JOURNAL OF CATALYSIS **142,** 448–454 (1993)

A Comparison of the Catalytic Activities of Ga_{13}–, Al_{13}–, $GaAl_{12}$–, and Chromium–Pillar Interlayered Clay Minerals and Ga–H-ZSM-5 Zeolite in the Dehydrocyclodimerization of Propane

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Received August 5, 1992; revised February 2, 1993

Pillar interlayered clay minerals (PILCs) prepared using Ga_{13}, $GaAl_{12}$, Al_{13}, and chromium pillars in combination with the clay mineral montmorillonite were studied for their reactivity in the dehydrocyclodimerization of propane. The results were compared to those obtained for Ga–H-ZSM-5, the zeolite catalyst which is used commercially in this type of reaction. Although the gallium-containing zeolite was found to be the most efficient catalyst under the conditions used, significant differences in reactivity were found among the pillared materials examined. These differences were attributed to the activity imparted by the pillars themselves. Of the pillared clays, the Ga_{13}-pillared montmorillonite was found to be most effective for this reaction, and it also exhibited better selectivity for benzene production than did the gallium zeolite catalyst.

1. INTRODUCTION

The "Cyclar" process, which was developed jointly by B.P. (British Petroleum) and U.O.P. (Universal Oil Products) is currently of great interest for the conversion of light paraffins to aromatics (*1, 2*). The process was developed in an attempt to convert liquid petroleum gas (LPG) into aromatics rich in benzene, toluene, and xylenes (BTX chemicals).

The reaction mechanism has been fairly well established. The first step is the dehydrogenation of the paraffin, forming an olefin and hydrogen. This is followed by the conversion of this olefin into alkanes and cycloolefins by dimerization and ring-closure reactions (cyclization). Finally, dehydrogenation of the cyclic compounds results in aromatics. Side products are typically olefins (particularly ethene) and methane. Strong acid sites, such as are present in zeolite minerals, are required for these activation steps. The rate-determining step is believed to be the dehydrogenation of the starting paraffin (*1–6*). For this reason, catalysts exhibiting dehydrogenation in addition to acidic activities are well suited to this reaction. The commercial catalyst which is now being utilized is a form of the zeolite Ga–H-ZSM-5. Minimum substitution levels of about 1% gallium in ZSM-5 have been required to produce effective promotion (*2*).

Another class of porous acidic catalyst is the pillar interlayered clay minerals (PILCs) which are made up of phyllosilicate sheets intercalated by metal polyoxocations, most commonly the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ ion (Al_{13}) (*7*). Calcination results in metal oxide pillars which serve to prop apart the sheets and thereby form a two-dimensional type of porous structure. Recent studies have found that Ga_{13} pillars which are analogous in structure to the Al_{13} ions can be formed (*8–11*), and also $GaAl_{12}$ ions in which the central tetrahedral position of the polyoxocation is occupied by gallium rather than aluminum (*10–14*). The base hydrolysis of chromium is also known to produce species which can be used as a pillaring agent, but

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0021-9517/93 $5.00

whose structure is unknown (*15–18*). Recent work has suggested that a polyoxocation similar in structure to the Al_{13} ion, but with the central tetrahedral position empty (i.e., a Cr_{12} polyoxocation) might be one species present in hydrolyzed chromium solutions (*10*). However this proposal has not been confirmed, so for the chromium–pillared clays discussed in this paper, the term Cr_x–PILC will be used.

The effectiveness of gallium as a promoter in the zeolites used in this process leads to the question of what type of activity will be exhibited by Ga_{13}–PILCs, in which much larger quantities of gallium can be readily substituted than is the case for Ga–H-ZSM-5. Elemental analyses of these Ga_{13}-PILCs showed that solution loadings of 10 meq Ga^{3+}/g clay results in a percentage gallium content of ca. 15% w/w (*10*). In addition, as chromium is known to exhibit strong dehydrogenation activity (*19*), chromium–pillared clay might be a useful catalyst for this reaction.

Studies of the acidic characters (by pyridine adsorption studies combined with IR spectroscopy) and activities for cumene conversion revealed that the $GaAl_{12}$ and Al_{13} pillars contribute to the acidity and also enhance the catalytic cracking behaviors of these clay-based catalysts (*20*). Conversely, the gallium pillars, although seen to contribute greatly to both the Lewis and Brønsted acidities, were found to form PILCs which exhibited much stronger dehydrogenation than cracking activity. Similar behavior was also observed for the Cr–PILCs (*20*). Catalytic studies which have been published for Ga–PILCs have indicated a strong efficacy for the dehydrogenation of propane to form propene (*21*), and also, for Pt-doped samples, a good selectivity for the production of C_7 isomers from *n*-heptane (*22*).

The relative activities of Al_{13}–, $GaAl_{12}$–, Ga_{13}–, and Cr_x–PILCs, as well as the zeolite Ga–H-ZSM-5 were therefore compared for the dehydrocyclodimerization of propane. Conditions were chosen which allowed the progress of the reaction to be followed by infrared spectroscopy.

EXPERIMENTAL

The PILCs prepared for these studies were made as previously described (*10, 11*). Metal ion solutions which gave loadings of 10 meq of M^{3+} per gram of montmorillonite were used in the preparations. Surface areas were measured using a Micromeritics model 2200 fast surface area analyzer, after degassing under nitrogen for 1 hr at 150°C.

Catalytic reactions of the oligomerization/aromatization of propane over the various PILCs were studied. In addition, a sample of Ga–H-ZSM-5 was examined for comparison. Samples of the catalysts (ca. 150 mg) were accurately weighed into a quartz boat, which was then placed in an evacuable quartz infrared cell fitted with KBr windows. The samples were heated under vacuum at a rate of 4°C per min to a temperature of 500°C. Oxygen was then introduced into the cell (to a pressure of about 0.5 atm), and the samples calcined overnight under these conditions. The following morning, they were outgassed under high vacuum for about 1 hr at 500° and then cooled under vacuum. The Ga–H-ZSM-5 sample had been twice ammonium exchanged and calcined as above. Elemental analyses revealed it to contain 42.2% Si(w/w), 4.9% Ga, and 0.16% Al.

To begin the catalytic reaction, propane would be introduced into the cell at room temperature, to the desired pressure (typically 150 mm Hg). The cell was then sealed and placed in a pre-heated furnace at time $t = 0$ and at 575°C, and the reaction would commence. Infrared spectra were run at various time intervals. The pressures of the different gasses present were calculated from the infrared spectra, using calibration curves prepared for this purpose.

RESULTS AND DISCUSSION

The surface areas of the pillared montmorillonites were 245, 210, and 195 m^2/g, for the $GaAl_{12}$, Al_{13}, and Ga_{13} pillared materials, and that of the Ga–H-ZSM-5 was 334 m^2/g. The chromium-pillared material showed a significant variability in surface area in different preparations; the sample used for this study had a surface area of about 200 m^2/g. The gallium and aluminum containing pillars are quite stable; previous results showed that even after prolonged heating at successively higher temperatures, including 12 hr at 500°C, the $GaAl_{12}$, Al_{13}, and Ga_{13} pillared montmorillonites all retained more than 85% of their initial surface areas (*11*). The chromium-pillared material was significantly less stable, although the results were, as mentioned above, preparation dependent. It may be that in this case the pillar has oxidized and collapsed during calcination.

Under the conditions used, the reaction was slow enough that the evolution of the products could be easily followed. Propane reacted over the various catalysts at very different rates; the time required for the propane pressure to drop to one half of its initial value was 1.0 days over the Al_{13}–PILC, 0.5 days over Ga_{13}–PILC, 1.2 days over $GaAl_{12}$–PILC, 0.6 days over Cr_x–PILC, and 0.4 days over Ga–H-ZSM-5. The spectra of the gas phase in contact with the Ga_{13}-PILC sample as a function of time are given in Fig. 1, as an example of the changes observed. Virtually every line present can be attributed to either propane itself, or one of the reaction products: propene, ethene, methane, benzene, or toluene. Only one weak band, at ca. 663 cm^{-1}, could not be identified. With the possible exception of this 663 cm^{-1} band, no evidence of the presence of the cycloolefins could be found. Presumably the dehydrogenation to benzene of any such species formed (see Introduction) is a very rapid process. While some molecular hydrogen very probably is formed during the dehydrogenation reactions, it is of course not detectable by infrared spectroscopy, and we were therefore not able to quantify the amount produced.

The efficiencies of the cracking and dehydrogenation sites on the different catalysts can be compared by looking at the pressures of the different compounds formed in the very early stages of the reaction, while secondary reactions are still minimal. Propene is produced by the dehydrogenation of propane, and the cracking of propane forms methane and ethene. After 30 minutes of reaction, the ratios of the pressures of propene to those of ethene obtained for the different catalyst were: Al_{13}–PILC, 0.87; Ga_{13}–PILC, 1.27; $GaAl_{12}$–PILC, 0.80; Cr_x–PILC, 1.02, and Ga–H-ZSM-5, 1.25. The significant differences in the ratios confirm that the exposed gallium in the Ga_{13} pillars and the Ga–H-ZSM-5 enhance the dehydrogenation activity. In the $GaAl_{12}$ pillars, the gallium is sequestered in the center of the cation, and presumably its only catalytic influence arises from the enhanced thermal stability it imparts; for this pillar, and for the Al_{13}, the cracking sites are more effective, and more ethene than propene is produced.

The differences in the cracking activities are also illustrated by the amount of methane formed. The $GaAl_{12}$–pillared clay produces substantially more methane than the other catalysts, even at later stages in the reaction, as seen in Fig. 2. The Cr–pillared clay, although it showed quite good dehydrogenation capability in the early stages (see propene-to-ethene ratio above), also produces high quantities of methane later in the reaction, probably because it is not efficient at converting the propene formed into aromatics (see below) and therefore more of it undergoes cracking.

The propene pressures increase initially and then decrease, as the propene is converted into other products. As shown in Fig. 3, this occurs most quickly over Ga–H-ZSM-5. Part of this activity (and of the subsequent conversion to benzene discussed below) will arise because the surface area of the Ga–H-ZSM-5 is $1\frac{1}{3}$ to $1\frac{2}{3}$ times larger than those of the pillared clay samples. While this is a significant difference, it does not appear to be large enough to account for the dramatic differences in propene and benzene formation. The Ga–H-ZSM-5 sample is simply a very efficient catalyst for such reactions.

The amount of benzene produced by the

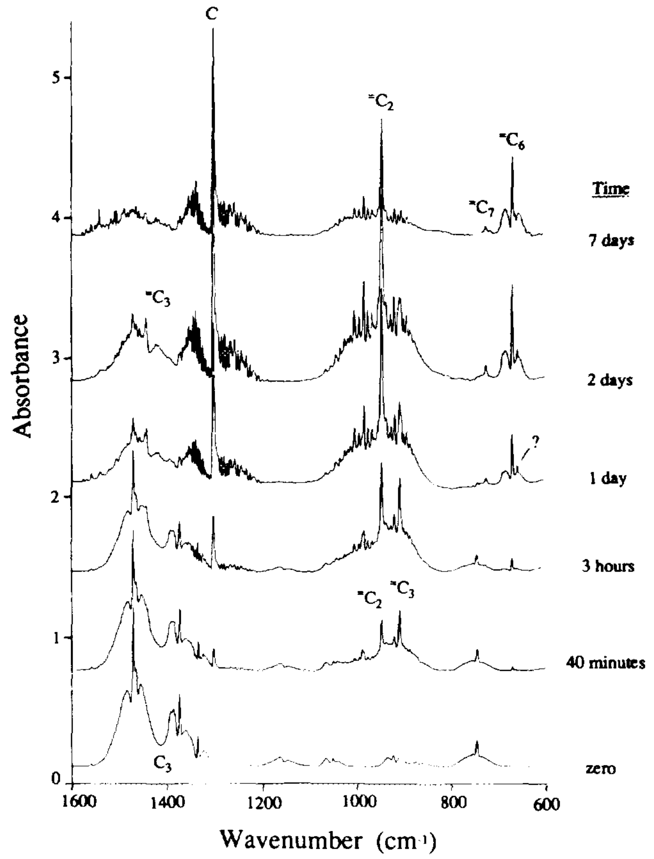

FIG. 1. Infrared spectra as a function of time for the propane dehydrocyclodimerization reaction employing the Ga_{13}-PILC catalyst.

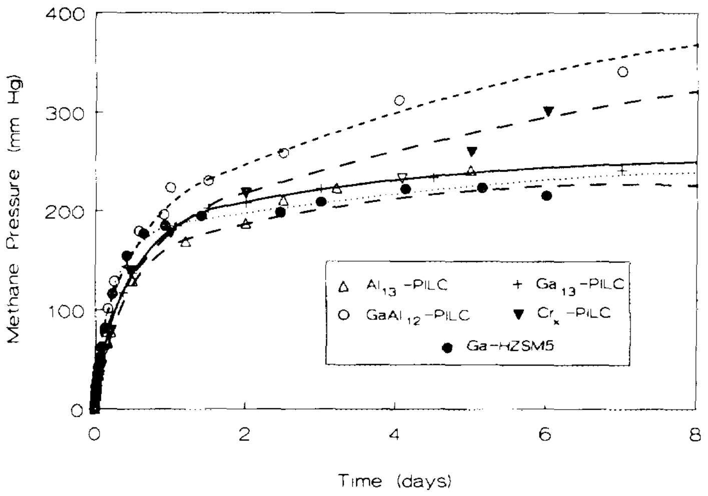

FIG. 2. Pressure of methane as a function of time over the different catalysts.

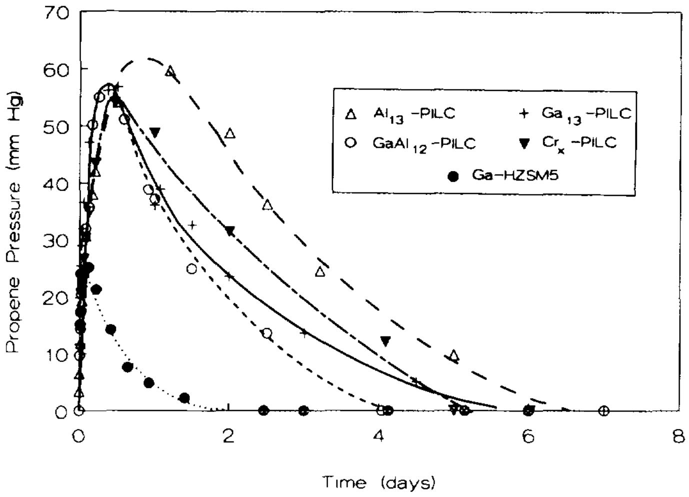

FIG. 3. Pressure of propene as a function of time over the different catalysts.

different catalysts is shown in Fig. 4. Clearly, the gallium zeolite, Ga–H-ZSM-5, is by far the most efficient catalyst for the overall propane dehydrocyclodimerization process. There are significant differences between the pillared clay mineral catalysts prepared with different pillaring cations, however. Of the pillared clays, the Ga_{13}–PILC is clearly the most effective. The Al_{13}–PILC is next most efficient, and the $GaAl_{12}$ and chromium pillared clays are least useful. It is interesting to compare the behavior of the different pillared clay minerals during the later stages of the reaction, after both the propane and propene have been completely used up (ca. 5 days). The only compounds present in appreciable quantities at this time are methane, ethene, and benzene. For the Ga_{13}-PILC, the benzene pressure continues to increase, while the

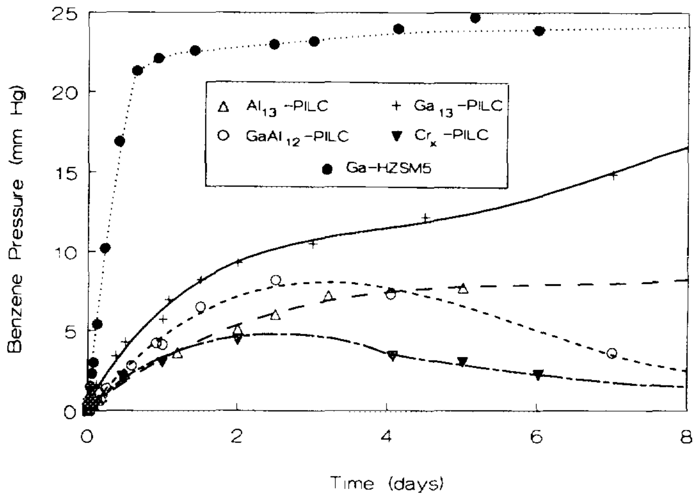

FIG. 4. Pressure of benzene as a function of time over the different catalysts.

methane pressure (Fig. 2) remains virtually constant. For the $GaAl_{12}$ PILC, the situation is very different; methane increases, while benzene actually decreases. Clearly, for the $GaAl_{12}$ pillared clay, the acidic nature of the surface dominates, and cracking (and possibly acid-catalyzed polymerization) occurs. For the Ga_{13}–PILC, the acidity is less, and the ethene is converted into aromatics instead.

While the pillared clay minerals are all much slower than the Ga–H-ZSM-5 zeolite to convert propane to aromatics under these conditions, there are differences in selectivity that are interesting. Rather surprisingly, the selectivity for benzene, as opposed to other aromatics, is much greater for the Ga_{13} pillared clay than for the Ga zeolite, despite the larger pores and wider range of pore sizes for the former. For example, the Ga_{13}–PILC catalyst eventually produced about 75% as much benzene as did the Ga–H-ZSM-5, but the toluene yield was only about 9% of that produced by the zeolite. Also, no xylenes at all were seen for the pillared clays, while small amounts were seen for the Ga–H-ZSM-5.

CONCLUSIONS

The results obtained confirm that the specific type of pillar present in a pillared clay mineral has a significant effect on its catalytic activity. However, for the dehydrocyclodimerization of propane under the conditions used, a gallium-containing zeolite, Ga–H-ZSM-5, has much higher activity than any of the pillared clay minerals studied. Among the pillared clays, the Ga_{13}–pillared montmorillonite was most effective at dehydrogenation, while the Al_{13} and particularly the $GaAl_{12}$ pillars promoted acidic reactions more effectively. The montmorillonite pillared with chromium initially exhibited dehydrogenation capability, but but at later stages cracking became more important; this change in activity may be associated with the lower thermal stability of the chromium-pillared material (*10*). The pillared clays did exhibit better selectivity for benzene production (as comapred to toluene and xylenes) than did the Ga–H-ZSM-5.

The primary purpose of this paper was to see if the different pillars did affect the catalytic activity, by studying the evolution of the products over the different materials. No attempt was made to optimize the conditions of the reaction (percentage gallium, reaction temperature, etc.) for either the Ga–PILC or the Ga–H-ZSM-5 samples. More detailed studies would have to be undertaken to determine if the Ga_{13}–PILCs would be suitable catalysts for the production of benzene from simple alkanes. However the fact that different activities were found for the various pillared montmorillonite samlpes in encouraging, in that it suggests that, within limits, it would be possible to "fine tune" the reactivity of the pillared clays for other reactions by selecting the pillaring agent with the desired properties.

ACKNOWLEDGMENTS

This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada (NSERC). One of us (S.M.B.) thanks NSERC, the Alberta Oil Sands Technology and Research Authority, the Killam Foundation, PetroCanada, Inc., and the University of Calgary Grants Committee for support in the form of graduate scholarships and grants. We also thank Mr. Karl Lifschitz and GFI Advanced Technologies for supplying the gallium chloride which was utilized in these studies.

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