords: catalysts; zeolite; Ga-ZSM-5; Zn-ZSM-5; conversion; *n*-butane; aromatics

1. Introduction

Zeolite catalysts are extensively being used in petroleum refining, as well as in the petrochemical and chemical industries. In many industrial processes, zeolites are employed as catalysts in their acid form. However, in recent years a number of new processes have been developed which are based on metal loaded zeolite catalysts. In processes like hydrocracking, selectoforming, dewaxing, hydroisomerization of C_6–C_5 alkanes, and hydroisomerisation of C_8 aromatic hydrocarbons, zeolite catalysts loaded with metals are used [1–3]. The relative abundance of propane and butane and large demand for aromatic hydrocarbons make it economically attractive to produce aromatic hydrocarbons by means of the aromatisation of propane and butane. The production of aromatic hydrocarbons such as benzene, toluene and xylene from light alkane over Ga, Zn and Pt modified ZSM-5 zeolite catalysts has been widely investigated [4,5]. The Ga, Zn and Pt modified ZSM-5 type zeolites exhibit very high catalytic activity in the transformation of light hydrocarbons into aromatics because of their unique shape selectivity, channel dimensions, low coke formation and acidic properties. The mode of introduction of metal into the zeolite is of crucial importance to many of these processes because of the dispersion of metals in the zeolite and their interaction within the zeolite framework or on external surfaces. Metal modified zeolite catalysts are extremely useful for reactions such as aromatisation, oxidation, dimerisation, oligomerisation and cyclisation because of different states of the metals, their mobility and their high catalytic activity [6,7]. Zeolite structures also affect the electronic properties of metals incorporated into them and this property of zeolites has been studied by Boudart et al. [8,9]. Metals are generally incorporated into zeolites by methods such as ion-exchange, impregnation and physical mixing. Taking into account the efficiency of metal uptake and its uniform distribution in zeolites these methods have both advantages and drawbacks. In this paper we report a novel method of preparation of Ga-ZSM-5 and Zn-ZSM-5 catalysts for the conversion of *n*-butane into aromatic hydrocarbons. In the method a metal impregnated silica fibre is used during the process of synthesis to modify the ZSM-5 zeolite with Zn and Ga metals.

2. Experimental

2.1. *Catalyst preparation*

2.1.1. *Na-ZSM-5 zeolite synthesis*

The Na-ZSM-5 zeolite was synthesised in the laboratory according to the method described in ref. [9] with slight modifications. Three different solutions, A, B and C, were prepared by mixing the appropriate amounts of reagents required for the zeolite synthesis. Solution A was prepared by dissolving sodium silicate (Merck) in distilled water, solution B was prepared by dissolving aluminium sulphate (Merck) and tetrapropylammonium bromide (Fluka) in dilute sulphuric acid (Merck), and solution C was prepared by dissolving sodium chloride (Merck) in distilled water. Solution A and solution B were added slowly and simultaneously to solution C under conditions of vigorous stirring. Immediately after the formation of a white gel, the pH of the gel solution was measured. After solutions A and B had been added to solution C, the gel solution was further stirred for 2 h at room temperature. The prepared gel was then transferred to a 300 ml autoclave (Parr) equipped with a Teflon cup. The synthesis was performed in an oven at 423 K. After the completion of the reaction, the content of the autoclave was cooled, washed and filtered. The zeolite was then dried at 373 K for 12 h and the Na-ZSM-5 zeolite was obtained after calcination at 813 K for 8 h.

2.1.2. Introduction of gallium and zinc during synthesis of the Na-ZSM-5 zeolite

The Ga-ZSM-5 and Zn-ZSM-5 zeolites were prepared by addition of gallium and zinc during the process of zeolite synthesis using gallium and zinc impregnated silica fibres. The silica fibre was obtained by burning a hybrid textile containing 30% silicic acid and 70% cellulose [10]. The hybrid textile also known as Visil fibre was provided by Kemira Ltd. The silica fibre, after being burnt at 1173 K temperature, is free from cellulose and has the same form and dimensions as the precursor viscose-silicic fibres. The silica fibre was impregnated with an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$, cut into small pieces and suspended in a solution containing sodium silicate and water. Two solutions, A and B, were prepared; solution A consisted of an organic base tetrapropylammonium bromide, aluminium sulphate and dilute sulphuric acid, and solution B consisted of sodium chloride dissolved in distilled water. The solution containing silica fibre and solution A were added to a beaker containing sodium chloride solution. The solutions were added gradually with stirring and a white gel formation took place instantaneously. The pH of the gel solution was regulated very carefully and the stirring was continued for 4 h. The gel was transferred into an autoclave equipped with a teflon cup and the synthesis was carried out in a preheated oven at a temperature of 423 K. When the synthesis was completed, the crystalline products from the autoclave were quenched, washed and filtered. The synthesised zeolite was dried and calcined to remove the organic compound. Zn containing ZSM-5 zeolite catalyst and the Na-ZSM-5 zeolite containing unimpregnated silica fibre were prepared in a similar way as the Ga-ZSM-5 zeolite. The Na-ZSM-5, Ga-ZSM-5 and Zn-ZSM-5 modified zeolites were further ion-exchanged with a NH_4Cl solution at room temperature for 24 h and washed free of Cl^- ions with distilled water. The catalysts were then dried at 353 K for 12 h and calcined at 803 K for 8 h. The zeolite catalysts prepared according to the above methods are denoted Ga-ZSM-5-DS, Zn-ZSM-5-DS and H-ZSM-5-SF.

2.2. Catalyst characterisation

The H-ZSM-5-SF, Zn-ZSM-5-DS and Ga-ZSM-5-DS zeolite catalysts were analysed for phase purity by using an X-ray powder diffractometer (Philips pw 1830) with Cu Kα radiation. The X-ray powder diffraction pattern obtained was found to agree well with those reported in the literature for Na-ZSM-5 (figs. 1 and 2). Consequently, the Ga and Zn introduced into ZSM-5 in this way did not destroy the basic structure of the Na-

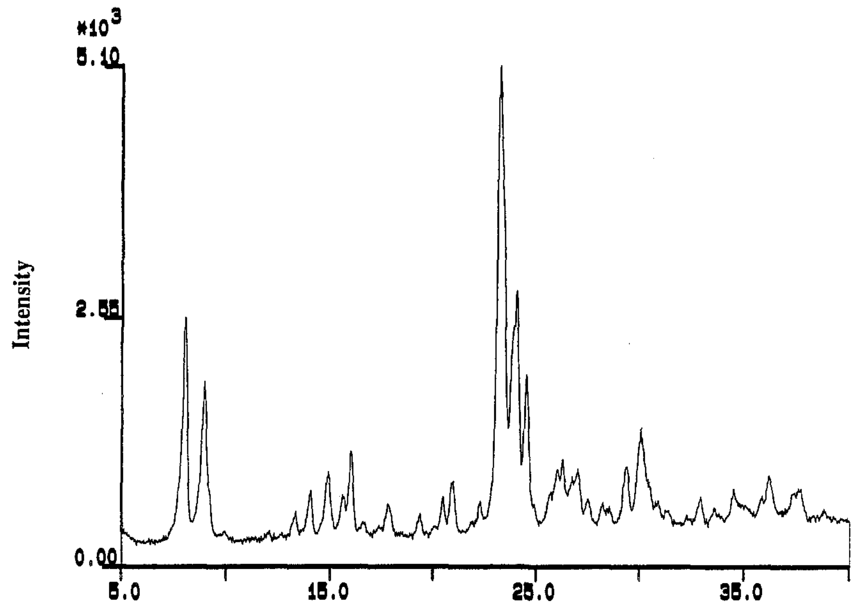

Fig. 1. X-ray powder diffraction pattern of H-ZSM-5-SF zeolite catalyst.

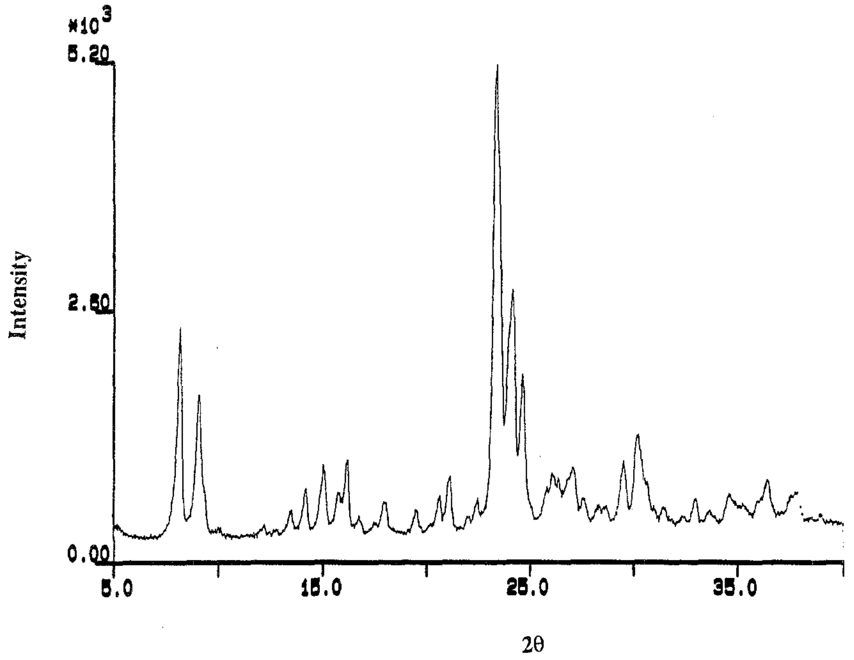

Fig. 2. X-ray powder diffraction pattern of Ga-ZSM-5-DS zeolite catalyst.

ZSM-5 zeolite. The morphology of the zeolite catalysts was investigated by means of scanning electron microscopy (Leica Cambridge Stereoscan 360). The SEM micrograph of the prepared zeolite catalysts shows the typical crystal size and form of the ZSM-5 zeolite. The SEM micrograph of H-ZSM-5-SF is given in fig. 3. The Si/Al ratio of the zeolite was determined by solid-state NMR (Bruker) and was found to be 39. The specific surface area of the H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts was measured by nitrogen adsorption using a Sorptomatic 1900 (Carlo Erba Instruments) and found to be 351, 372 and 384 m^2/g, respectively. The adsorption isotherm and specific surface area obtained are typical of those found for solids with microporous structures. The Ga and Zn content of the modified ZSM-5 was determined by an X-ray fluorescence analyser X-MET 880 (Outokumpu) and was found to be 1.6 and 1.5 wt%, respectively.

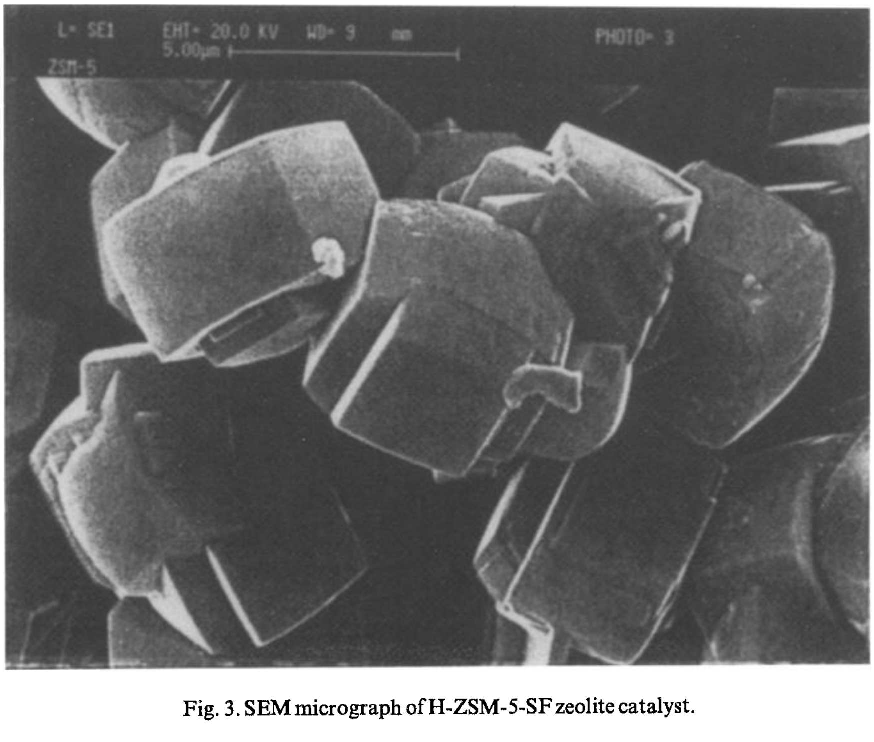

Fig. 3. SEM micrograph of H-ZSM-5-SF zeolite catalyst.

2.3. The temperature programmed desorption of ammonia

The number of acid sites and their strengths are important factors in influencing the catalytic activity of the prepared zeolite catalysts for the reaction of *n*-butane. The investigation of the acidity of H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS was performed by determining the TPD of ammonia using a mass spectrometer (Carlo Erba Instruments) equipped with a QTMD detector. The TPD of ammonia was carried out after activating the sample of 0.1 g in a pyrex reactor for 1 h at 773 K in helium flow. The sample was cooled to 373 K and ammonia adsorption was performed for 45 min. The physically adsorbed ammonia was removed by flushing with helium at 373 K for 1 h. The ammonia was thermally desorbed at a heating rate of 10 K/min in a helium flow (60 ml/min) from 373 to 873 K. The desorbed ammonia was detected by the QTMD detector and the signals of AMU 17 (ammonia), 14 (nitrogen) and 18 (water) were continuously monitored by the mass spectrometer. The comparison of the TPD curves of the H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS catalysts reveals that a high temperature peak corresponds to the desorption of ammonia from structural OH groups. The acid sites represented by a low temperature peak have considerably lower acidic strength and are assumed not to play a major role in the transformation of hydrocarbons. The number of Ga^{3+} and Zn^{2+} cations at exchangeable sites does not influence the number of acid sites significantly. The TPD ammonia curve for the Zn-ZSM-5-DS catalyst is given in fig. 4.

2.4. Catalyst testing

The prepared H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts were tested for the conversion of *n*-butane into aromatic hydrocarbons. The reaction was carried out in a continuous flow fixed-bed reactor operating at atmospheric pressure. The reactor was packed with 0.5 g of catalyst, which was kept in place with glass beads, sand and quartz wool before and after the catalyst bed. The reactor was placed in a vertical oven and the reaction was carried out at atmospheric pressure. The reactant *n*-butane (99.9% purity, AGA) was preheated to 343 K prior to the entry into the reactor. The reactant was fed into the reactor with a space velocity (weight hourly space velocity, WHSV) of 2.5 h^{-1}. The flow rate of N_2, which was used as the carrier gas was 36 ml/min. The reactor output was fed to the GC via tubing and a control valve, both of which were heated to ensure that all of the products would remain in the gas phase. The cracking and aromatic products were analysed on-line by a gas chromatograph (Varian 3700) equipped with a GS-alumina fused-silica PLOT Al_2O_3–KCl capillary column and a FID detector. Hydrogen was analysed by a gas chromatograph (Mikrolab 82-22) equipped with a molecular sieve packed column and a TCD detector. Prior to the catalytic testing, the contribution made by thermal cracking was investigated in an empty reactor at the highest reaction temperature, 803 K; it was observed that the thermal cracking was negligible. The flow diagram of the catalyst testing system is given in (fig. 5).

3. Results and discussion

The different characterisation techniques confirmed that Ga and Zn introduced into ZSM-5 by this method have not affected the structure of the zeolite which was found to be identical to the ZSM-5 structures reported in the literature. It was assumed that most of Ga and Zn introduced in such a way is situated in the channels, channel intersections of ZSM-5, and some of it was also situated in the ion-exchange position and on the external

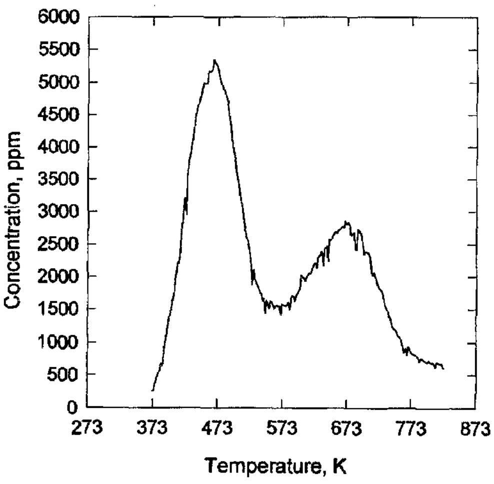

Fig. 4. TPD of ammonia curve of Zn-ZSM-5-DS zeolite catalyst.

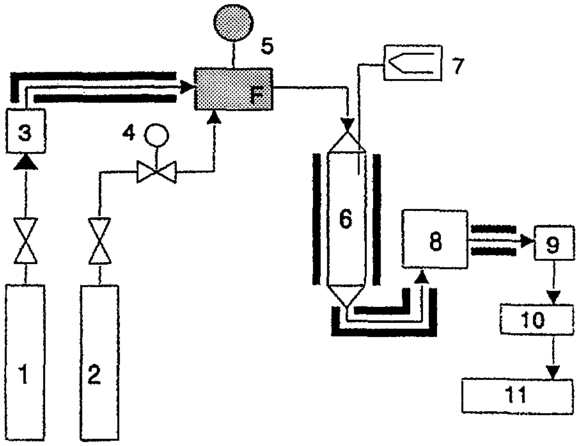

Fig. 5. Catalyst testing system: (1) reactant feed (*n*-butane), (2) carrier gas (nitrogen), (3) water bath, (4) pressure regulator, (5) mass flow controller, (6) reactor and oven, (7) thermocouple, (8) GC (FID), (9) GC (TCD), (10) integrator and (11) computer.

surface of the zeolite. (The exact location of Ga and Zn in the ZSM-5 zeolite structure is still under investigation.) The energy dispersive X-ray analysis revealed that a larger amount of Ga than Zn cations were situated on the external surface of the ZSM-5 zeolite, which could be due to the larger atomic radius and valence state of Ga as compared to Zn. The acidity measurements of H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS catalysts by the TPD of ammonia indicated similarity in their acid strength; however, the introduction of cations in large quantity by this method and subsequent pretreatment by hydrogen may affect the acidity of the Ga and Zn modified ZSM-5 zeolite catalysts.

The effect of temperature on the conversion of *n*-butane over H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS catalysts was investigated at temperatures of 713, 743, 773 and 803 K with a WHSV of 2.5 h^{-1}. The catalysts were pretreated with dry air for 3 h and in a flow of nitrogen for 30 min prior to the catalytic activity measurements. The transformation of *n*-butane over H-ZSM-5-SF, Zn-ZSM-5-DS and Ga-ZSM-5-DS catalysts produced gaseous and aromatic products such as hydrogen, methane, ethane, ethene, propane, propene, butenes, benzene, toluene, xylene and ethylbenzene. The observation that similar products were obtained for Ga and Zn modified ZSM-5 zeolite catalysts further confirmed that the support of both the metals had the ZSM-5 structure. The conversion of *n*-butane over H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS increased with increasing temperature and maximum conversion over all the three catalysts was obtained at 803 K (fig. 6). The formation of aromatic hydrocarbons over these catalysts also increased with increasing temperatures and was maximum at the highest temperature investigated, 803 K (fig. 7). Besides the gaseous and aromatic products small amounts of non-aromatic hydrocarbons of C_5–C_6 were also formed. Toluene constituted almost 50% of the aromatic hydrocarbons formed while benzene, xylene and ethylbenzene formed the rest. In xylene distribution *p*-xylene and *m*-xylene were favoured in comparison with *o*-xylene. The Ga-ZSM-5-DS and Zn-ZSM-5-DS catalysts exhibited higher catalytic activity and transformation into aromatic hydrocarbons than the H-ZSM-SF catalyst. The main function of Ga and Zn was the dehydrogenation of *n*-butane and cycloolefins, whereas Brønsted acid sites promoted the reactions of cracking and oligomerisation. It was also observed that hydrogen pretreatment of the Ga-ZSM-5-DS and Zn-ZSM-5-DS catalysts brought about an increase in the *n*-butane conversion and aromatic hydrocarbon formation as compared to the oxidised form of Ga and Zn modified ZSM-5 catalysts (table 1). The positive behaviour of the reduced catalysts could be explained on the basis of the better dispersion of Ga and Zn in the ZSM-5 zeolite structure prepared by this method.

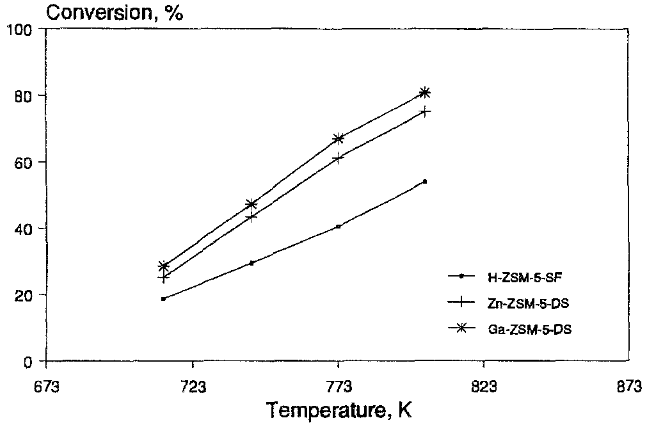

Fig. 6. Effect of temperature on the conversion of *n*-butane over H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts.

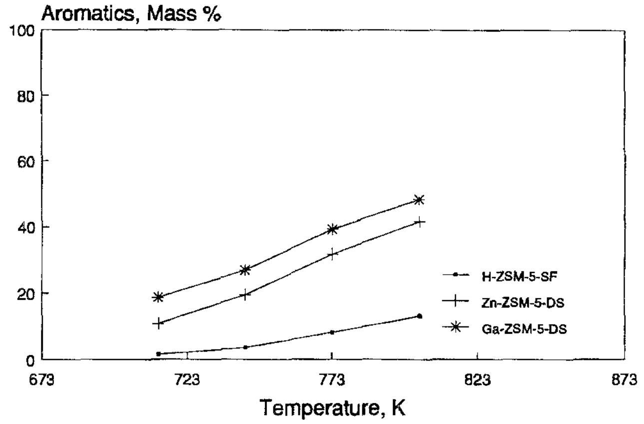

Fig. 7. Effect of temperature on the formation of aromatic hydrocarbons over H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts.

The effect of time on stream was studied at 803 K for 4.5 h and it was found that the catalysts were stable for *n*-butane conversion (fig. 8) and aromatic hydrocarbon formation (fig. 9). The visual observation of the reactor revealed that the catalysts did not turn black and were thus resistant to coke formation. Of the three catalysts, the Ga and Zn modified catalysts were more stable than the H-ZSM-5-SF catalyst, indicating that Brønsted acid sites of the proton form catalyst deactivated due to coke formation faster than the modified ZSM-5 zeolite catalysts.

Table 1
Conversion of *n*-butane and formation of aromatic hydrocarbons over oxidised and reduced Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts at 773 K

Catalysts	Aromatics (mass%)	Conversion (%)
Ga-ZSM-5-DS (oxidised)	39.25	67.54
Ga-ZSM-5-DS (reduced)	44.63	76.34
Zn-ZSM-5-DS (oxidised)	31.25	61.23
Zn-ZSM-5-DS (reduced)	35.78	68.32

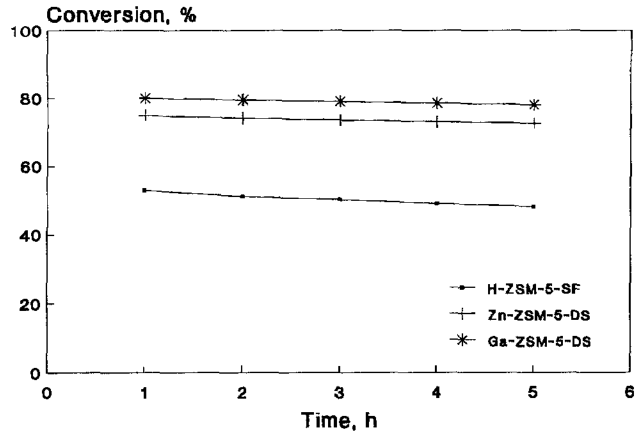

Fig. 8. Effect of time on stream on the conversion of *n*-butane over H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts.

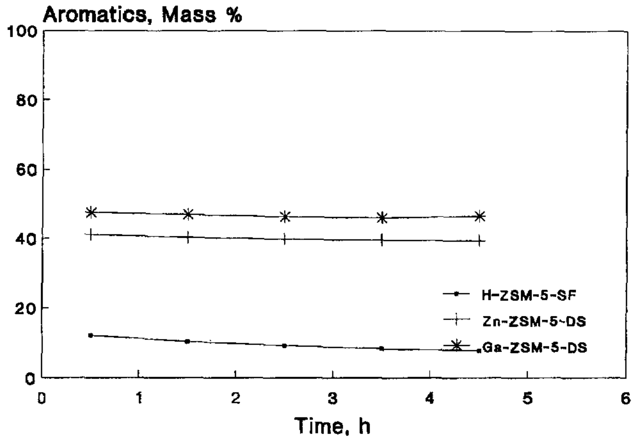

Fig. 9. Effect of time on stream on the formation of aromatic hydrocarbons over H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts.

4. Conclusions

H-ZSM-5-SF, Ga-ZSM-5-DS and Zn-ZSM-5-DS zeolite catalysts have been prepared using Ga and Zn impregnated silica fibres. The hydrothermal synthesis of ZSM-5 containing Ga and Zn impregnated silica fibres by the above-mentioned method offers a new possibility of metal introduction, especially for those cations which are large in size and difficult to introduce by methods such as ion-exchange. The catalysts synthesised consisted of Brønsted and Lewis types of acid sites with uniform dispersion of Ga and Zn cations. The catalysts were found to be very active for *n*-butane conversion and for transformation into aromatic hydrocarbons. The Ga and Zn cations balanced together with Brønsted acid sites were the active sites for this reaction. The deactivation due to coke formation was very low for the Ga and Zn modified zeolite catalysts.

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