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Methanol to hydrocarbons: enhanced aromatic formation using a composite Ga_2O_3–H-ZSM-5 catalyst

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Addition of β-Ga_2O_3 to H-ZSM-5, as a physical mixture, enhances the formation of aromatic hydrocarbons in the methanol to hydrocarbons reaction.

Methanol conversion to hydrocarbons has been extensively studied using zeolite catalysts[1] since Chang and Silvestri reported this reaction for the zeolite H-ZSM-5.[2] The reaction has been demonstrated over a range of zeolites and microporous materials, *e.g.* zeolite Y,[3] zeolite β,[4] mordenite,[5] Me-APO-5,[6] SAPO-34,[7] as well as non-microporous catalysts e.g. WO_3–γ-Al_2O_3.[8] During these studies most attention has focussed on the reaction mechanism for the formation of the first carbon–carbon bond.[1] In addition, significant attention has been given to the control of the product distribution e.g. the formation of light alkenes or gasoline.[1] In all these previous studies it is surprising that no attention has been given to the use of composite catalysts in which an oxide and zeolite are mixed together. We have now addressed this, and we have found that the addition of β-Ga_2O_3 to H-ZSM-5 can dramatically enhance the yield of aromatic hydrocarbons and in this communication we present our preliminary results.

H-ZSM-5 (Si : Al mol ratio = 80; calcined at 350 °C, 3 h; PQ Corporation) and β-Ga_2O_3 (Aldrich, 99.99%) were obtained commercially and used without further purification or treatment. The methanol to hydrocarbons reaction was carried out using a standard laboratory microreactor. Methanol was fed using a calibrated syringe pump to a vaporisor, mixed with helium diluent (60 ml min^{-1}) and was reacted over the catalyst (0.25 g) in the heated zone of a tubular microreactor (id = 9 mm). Product analysis was carried out using on-line gas chromatography and the lines to and from the reactor were heated to avoid condensation of the products.

H-ZSM-5 and β-Ga_2O_3 were separately reacted with methanol (400 °C, 3.1 g methanol g $catalyst^{-1}$ h^{-1}) and the results are shown in Table 1. It is apparent that β-Ga_2O_3 is not active for this reaction under these conditions (experiment 3), whereas, as expected H-ZSM-5 gives complete conversion of the methanol to hydrocarbons (experiment 1).

Subsequently, the zeolite (0.125 g) and β-Ga_2O_3 (0.125 g) were mixed together as a physical mixture. This was achieved by mixing either the powders or pellets (β-Ga_2O_3, 250–300 μm; H-ZSM-5, 600–1000 μm) together in a glass tube without crushing. This simple physical mixture gave a significantly higher yield of aromatic compounds and lower yields of $C_4 + C_5$ hydrocarbons, when compared with the same mass of H-ZSM-5 alone (experiment 4). A blank experiment in which BN (0.125 g), a material that is totally unreactive for the conversion of methanol under these reaction conditions, was physically mixed in the same way with H-ZSM-5 (0.125 g) gave no enhancement in the yield of aromatic hydrocarbons (experiment 2). In a subsequent set of experiments, separate beds of β-Ga_2O_3 (0.125 g) and H-ZSM-5 (0.125 g) were reacted with methanol. In these experiments the two beds were separated by glass beads so that there was no physical contact between the two materials. The results (experiments 5 and 6, Table 1) show that no enhancement in the yield of aromatic compounds was observed. This indicates that the effect is the result of physical contact between the two materials. To demonstrate this, an experiment was carried out using a physical mixture of H-ZSM-5 pellets (0.125 g, particle diameter = 600–1000 μm, prepared by pelleting and sieving the zeolite) and β-Ga_2O_3 powder (0.125 g, particle diameter < 80 μm). The results for methanol conversion (400 °C, 3.1 g methanol g $catalyst^{-1}$ h^{-1}) are shown in Fig. 1, and a yield of aromatic hydrocarbons > 20 wt% is observed. After 270 min time on line, the flow of methanol was stopped and the catalyst was cooled in He to ambient temperature. Once cooled, the β-Ga_2O_3 (powder)–H-ZSM-5 (pellets) mixture was sieved to separate the β-Ga_2O_3 from the zeolite. Analysis of the two components by powder X-ray diffraction indicated that no changes had occurred during the reaction to the crystallinity of these materials, althouth it is recognised that this technique cannot provide information on the formation of nano-crystalline material. In addition, analysis of the zeolite pellets using atomic absorption spectroscopy confirmed that it did not contain any gallium. Both materials were retested for methanol conversion using the same conditions that had been used for the previous

Table 1 Methanol conversion to hydrocarbons over H-ZSM-5, β-Ga_2O_3 and β-Ga_2O_3–H-ZSM-5[a]

Experiment No.	Catalyst	Methanol conversion (%)	Product selectivity (%)[b] CH_4	C_2	C_3	C_4	C_5	C_{6+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	Aromatic yield (%)
1	H-ZSM-5–glass beads[c]	100	0.2	8.8	38.4	27.6	10.4	5.5	2.4	1.4	3.4	2.7	10.4
2	H-ZSM-5–BN[d]	100	0.2	6.3	36.1	28.2	12.6	7.3	3.1	1.1	2.7	2.5	9.3
3	β-Ga_2O_3–glass beads[e]	0.5	tr[f]	tr	tr	tr	tr	—	—	—	—	—	0
4	β-Ga_2O_3–H-ZSM-5[g]	100	0.3	6.5	35.5	21.9	12.7	4.9	4.6	2.2	5.9	5.5	18.2
5	β-Ga_2O_3–H-ZSM-5[h] Sandwich	100	1.5	5.1	40.8	31.1	8.9	5.1	3.8	0.7	1.6	1.4	7.5
6	H-ZSM-5–β-Ga_2O_3[i] Sandwich	100	0.2	8.0	43.9	24.9	10.2	4.3	4.0	0.8	2.1	1.6	8.5

[a] 400 °C, 3.1 g methanol g $catalyst^{-1}$ h^{-1}. [b] Selectivity for alkenes and alkanes are combined. [c] H-ZSM-5 (0.125 g, pellets) + glass beads (0.125 g) mixed. [d] H-ZSM-5 (0.125 g, pellets) + boron nitride (0.125 g, pellets) mixed. [e] β-Ga_2O_3 (0.125 g, pellets) + glass beads (0.125 g) mixed. [f] tr = trace. [g] H-ZSM-5 (0.125 g, pellets, 600–1000 μm) + β-Ga_2O_3 (0.125 g, pellets, 250–300 μm) mixed. [h] Bed of β-Ga_2O_3 (0.125 g, pellets) upstream of H-ZSM-5 (0.125 g, pellets), the two beds separated by glass beads. [i] Bed of H-ZSM-5 (0.125 g, pellets) upstream of β-Ga_2O_3 (0.125 g, pellets), the two beds separated by glass beads.

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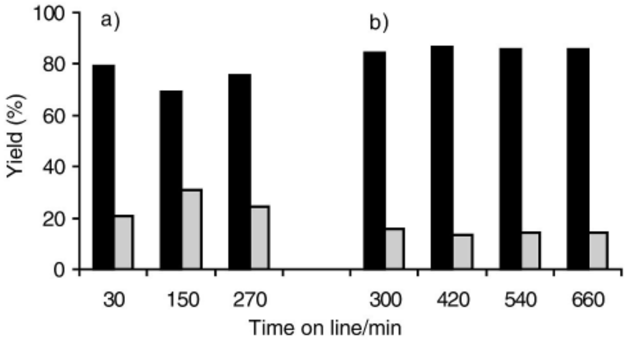

Fig. 1 Methanol conversion to hydrocarbons over (a) β-Ga_2O_3 (powder)–H-ZSM-5 (pellets) physical mixture until 270 min time-on-line and (b) H-ZSM-5 (pellets) following removal of β-Ga_2O_3 (powder) by sieving. Reaction conditions: 400 °C, 3.1 g methanol g catalyst^{-1} h^{-1}. Key: black = aliphatic hydrocarbons, grey = aromatic hydrocarbons. All data recorded at 100% methanol conversion.

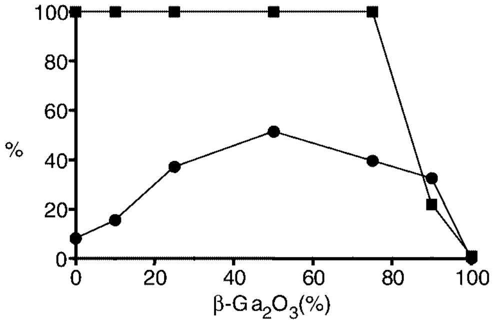

Fig. 2 Methanol conversion to hydrocarbons over β-Ga_2O_3–H-ZSM-5 physical mixtures prepared by grinding as a function of H-ZSM-5 (wt%). Reaction conditions: 400 °C, 0.7 g methanol g catalyst h^{-1}. Key: ■ methanol conversion, ● aromatic yield.

physical mixture experiment. The β-Ga_2O_3 was found to be inactive. The results for the H-ZSM-5 pellets (Fig. 1) show that the yield of aromatic hydrocarbons was now much lower (typically 13–14 wt%), and typical for that expected for H-ZSM-5 alone. This experiment demonstrates that the β-Ga_2O_3–H-ZSM-5 composite catalyst exhibits a new catalytically active site that gives enhanced yields of aromatic hydrocarbons. It is proposed that this new site involves contact synergy between the crystallites of β-Ga_2O_3 and H-ZSM-5. Furthermore, it is apparent that these sites can be removed by separating the physical mixture. To confirm this effect, a further experiment was conducted in which β-Ga_2O_3 (0.125 g) and H-ZSM-5 (0.125 g) were ground together to achieve a uniform intimate mixture. When this intimately mixed material was tested for methanol conversion (400 °C, 0.7 g methanol g catalyst^{-1} h^{-1}) the yield of aromatic hydrocarbons increased to 51.4 wt% (24.2% C_8H_{10}, 20.6% C_9H_{12}). Investigation of other ratios of Ga_2O_3–H-ZSM-5 confirmed that the 1 : 1 physical mixture gives the most marked enhancement in the yield of aromatic hydrocarbon (Fig. 2) which is consistent with the proposal of the active site for enhanced aromatic formation being at the junction of the β-Ga_2O_3 and H-ZSM-5 particles. It is proposed that at this site alkenes are dimerised and aromatised in a similar manner to the aromatisation of propane in the Cyclar process which is observed at temperatures >600 °C using Ga^{3+}-doped H-ZSM-5.[9] Indeed, recently Lunsford and co-workers[10] showed that ethene could be converted to aromatic products using a Ga–H-ZSM-5 catalyst at temperatures in the range 500–550 °C. To demonstrate the generality of the observed effect, we have also investigated β-Ga_2O_3–zeolite β and β-Ga_2O_3–WO_3–γ-Al_2O_3 physical mixture and have observed similar effects of contact synergy. It is therefore considered that composite catalysts, comprising oxides and microporous materials, may generate new types of catalyst for hydrocarbon formation from methanol and these catalysts can be used to control the product distribution.

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