

Enhancement in Propane Aromatization with Ga₂O₃/HZSM-5 Catalysts

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A strong enhancement in the propane aromatization activity of Ga/HZSM-5 catalysts may be achieved by mechanically mixing Ga₂O₃ with HZSM-5 and activating the catalyst by either hydrogen pretreatment or long term exposure to a propane reactant.

A new catalytic process called Cyclar, based on Ga-doped zeolite catalysts for converting light paraffins into aromatic hydrocarbons, has been announced recently.¹ Ion-exchanged² or impregnated gallium³ as well as gallosilicates⁴ and even mechanical mixtures of Ga₂O₃ and ZSM-5 zeolites^{5,6} have been shown to exhibit catalytic activity for the aromatization of light paraffins. Nevertheless, the state of the active Ga component, its interaction with the zeolite, and the mechanism of the catalytic action of these new catalysts remain unclear. In the present work we have found that mechanically

mixing Ga₂O₃ with HZSM-5 zeolite followed by pretreatment causes an increase in the conversion of propane into aromatic hydrocarbons at much lower Ga₂O₃ contents than those reported recently.⁶ The second important observation in this investigation is the strong increase in the aromatization activity and selectivity either with the time on stream (propane/helium feed), or resulting from a hydrogen pretreatment.

Catalysts of 2, 5, and 10 wt% Ga were prepared by mixing powdered β-Ga₂O₃ (4N5-grade, lot no. 3038, Ingal Inter-

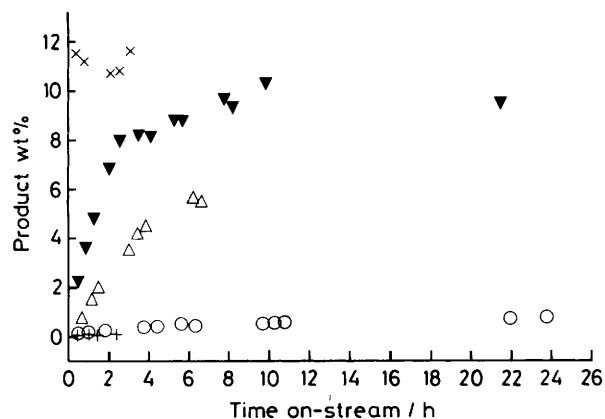


Figure 1. Yield of aromatics from propane reactant over various catalysts at 803 K, 1.2 WHSV; (▼) 10% Ga; (△) 5% Ga; (○) 2% Ga; (+) HZSM-5; (×) 2% Ga, H₂ pretreated.

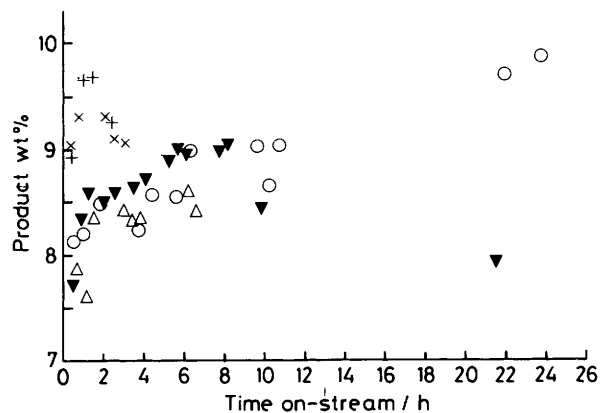


Figure 2. Yield of C₁ + C₂ hydrocarbons from propane reactant over various catalysts at 803 K, 1.2 WHSV; (▼) 10% Ga; (△) 5% Ga; (○) 2% Ga; (+) HZSM-5; (×) 2% Ga, H₂ pretreated.

national Co.) and HZSM-5 zeolite (Union Carbide Co., Linde Div., Type ELZ-105-6) for 3 h in a stainless steel ball-mill, then forming pellets, crushing, and sieving to 40–60 mesh. Prepared catalysts were stored in a desiccator over an NH₄Cl solution (1 M) prior to use. The catalysts were characterized by X-ray powder diffraction (Scintag PAD V, Cu-K_α radiation) and temperature-programmed reduction in a microbalance (Perkin-Elmer TGA-7). Catalytic testing was done in a tubular reactor with 0.8 g catalyst and 6.1×10^{-6} mol s⁻¹ (1.2 WHSV) of propane (Matheson, Instrument grade) at a partial pressure of 14 kPa with He as diluent gas at 109 kPa. Chromatographic analysis of the reactor feed and effluent was performed on-line with a 30 m wide bore capillary column (Supelco SPB-1) installed in a Hewlett-Packard 5880 GC equipped with an FID detector.

The effect of the time on-stream with a propane reactant at 803 K (after thermal pretreatment in 60 ml min⁻¹ pure He at 843 K) can be seen in Figures 1 and 2. For the Ga-containing samples that have not been reduced in H₂, there is a sharp increase in the yield of aromatic hydrocarbons (Figure 1) but only a small change in the C₁–C₂ yield (Figure 2, note the y-axis scale of 7–10%). For the parent HZSM-5 sample, a time on-stream effect was not observed, the C₁–C₂ yield was virtually the same as the Ga-containing samples, and production of aromatics was negligible. A 2% Ga sample pre-reduced in H₂ did not exhibit a long activation period, and gave a high yield of aromatics compared to all other samples. Similar runs show that this high selectivity can be maintained for at least 20 h. C₁–C₂ and aromatic hydrocarbons account for more than 90% of the total propane conversion. The remainder consists mainly of C₄ hydrocarbons whose yield also increases with the time on-stream. It appears that neither Ga content nor time on-stream affect the distribution of the aromatic hydrocarbons, which consists of roughly equal parts of benzene and toluene with about 15% xylenes and less than 1% C₉+ aromatics.

Gnep *et al.*⁶ conducted experiments with HZSM-5 using a propane feed at the same temperature (803 K) as in this investigation, and they reported a total conversion of roughly 5% with a 0.1% yield of aromatics. When Ga₂O₃ was mixed with HZSM-5, they registered a strong increase in activity (about 60%) and production of aromatics (about fifteen-fold increase) at a Ga₂O₃ content of 300 wt% (1 part ZSM-5 to 3 parts Ga₂O₃). Our data show an even stronger enhancement with only 2% Ga. At a similar level of propane conversion as the parent HZSM-5 in ref. 6, we observed a ten-fold increase in aromatics production after 27 h on-stream with propane.

There is also evidence of a key role for hydrogen in creating an active state of the catalyst. If the propane flow is stopped and the catalyst treated at 843 K for 2 h in hydrogen, a further increase in the yield of aromatics corresponding to a total increase of 150-fold is realized, and the overall selectivity to aromatics reaches 52%. Also, the period of time required to develop maximum aromatization activity with a propane feed is reduced to zero upon preliminary thermal treatment in a hydrogen/helium mixture at 843 K for 2 h.

The X-ray and microbalance experiments provide further indication of a strong interaction between the acidic HZSM-5 and Ga₂O₃. After pretreatment with H₂ or prolonged exposure to a propane feed at 800–850 K, X-ray diffraction shows a decline in the β-Ga₂O₃ phase relative to the HZSM-5 phase. Microbalance experiments show a loss corresponding to a 0.5–2% weight reduction upon contacting H₂ with samples that contain Ga₂O₃; such a loss is not found for the parent HZSM-5. Well known gallium chemistry suggests that Ga₂O₃ can be converted to gallium suboxide (Ga₂O) *via* hydrogen reduction at about 870 K (for example, see ref. 7), which is near the temperature range of our catalytic investigation; we suggest that catalytic effects are dependent upon this conversion process. Finally, the results presented are unusual since activation rather than deactivation of the catalyst is manifested in this high temperature range. Activation periods of a week or more are not uncommon, therefore investigators should be careful in designing experiments in similar systems.

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