

Influence of catalyst binder on the acidity and activity/selectivity of Ga/H-ZSM-5 zeolite in propane aromatization

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Abstract. The acidity and initial and time-on-stream activity in propane aromatization (at 550°C, space velocity of $3100 \text{ cm}^3 \text{ g}^{-1} (\text{zeolite}) \text{ h}^{-1}$) of Ga-impregnated H-ZSM-5 zeolite without or with binders (50 wt%), such as silica, alumina and kaolin, have been investigated. Both the acidity and catalytic activity of the zeolite are influenced by the presence of binder in the catalyst, depending upon the binder. The influence is found to be lowest for alumina and highest for kaolin. Among the binders, alumina is the most preferred binder for the zeolite catalyst.

Keywords. Catalyst binder; alumina; silica; kaolin; Ga/H-ZSM-5 zeolite; propane aromatization; acidity of zeolite.

1. Introduction

In most commercial catalysts, a binder (e.g. synthetic material, such as silica and alumina or natural clay, such as kaolin, kaolinite etc.) is used to provide the catalyst necessary mechanical strength and/or resistance towards attrition loss. For zeolite catalyst, the binder often forms the major part (50–90%) of the catalyst. Binders in general, are not chemically inert to zeolites, particularly at high temperatures, and are also not catalytically inactive. Binder–zeolite interaction can therefore have a strong influence on the catalytic activity, selectivity and deactivation (by coking) of zeolites due to changes in the zeolitic acidity and/or trapping by the binder of coke precursors.

A few studies showing the strong influence of the binder on the acidity and catalytic properties of zeolites have been reported earlier^{1–3}. Activity of the ZSM-5 for acid catalyzed reactions was enhanced by zeolite–alumina interactions during the catalyst pre-treatment¹. An improvement in the stability of dealuminated mordenite zeolite against coking was observed due to trapping of coke precursors by the kaolin binder². Alumina was found to act as a sink for Na cations³. The binder can also influence the catalytic performance of zeolite by trapping metal poisons (e.g. Ni, V etc.) from feed stock of petroleum origin^{4,5}. The influence of the binder on catalytic performance and deactivation due to coking of zeolite catalysts was also observed in other studies^{6–8}. Recently, we have observed the strong influence of binders (viz. alumina, silica and kaolin) on the acidity, catalytic activity/selectivity and deactivation due to coking of H-galloaluminosilicate

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(MFI) zeolite in propane aromatization^{7,8}. These studies show that information on the influence of the binder on the acidity and catalytic performance of zeolite is very important for developing an industrial zeolite catalyst. However, the manufacture of any industrial catalyst is regarded as a closed secret and very little information on zeolite–binder interactions causing beneficial as well as deleterious effects on the surface properties and performance of commercially important zeolite is available in the open literature.

Ga-impregnated H-ZSM-5 (Ga/H-ZSM-5) zeolite shows high activity in the aromatization of lower alkanes^{9–11}, which is a process of great practical importance. This catalyst, however, is deactivated very quickly in the aromatization process due to coking^{12–14}. For developing a commercial Ga/H-ZSM-5 zeolite catalyst for the aromatization of lower alkanes, it is interesting to study the influence of various binders, such as alumina, silica and kaolin, on the acidity and initial activity/selectivity of the zeolite catalyst. It is also interesting to study the influence of binder on zeolite catalyst deactivation due to coking. This investigation was undertaken with these objectives in mind.

2. Experimental

Ga/H-ZSM-5 zeolite (Ga-loading = 1.0 wt%) was prepared by depositing Ga-nitrate (Aldrich) on NH₄-ZSM-5 zeolite (Si/Al = 35, Na/Al = 0.02) using the incipient wetness impregnation technique, drying at 120°C for 10 h and calcining the impregnated zeolite under static air at 600°C for 4 h. NH₄-ZSM-5 zeolite in turn was prepared by exchanging calcined Na-ZSM-5 (Si/Al = 35) with aqueous 1 M ammonium nitrate solution at 80°C for 1 h; the exchange was repeated five times. Na-ZSM-5 zeolite was prepared and characterized by procedures described elsewhere¹⁵.

The MFI structure of the zeolite was confirmed by XRD (using Philips Defractometer 1730 series and CuK_α source of radiation). The ²⁷Al MAS NMR of the zeolite indicated that all the aluminium atoms in the zeolite are tetrahedral¹⁴.

The binder (50 wt%) containing zeolite catalyst was prepared by physically mixing powdered binder [viz. silica gel (Fuji Division), alumina (Catapol B), and kaolin (Aldrich)] and the Ga/NH₄-ZSM-5 zeolite [binder/zeolite (wt/wt) ratio = 1.0]. The zeolite samples were pressed and crushed to particles of 52–72 mesh size and calcined at 600°C in static air for 4 h.

The number of strong acid sites on the Ga/H-ZSM-5 zeolite and the binder containing zeolite catalysts was measured in terms of the pyridine chemisorbed at 400°C. The acidity was determined by using the GC adsorption/desorption technique¹⁶.

Propane aromatization reaction (at 550°C) was carried out at atmospheric pressure in a continuous flow quartz reactor (i.d. 13 mm) provided with a chromel–alumel thermocouple in the centre of the catalyst bed (containing 1–2 g catalyst), using a propane–nitrogen mixture (33 mol% propane) as a feed with a space velocity of 3100 cm³g⁻¹_(zeolite)h⁻¹. Catalytic activity and selectivity were measured as functions of time-on-stream (up to about 6.7 ± 0.2 h). Reaction products were analysed by an online GC with FID, using Poropak-Q (3 mm × 3 m) and Benton-34 (5%) and dinonylphthalate (5%) on Chromosorb-W (3 mm × 5 m) columns.

In order to determine the influence of binder on the product selectivity at the isoconversion of propane, the activity and selectivity data at different space velocities [2000–60,000 cm³g⁻¹_(zeolite)h⁻¹] in the absence of catalyst deactivation (i.e. initial activity/selectivity) at 550°C were obtained by the square pulse technique by passing the

gaseous reactant mixture at different space velocities over fresh catalyst for a short period (2–5 min) under steady state conditions and then replacing the reactant mixture by pure H₂. The reaction products of the square pulse experiment were analysed by online GC.

The space velocity in this work is defined as the volume of total gaseous feed mixture (measured at 0°C and 1 atm) passed over a unit mass of the zeolite (present in the catalyst) per unit time and expressed in units of cubic centimetres per gram of zeolite per hour. Before carrying out the catalytic reaction, the zeolite catalyst (without or with binder) was pretreated *in situ* in a flow of moisture-free N₂ at 600°C for a period of 1 h and then in H₂ at 600°C for 1 h. Conversion and selectivity in the catalytic reactions were obtained from the product distribution, as follows: conversion (%) = 100–wt% of reactant in products; product selectivity (%) = [(wt% of particular product in products)/(100–wt% of reactant in products)] × 100. The aromatization/cracking (A/C) and dehydrogenation/cracking (D/C) activity ratios were obtained from the product selectivities as follows. A/C activity ratio = [(selectivity for aromatics)/(selectivity for C₁ and C₂)] and D/C activity ratio = [(100–selectivity for C₁ and C₂)/(selectivity for C₁ and C₂)].

3. Results and discussion

3.1 Influence of binder on the acidity of Ga/H-ZSM-5 zeolite

Strong zeolitic acid sites of the zeolite catalysts (without or with binder) were measured in terms of the chemisorption of pyridine at 400°C¹⁶. Results showing the strong influence of binder on the strong acid sites of the zeolite catalyst are presented in table 1. The acidity (which is expressed per gram of the Ga/H-ZSM-5 zeolite present in the catalyst containing both the zeolite and binder) is decreased due to the presence of the different binders in the zeolite catalyst. The decrease in the acidity is however lowest for the alumina binder and highest for the silica binder. The decrease in the acidity is expected mostly due to hydrothermal treatment of the zeolite during its calcination at 600°C because of the water vapour produced by the dehydration of the different binders. Earlier studies¹⁷ showed a strong influence of hydrothermal treatment on the acidity of H-ZSM-5 zeolite. The decrease in the acidity for the kaolin binder may also be due to migration of sodium cations from binder to zeolite channels, causing neutralization of some of the zeolitic Bronsted acid sites.

3.2 Influence of binder on initial activity/selectivity of Ga/H-ZSM-5 zeolite

Results showing the influence of binder on the initial activity and also on the distribution of aromatics formed in the propane aromatization are presented in table 1. The initial propane conversion/aromatization activity of the zeolite is decreased because of the presence of different binders and the decrease in the activity is quite consistent with the decrease in the acidity of the zeolite because of the different binders. The distribution of aromatics formed in the propane aromatization is also influenced significantly by the different binders. A comparison of the results for different binders shows that, among the three binders (*viz.* alumina, kaolin and silica), alumina is the best binder for the zeolite catalyst. A similar observation was also made for the binder containing H-gallosilicate (MFI) catalyst^{7,8}.

In order to study the influence of the binders on product selectivity, D/C activity ratio and aromatics/(methane + ethane) mass ratio, results for zeolite catalysts without and with

Table 1. Data on the acidity, initial activity, aromatics distribution and carbon deposition on Ga/H-ZSM-5 zeolite without and with binder (50 wt%) in propane aromatization ($\text{GHSV } 3100 \text{ cm}^3 \text{ g}^{-1} \text{ (zeolite)} \text{ h}^{-1}$).

Catalyst	Initial activity		Aromatics distribution* (wt %)					Carbon deposited (wt %)
	Strong acid sites [mmol g^{-1} (zeolite)]	Propane conversion (%)	Conversion to aromatics (%)	B	T	C ₈	C ₉₊	
Without binder	0.28	30.8	15.4	42.7	40.3	15.2	1.8	6.5
Alumina	0.20	25.0	12.0	37.1	39.9	20.0	3.0	6.7
Kaolin	0.14	9.0	1.5	54.2	36.6	8.9	0.0	6.8
Silica	0.11	8.4	1.6	45.8	40.3	13.9	0.0	6.5

*Not affected by catalyst deactivation due to coking; B = benzene, T = toluene

Table 2. Data on the product selectivity, D/C activity ratio and Ar/(CH₄ + C₂H₆) mass ratio in the aromatization of propane over Ga/H-ZSM-5 without or with binder at isoconversion of propane.

Binder	Propane conversion (%)	Product selectivity (%)						D/C activity ratio	Ar/(CH ₄ +C ₂ H ₆) mass ratio
		Aromatics	Propylene	Ethylene	Ethane	Methane	C _{4+al} *		
Without binder	25.0	46.5	24.5	15.0	3.6	7.8	3.8	2.8	3.7
Alumina	25.5	47.8	20.4	15.2	3.3	7.7	5.6	2.8	4.3
Without binder	8.6	17.6	57.8	15.4	1.2	6.1	1.8	3.2	2.4
Kaolin	8.5	18.5	55.2	15.2	1.5	5.2	4.2	3.6	2.8
Silica	8.6	24.5	39.1	19.9	2.1	8.6	5.9	2.3	2.3

*al - aliphatics

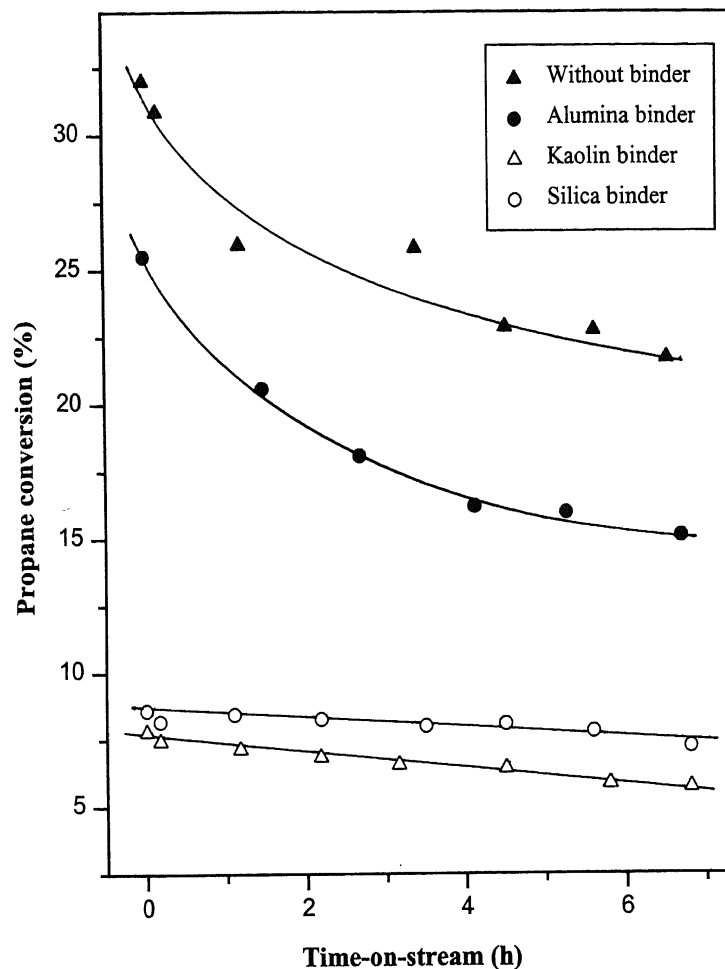


Figure 1. Variation with time-on-stream of propane conversion over Ga/H-ZSM-5 zeolite with different binders (at 550°C and GHSV = 3100 cm³ g⁻¹(zeolite)h⁻¹).

the different binders are compared at isoconversion of propane in table 2. Data for the isoconversion of propane were obtained from the initial activity/selectivity data at different space velocities, given elsewhere¹⁴.

The comparison (table 2) shows that, in general, all the three binders cause an increase in the aromatics selectivity and a decrease in the propylene selectivity. However, for the selectivity of ethylene, ethane, methane and C₄₊ aliphatics, the influence of the binder is not the same but varies from binder to binder (table 2). The D/C activity ratio is not affected by the alumina binder, it is increased to a small extent by the kaolin binder but is decreased appreciably by the silica binder. The aromatics/(methane + ethane) mass ratio is increased by the alumina and kaolin binders but is decreased to a very small extent by the silica binder.

3.3 Influence of binder on the time-on-stream activity/selectivity of Ga/H-ZSM-5 zeolite

In order to study the influence of the binder on the time-on-stream activity and selectivity of zeolite catalyst, propane aromatization over the catalyst without or with

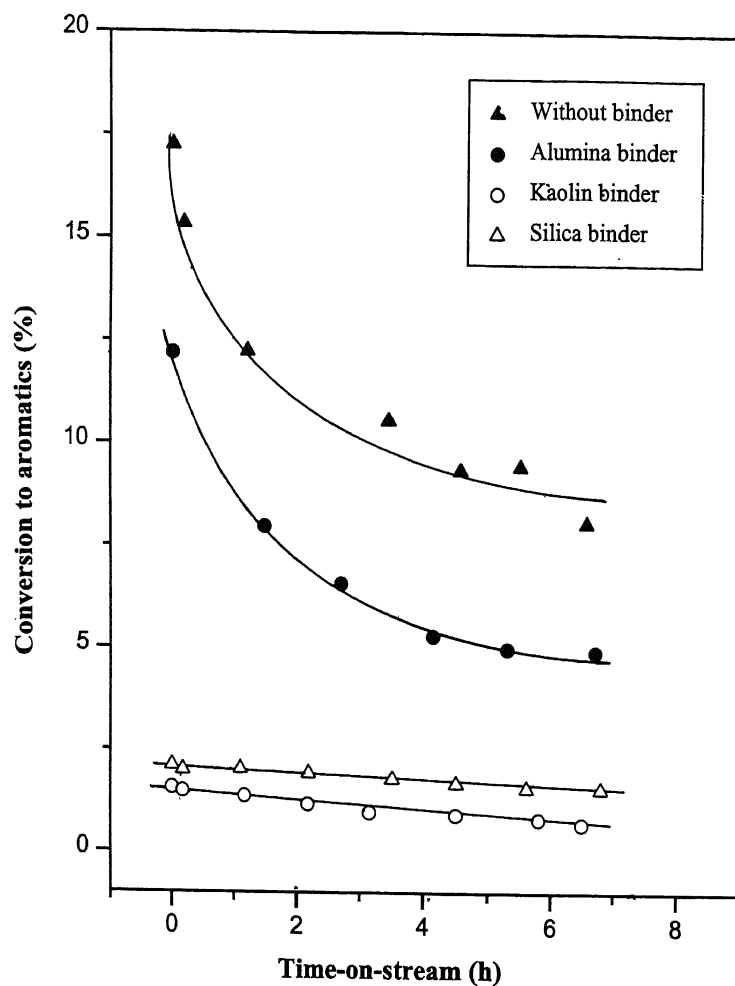


Figure 2. Variation with time-on-stream of propane conversion to aromatics over Ga/H-ZSM-5 zeolite with different binders (at 550°C and GHSV = $3100 \text{ cm}^3 \text{ g}^{-1} (\text{zeolite}) \text{ h}^{-1}$).

binder (GHSV = $3100 \text{ cm}^3 \text{ g}^{-1} (\text{zeolite}) \text{ h}^{-1}$) has been carried out for a period of $6.7 \pm 0.2 \text{ h}$. The results in figures 1 and 2 show that the deactivation in the initial short period is highest for the zeolite with alumina binder and lowest for kaolin and silica binder. However, after the initial fast deactivation, the alumina-containing zeolite catalyst undergoes very slow deactivation. The deactivation of Ga/H-ZSM-5 zeolite in propane aromatization is mainly due to coking; the deactivated catalyst can be regenerated by its oxidative treatment.

Results showing the influence of time-on-stream on the product selectivity of the zeolite catalyst without and with the different binders are presented in table 3. The results show the strong influence of the binder on product selectivity at different times-on-stream.

Table 3. Data on the product selectivity at different times-on-stream for the zeolite catalyst without and with different binders.

Time-on-stream (h)	Selectivity (%)															
	Without binder				With alumina				With silica				With kaolin			
	0.0 ^a	1.0	5.5	0.0 ^a	1.0	5.5	0.0 ^a	1.0	5.5	0.0 ^a	1.0	5.5	0.0 ^a	1.0	5.5	
Aromatics	53.9	47.2	41.4	47.8	38.7	31.3	24.5	24.0	20.2	18.5	19.2	14.2	18.5	19.2	14.2	
Propylene	16.8	20.0	24.5	20.6	22.9	29.8	39.1	39.5	46.5	55.2	54.3	60.6	55.2	54.3	60.6	
Methane	9.2	8.1	7.8	7.8	8.2	8.6	8.6	8.5	8.4	8.4	5.3	5.2	5.2	5.3	5.2	
Ethane	4.7	3.9	3.2	3.4	3.4	3.1	2.1	2.0	1.9	1.9	1.5	1.1	1.5	1.5	1.1	
Ethylene	16.3	15.8	16.9	15.4	18.4	19.5	19.9	20.0	18.8	15.2	15.3	14.4	15.2	15.3	14.4	
C ₄₊ -aliphatic	4.6	5.1	6.1	5.6	7.3	7.1	5.9	5.8	5.0	4.5	4.3	1.9	4.5	4.3	1.9	

^aObtained from extrapolation of the data to zero time-on-stream

4. Conclusions

Acidity and initial activity/selectivity and time-on-stream activity/selectivity in propane aromatization of Ga-impregnated H-ZSM-5 zeolite catalyst containing 50 wt% binder, such as alumina, silica and kaolin, vary from binder to binder. Both the acidity and the catalytic activity of the zeolite are decreased due to the presence of binder; the influence of binder on the acidity and activity of the zeolite is in the following order: alumina \ll kaolin $<$ silica. The time-on-stream activity and product selectivity of the zeolite are also strongly influenced by the presence of the binder. Among the binders (viz. alumina, kaolin and silica) used for the Ga/H-ZSM-5 zeolite catalyst, alumina is the best binder as its influence on the zeolitic acidity and catalytic activity/selectivity in the propane aromatization is small.

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