Catalysis Letters 9 (1991) 145–150

THE DEHYDRATION OF METHYLBUTYRALDEHYDE CATALYZED BY FLUORINE MODIFIED SmNa-Y ZEOLITES

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Received 21 November 1990; accepted 22 March 1991

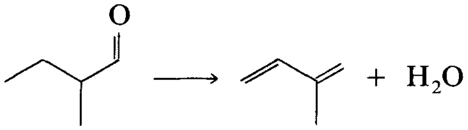
Na-Y zeolites exchanged with samarium (III) were modified with various loadings of fluorine using NH_4F. These zeolites were found to be effective catalysts for the selective dehydration of methylbutyraldehyde to isoprene. These results are compared with other acid zeolite catalysts.

Keywords: Fluorine, SmNa-Y, Dehydration, Methylbutyraldehyde, Isoprene

1. Introduction

Fluorine modification has clearly been shown to affect the properties of oxide catalysts [1]. In particular synthetic faujasite type zeolites exhibit significant changes in activity associated with acid catalyzed reactions after fluorination [2–6]. The fluorine modification of H-Y and Na-Y zeolites results in loss of catalytic activity and crystallinity [6,7]. However, fluorination of H-Y zeolites exchanged with trivalent aluminum enhances the catalytic activity with retention of crystallinity [2–4]. The apparent stabilizing effect of polyvalent cations in the fluorine modified Y type zeolites prompted us to examine the fluorination of rare earth exchanged Y type zeolites. Although samarium is a component of commercial REY catalysts it has received little attention. We are interested in reactivity of zeolites containing those lanthanides that generally comprise only a few percent of the rare earth ores used to prepare commercial catalysts. Therefore, we have studied the reactivity of samarium(III) exchanged Na-Y zeolites modified with NH_4F. We observed both stability to dealumination and no significant loss in crystallinity as well as enhanced catalytic activity [8].

The production of dienes via the dehydration of aldehydes is an attractive alternative to naphtha cracking. Isoprene, a precursor to synthetic rubber, can be prepared by the acid catalyzed dehydration of methylbutyraldehyde. It has



been suggested that the production of isoprene by a zeolite catalyzed process may be of commercial interest [9]. We wish to report here the high activity and selectivity of fluorine modified Sm(III)Na-Y in the catalyzed dehydration of methylbutyraldehyde to isoprene.

2. Experimental

The Na-Y (LZY-52) was obtained from Union Carbide and exchanged with samarium(III) acetate at 80°C, dried at 100°C. The SmNa-Y (5% Sm by wt) was fluorinated with NH_4F using an incipient wetness technique, then dried and eventually calcined at 450°C for 16 hours. Samples designated SmNaF-Y-1, -2,-3, and -4 contain 0.3, 1.4, 1.9, and 5.5% fluorine respectively. Control samples were prepared by treating SmNa-Y with ammonium carbonate. Catalytic reactivity was measured using a pulsed microreactor connected to a gas chromatograph. Analysis of products from 0.5 μL injections of 2-methylbutyraldehyde was made using a 20M carbowax on chromosorb W column (1/8″ S.S., 6 ft) with a nitrogen carrier gas flow rate of 20 mL min^{-1}. The reactor was loaded with 10 mg of zeolite then activated at 450°C in a carrier gas stream for 0.5 hour prior to catalytic studies.

3. Results and discussion

The results for conversion of methylbutyraldehyde at 280°C over SmNa-Y and the fluorine modified zeolites are shown in fig. 1. At this temperature all of these catalysts were 100% selective for isoprene. Clearly, fluorination enhances the activity of SmNa-Y in this reaction except for the highest loading which is less active than SmNa-Y. The maximum in activity is found with sample SmNaF-Y-3 containing 1.9% fluorine. This is in contrast to reactions such as cumene cracking or toluene disproportionation where the maximum in activity was observed at a much lower loading of fluorine [8]. 100% conversion of methylbutyraldehyde can be achieved using SmNaF-Y-3 at 320°C. Also shown are the results for the control samples that were prepared from ammonium carbonate using amounts of NH_4^+ equivalent to those employed in the preparation of the corresponding

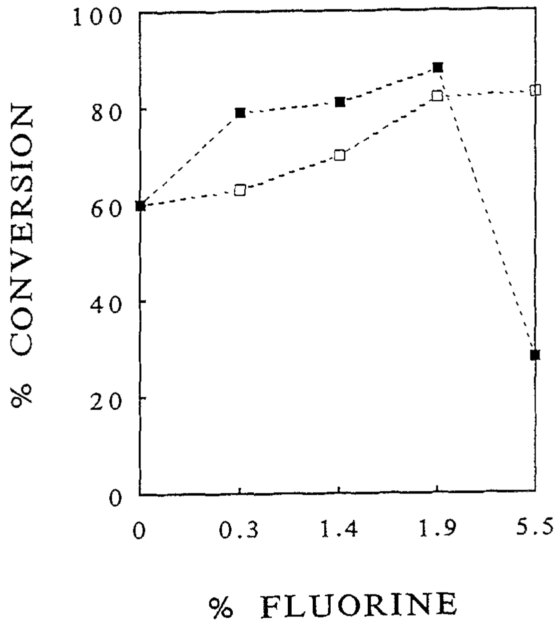


Fig. 1. Conversion of methylbutyraldehyde at 280°C and a flow rate of 20 mL min^{-1} as a function of fluorine loading in the SmNa-Y catalysts (-■-) for the first pulse. The control samples (-□-) are SmNa-Y treated with ammonium carbonate.

fluorinated samples. This indicates that there may be some activity enhancement associated with Bronsted sites generated by the ammonium ions. However, these results, which are reproducible to within less than ±1%, support the fact that fluorination further enhances activity.

There is some evidence of coking as the catalysts are exposed to several pulses. A plot of percent methylbutyraldehyde conversion as a function of pulse number is shown in fig. 2 for SmNa-Y and the fluorine modified samples. The initial activity falls off ~ 10–20% after the first pulse but starts to level off after several pulses. The trend in activity as a function of fluorine loading is maintained. The control samples (not shown) parallel this deactivation with increasing pulse number.

The enhanced activity of SmNa-Y after fluorination may result from a strengthening of Bronsted sites, generated during Sm(III) exchange as well as from NH_4^+, via inductive effects. In order to evaluate the importance of Bronsted acid strength we compared the activity of the fluorine modified SmNa-Y with a series of strong acid zeolites including H-ZSM-5 (Si/Al = 16), H-Mordenite (Si/Al = 5) and H-Y. The results for conversion of methylbutyraldehyde as a function of pulse number is plotted in fig. 3 for these zeolites as well as SmNaY and SmNaF-Y-3. After the first pulse the most active catalyst is H-Y but this activity rapidly decreases to the point where it is the worst catalyst after 10

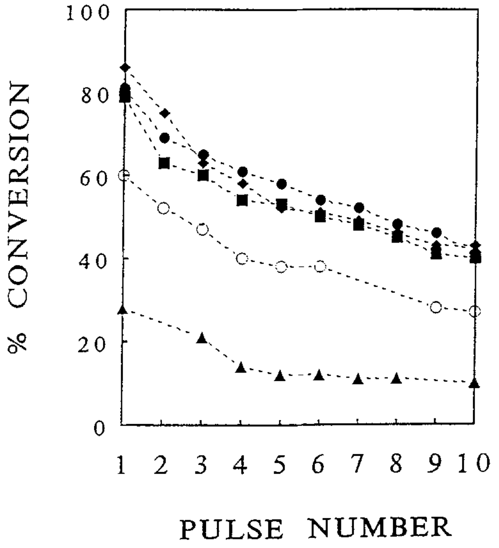


Fig. 2. Conversion of methylbutyraldehyde at 280°C and a flow rate of 20 mL min^{-1} catalyzed over different SmNa-Y catalysts as a function of pulse number. -○- SmNa-Y, -■- SmNaF-Y-1, -●- SmNaF-Y-2, -◆- SmNaF-Y-3, -▲- SmNaF-Y-4.

pulses. This be the result of polymerization of isoprene and coking. The rare earth exchanged zeolite are stabilized towards this form of deactivation as evidenced from control reactions. Oligomer deposits can also be removed and activity

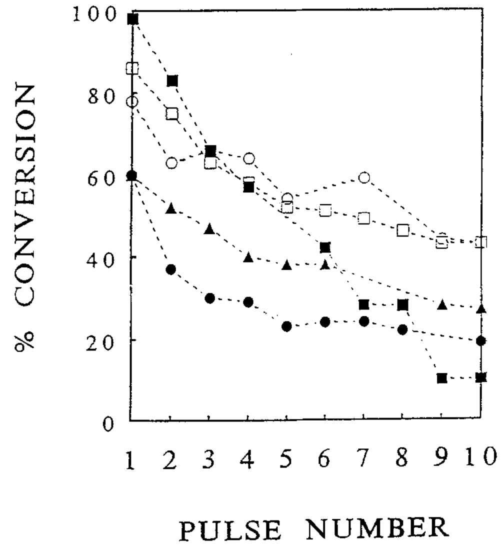


Fig. 3. Conversion of methylbutyraldehyde at 280°C and a flow rate of 20 mL min^{-1} catalyzed by different zeolite catalysts as a function of pulse number. -■- H-Y, -●- H-Mordenite, -○-H-ZSM-5, -▲- SmNa-Y, -□- SmNaF-Y-3.

restored after increasing the temperature. There is a report of high methybutyraldehyde conversions over USY in a flow system at 400°C but the selectivity was only 2.4% for isoprene [10]. Since our experiments were conducted at 280°C in a pulsed reactor it is difficult to compare the activity and selectivity of our H-Y sample. However, we expect the fluorine modified SmNa-Y zeolites would still be superior catalyts in a flow system. H-Mordenite is very selective but surprisingly not very active at this temperature. We suspect the strongest acid sites might be deactivated after the first pulse because of isoprene polymerization. This is in contrast to H-ZSM-5 which is nearly as active as SmNaF-Y-3 but is only ~ 70% selective for isoprene at this temperature. The difference in shape selectivity associated with the medium pore ZSM-5 may result in less polymerization and a small decrease in activity with increasing pulse number. On the other hand the channel geometry of ZSM-5 appears to facilitate the undesirable formation of arenes. From this set of data the SmNaF-Y-3 zeolite appears to be the prefered catalyst.

4. Conclusions

Samarium (III) exchanged Na-Y type zeolites have been shown to be effective catalysts for the selective conversion of methylbutyraldehyde to isoprene. We have also shown that fluorine modification of SmNa-Y enhances the activity of this catalyst. We are currently examining the other variables in this system such as the type and concentration of rare earth cations as well as the Si/Al ratio. We are encouraged by the high activity and selectivity of fluorine modified zeolites in the pulsed system so we plan to study this reaction in a flow system in order to better evaluate its commercial potential.

Acknowledgements

We thank the Robert A. Welch Foundation and the donors of the Petroleum Research Fund administered by the American Chemical Society for financial support.

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