

Gallosilicate Molecular Sieves: The Role of Framework and Nonframework Gallium on Catalytic Cracking Activity

INTRODUCTION

The acid properties of a molecular sieve zeolite can be modified by changing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio or through isomorphous substitution, e.g., replacement of aluminum in the tetrahedral framework sites. Numerous examples of gallosilicates (isomorphous substitution of gallium for aluminum) have been reported (1-5). However, little is known of the ability of these materials to act as acid catalysts in the catalytic cracking of hydrocarbons. In addition, gallium oxide itself may be catalytically active. It is therefore important to understand the role a secondary phase or impurity of gallium oxide would have on the apparent acid activity of a gallosilicate containing such an impurity or secondary phase. This paper presents the results of *n*-butane cracking studies with the gallosilicate analog of zeolite ZSM-5, i.e., [Ga]ZSM-5, and a hydrothermally modified gallosilicate ZSM-5 material containing nonframework gallium.

METHODS

Preparation of gallosilicate [Ga]ZSM-5 ($\text{SiO}_2/\text{Ga}_2\text{O}_3 = 80$). 5.94 g $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich Chemicals, 99.999% purity) in 200 g H_2O with 16 g H_2SO_4 (96%) was added to 200 g N-brand silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 3.22$, 41.0° Baume, PQ Corp.) in 200 g water. To the resulting gel was added 24 g tetrapropylammonium bromide (Aldrich Chemicals) in 100 g water. After agitating for several minutes, the mixture was placed in an autoclave (Autoclave Engineers, 1-liter capacity, stirred) under autogeneous pres-

sure for 3 to 4 days at 170°C. Gallosilicate samples of other $\text{SiO}_2/\text{Ga}_2\text{O}_3$ molar ratios were prepared by adjusting the amount of gallium ion and H_2SO_4 in the reaction mixture. Atomic absorption spectroscopy was used to determine elemental composition. The aluminum content of the gallosilicates was analyzed: $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were determined to be greater than 1500. Thermal decomposition of the organic quaternary amine (still associated with the molecular sieve structure) was performed in flowing N_2 to alleviate framework gallium loss, which would otherwise occur through inadvertent steaming from oxidative decomposition of the amine. After 8 h at 550°C, air was introduced to burn off the residual coke. The samples were cooled to room temperature and converted to the NH_4^+ form by exchange with 1 M NH_4NO_3 ; they were then recalcined in dry flowing air at 550°C for 4 h to generate the acid form (H-[Ga]ZSM-5). The K^+ forms were prepared by titrating the acid form with KOH at room temperature to pH 8.

Preparation of zeolite ZSM-5. The method of Rollman and Valyocsik was used to synthesize the aluminosilicate zeolite ZSM-5 (6). Calcination, ammonium exchange, and hydrothermal treatment were identical to those used for the gallosilicate materials.

n-Butane cracking. The acid forms of the gallosilicate, H-[Ga]ZSM-5, and aluminosilicate, H-ZSM-5, were examined for catalytic cracking activity with 2% *n*-butane in helium in a microreactor at 500°C: this hydrocarbon is difficult to crack and has been shown to be suitable for measuring

activity of ZSM-5 materials (7). Reactions were conducted at 500°C in order to obtain suitable conversion levels (15% nominal) while utilizing reasonable amounts of catalyst (catalyst weights were varied). No external mass transfer or intraparticle effects were observed; the pseudo-first-order rate constant K_a was also not affected by varying *n*-butane feed concentration. Products were analyzed on a 1.8-m Chromosorb 102 column (Perkin-Elmer) isothermally at 80°C for good GC reproducibility.

Steaming. The H-[Ga]ZSM-5 was steamed from 1 to 4 h at 550°C in 100% steam to remove the trivalent component from the framework sites (8-11). Partial framework gallium removal was confirmed by observing the decrease in ion-exchange capacity.

Confirming framework incorporation. In the gallosilicate analog of the zeolite ZSM-5 ([Ga]ZSM-5), the gallium is found to occupy both framework and nonframework sites, depending on the method of treatment of the material. Gallium behaves very similarly to aluminum during the crystal growth phase of synthesis: the gallium in the reaction mixture incorporates into the ZSM-5 framework structure. The unit cell volume of the as-synthesized gallosilicate expands linearly with decreasing SiO₂/Ga₂O₃ ratio, indicating successful incorporation of the larger gallium ion during synthesis (unit cell volumes: 5432 Å³ for [Ga]ZSM-5 (SiO₂/Ga₂O₃ = 69); 5386 Å³ for silicalite). X-ray line intensity and the *n*-hexane adsorption capacity of these materials both show that the materials are highly crystalline. The presence of ion-exchange sites, which would arise from framework gallium, is demonstrated by K⁺ exchange experiments: molar ratios of K/Ga near unity are observed confirming complete framework gallium incorporation. After 4 h of steaming, ion-exchange capacity decreases 50%, indicating loss of framework gallium. A sample of zeolite H-ZSM-5 similarly treated for comparison shows comparable reductions in exchange

capacity. The steamed materials maintain high crystallinity as determined by XRD and *n*-hexane adsorption capacity.

Catalytic activity of framework and non-framework gallium. Two types of studies were conducted (12): (1) the activity vs silica-to-metal oxide molar ratio (SiO₂/M₂O₃, M = Al or Ga) was determined for the parent (unsteamed) materials, and (2) the activity vs steaming time was measured for both H-[Ga]ZSM-5 and H-ZSM-5. Table 1 shows that catalytic activity (K_a) increases with increasing concentrations of gallium or aluminum in the ZSM-5 framework. The results presented in this table also reveal that the gallosilicate, H-[Ga]ZSM-5, is a weaker acid catalyst than zeolite H-ZSM-5. The activity of H-[Ga]ZSM-5 is considerably less than that of H-ZSM-5 for a given SiO₂/M₂O₃ molar ratio. This result is augmented by observing the thermal desorption of ammonia from the ammonium-exchanged materials (Fig. 1): a temperature of up to 500°C is required to drive off all the ammonia from zeolite ZSM-5, whereas the gallosilicate is free of ammonia by ca. 400°C.

A second study (results are in Table 1) shows that hydrothermal treatment of H-[Ga]ZSM-5 considerably enhances catalytic activity, while zeolite H-ZSM-5 activity decreases upon steaming under the conditions chosen. The important feature observed in this study is the role of the nonframework gallium on the apparent acid activity of the material. With mild steaming, a 10-fold increase in cracking activity is observed accompanied by marked changes in product distribution (discussed below). This increase is attributed to the presence of a very active amorphous gallium oxide phase generated upon steam treatment: dispersed Ga₂O₃ on silicalite similarly exhibits considerable cracking activity (Table 1). The enhanced activity observed decays as the gallosilicate material is steamed for longer periods, suggesting that dispersion of the gallium oxide phase may be reduced by agglomeration. This basic feature of

TABLE I

n-Butane Cracking Activity^a of Gallosilicate H-[Ga]ZSM-5 and Zeolite H-ZSM-5

	Composition SiO ₂ /M ₂ O ₃ molar ratio	Cracking activity [$K_a = \text{cm}^3/\text{g}\cdot\text{min}$] ^a		
		Unsteamed	Steamed (h)	
			1	2
H-[Ga]ZSM-5	69	7.1		
	88	5.8	31.3	18.6
	180	2.7		
Ga ₂ O ₃ /silicalite	90	25.2		
Pure Ga ₂ O ₃	—	1.7 ^b		
H-ZSM-5	62	69.3		
	70	45.5	15.8	13.2
	82	19.5		
	110	14.2		
	280 ^c	2.6		

^a See Rastelli *et al.* (7).

^b Deactivates rapidly.

^c Silicalite (Union Carbide Experimental product S-115).

activity enhancement and altered product selectivity in steamed gallosilicates and activity decline in steamed aluminosilicates was found to hold for other ratios of SiO₂/M₂O₃ studied.

The gallium oxide phase also significantly affects the cracked product distribution for *n*-butane cracking (Fig. 2). The H-[Ga]-ZSM-5, where all of the gallium occupies framework sites, exhibits a product distri-

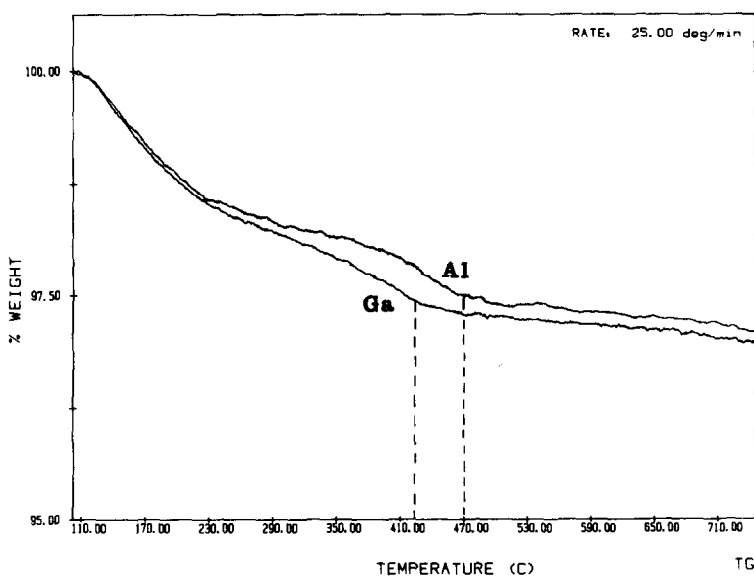


FIG. 1. Thermogravimetric analysis of ammonium-exchanged zeolite NH₄-ZSM-5, "Al" (SiO₂/Al₂O₃ = 82) and gallosilicate NH₄-[Ga]ZSM-5, "Ga" (SiO₂/Ga₂O₃ = 69) showing approximate maximum temperature for complete desorption of ammonia.

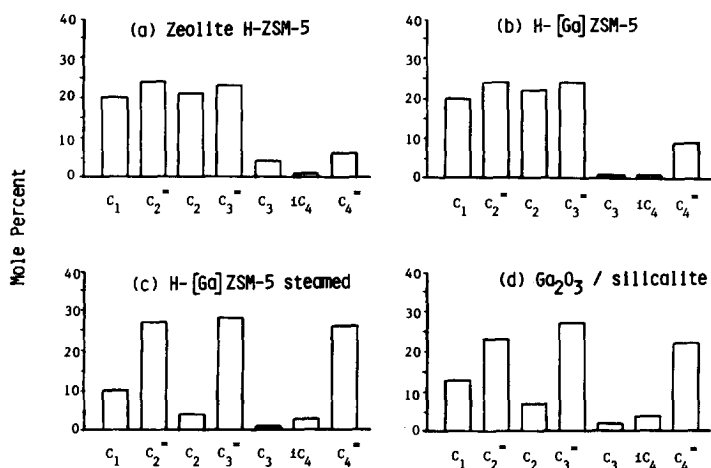


FIG. 2. Cracked products from *n*-butane at 15% conversion (12): (a) zeolite H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 70$), (b) gallosilicate H-[Ga]ZSM-5 ($\text{SiO}_2/\text{Ga}_2\text{O}_3 = 88$), (c) H-[Ga]ZSM-5 (88) steamed 1 h, (d) Ga_2O_3 deposited on silicalite (effective $\text{SiO}_2/\text{Ga}_2\text{O}_3 = 90$). Products: methane, ethylene, ethane, propylene, propane, isobutane, mixed butenes. Zeolite H-ZSM-5 (70) steamed 1 h (not shown) differs only slightly from (a) due to an altered effective $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (verified by comparing product distribution vs $\text{SiO}_2/\text{M}_2\text{O}_3$ ratio) (12). Average carbon balance: 98%, except (d): 90% (due to coking). C_3^+ products are negligible.

bution (Fig. 2b) comparable to that of the aluminosilicate zeolite (Fig. 2a). Upon steaming, however, a drastic change in the gallosilicate product distribution occurs (Fig. 2c): the cracked product distribution is altered with olefins predominating. An amorphous gallium oxide/silicalite catalyst prepared for comparison (incipient wetness impregnation of $\text{Ga}(\text{NO}_3)_3$ on silicalite followed by air calcination) yields a product distribution (Fig. 2d) comparable to the steamed gallosilicate (Fig. 2c). The catalytic activity of the amorphous Ga_2O_3 /silicalite catalyst ($\text{SiO}_2/\text{Ga}_2\text{O}_3 = 90$) is also comparable to the activity of the steamed gallosilicate (H-[Ga]ZSM-5 (88), steamed 1 h). This further verifies the role of the amorphous gallium-containing phase on the conversion of *n*-butane under these reaction conditions.

CONCLUSIONS

The carefully synthesized and calcined H-[Ga]ZSM-5 cracks *n*-butane to yield products similar to those observed with zeolite H-ZSM-5, indicating that gallium-occupy-

ing framework sites exhibit acid behavior similar to the aluminosilicate. Lower K_a values indicate a weaker acid strength also confirmed by ammonia desorption studies. Once the gallosilicate material has been subjected to steaming conditions (even if only through careless calcination procedures), a secondary amorphous gallium oxide phase is produced which significantly alters the overall catalytic activity of the material and the product distribution. The results of this study verify the need to identify both framework and non-framework species present in these materials before interpreting catalytic behavior of nonaluminosilicate molecular sieves.

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