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Adamantanes from petroleum with zeolites

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Abstract

Experiments with zeolite Beta and zeolite Y demonstrate that adamantane and methyl adamantanes can be isolated very effectively from modern refinery streams by mild hydrocracking over Pt- and Pd-containing large pore zeolites. Yield depends importantly on individual refinery crude source and process configuration. Heavy crudes and refineries with conventional hydrocracking and FCC feed hydrotreater facilities are particularly desirable, and an ideal feed for adamantane isolation in such a situation is the 150–250°C fraction of the hydrocracker (HDC) recycle stream. When Pt- or Pd-containing zeolite Beta was used with such a stream, temperatures of some 250°C and pressures below 3.5 mPa (500 psig) sufficed to remove selectively well over 90% of the non-adamantane hydrocarbon, with little conversion of adamantanes. High selectivity for adamantanes is attributed in large part to size-selective exclusion of these molecules from the pores of zeolite Beta.

Keywords: Adamantanes from petroleum; Petroleum; Zeolites

1. Introduction

Adamantanes were first identified in the early 1930s in the heavy Hodonin crude oil of eastern Czechoslovakia [1]. Although adamantanes are found in certain natural gas condensates [2], their commercial isolation or manufacture from crudes has not been achieved. Isolation has been restricted to the laboratory and has been characterized by multistep fractionation, adsorption, and solvent separation sequences [3]. In an interesting and pertinent result, when the product of such a multistep concentration process was subjected to hydrocracking over 10% Pt on diatomite at 400–430°C, only the adamantanes were preserved [4]. The yield was low of course, since it was defined by the concentration of adamantanes in the original crude, said never to exceed about 0.02–0.04% [5].

Increased yield would be possible in a refinery if the polycyclic structures in a crude (tricyclics in particular) could be converted to adamantanes, and there is reason to believe such conversion can occur. The original discovery of a facile chemical route to adamantane, the $AlCl_3$-catalyzed isomerization of hydrogenated cyclopentadiene dimer, tetrahydrodicyclopentadiene (THDCP) [6], was quickly extended to include such tricyclic hydrocarbons as perhydrofluorene (PHF), perhydroacenaphthenes, and perhydrophenanthrenes [7,8]. All such structures, together with their aromatic analogs, are common constituents of crude oil. An example of perhydrofluorene conversion to adamantanes is shown in Fig. 1.

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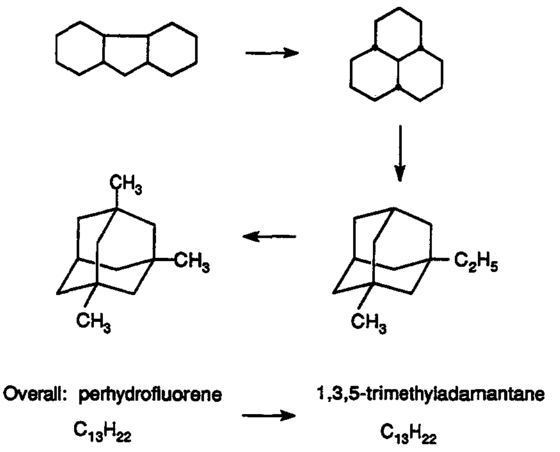

Fig. 1. Reaction sequence for the conversion of PHF to 1,3,5-TriMA [7].

Furthermore, acid catalysts common to refinery processes have now been shown to be effective in converting both THDCP and petroleum-related tricyclic hydrocarbons to adamantanes. Examples include chlorinated Pt/Al_2O_3 [9], silica-alumina [10,11], silica-alumina with Group VIII metal [12], and zeolites X and Y, often with Group VIII metal [13–15].

Based on the above, it was reasonable to conclude that virtually any fused-ring tricyclic perhydroaromatic, if present in a refinery stream, might tend to rearrange into the adamantane structure in the presence of a large-pore zeolite catalyst [16]. The following experiments explore zeolite pore size constraints on the formation and conversion of methyl adamantanes, using zeolites Beta and Y as examples.

2. Experimental

Two zeolite catalysts were used in the experiments, both generated in-house, both containing alumina binder, and both in the "hydrogen" form. Framework SiO_2/ Al_2O_3 ratios for the two zeolites were approximately 50 for Beta (HiAct-Beta, see below) [17] and 200 for "ultra-stable" Y (USY) [18]. For better comparison with the USY, a third catalyst, "low activity" Beta (LoAct-Beta), was dealuminated to a similar framework SiO_2/ Al_2O_3 ratio. In the experiments, all catalysts were 24/60 mesh, all contained 0.5% Pt or Pd, and all were brought to initial operating conditions (232°C and 2.5 MPa) in flowing hydrogen. All experiments were conducted in a downflow tubular reactor, at 2.5 MPa, with a H_2/hydrocarbon (H_2/HC) mole ratio of 3–4, at temperatures of 230–350°C, and at 1–4 WHSV (weight hourly space velocity). Day-to-day catalyst aging was not significant in these experiments.

Refinery streams selected for testing included a 135–210°C HDC heavy naphtha, a 175–260°C portion of the HDC recycle stream, and a 120–245°C hydrotreated kerosene, all from a refinery sourced largely with heavy crude. In addition, a 175–290°C analog of the above HDC recycle stream was obtained from a refinery sourced with light, conventional crude. Pure compounds (PHF, decalin, 1- and 2-methylnaphthalene, and phenanthrene) were obtained from Aldrich.

Gas chromatography (GC) results were obtained with a 60 m DB-1 capillary column (J&W Scientific, 0.25 mm i.d., 0.25 μm film). The GC–mass spectrometer (GC–MS) analyses were performed on a Kratos model MS80RFA, with a Hewlett Packard series II 5890 GC and a 30 m DB-5HT column (J&W, 0.32 mm i.d., 0.1 μm film). Ionization was by electron impact.

3. Zeolite Beta

3.1. High-activity Beta

3.1.1. Demonstration of adamantanes

Conversion of HDC heavy naphtha over HiAct-Beta provided the first evidence of adamantanes. As reaction severity was increased, a distinctive gc signature emerged for the remaining high-boiling hydrocarbons, as shown in Fig. 2. These hydrocarbons represented approximately 1% of the feed; they boiled above about 190°C; and GC–MS showed them all to be

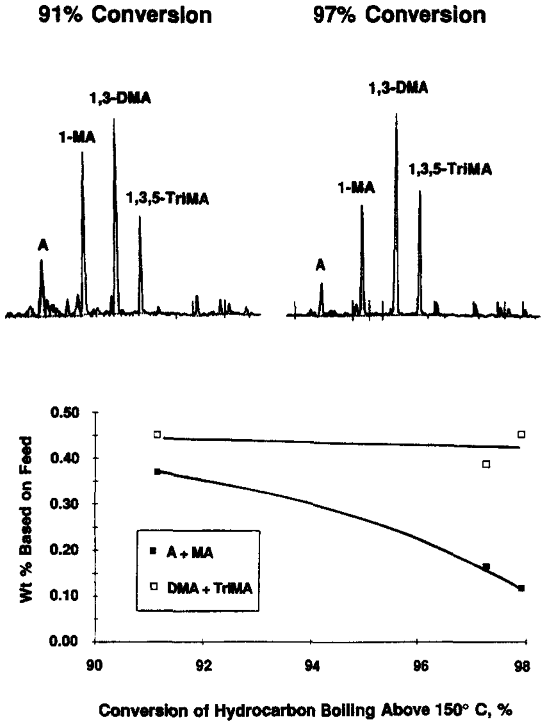

Fig. 2. Adamantanes isolated from HDC heavy naphtha. "Conversion" refers to total feed material boiling above 150°C. Abbreviations are adamantane (A), 1-methyl adamantane (1-MA), 1,3-dimethyl adamantane (1,3-DMA), and 1,3,5-trimethyl adamantane (1,3,5-TriMA).

adamantanes. As shown by the GC traces in Fig. 2, the compounds were adamantane (A), 1-methyl adamantane (1-MA), 1,3-dimethyl adamantane (1,3-DMA), and 1,3,5-trimethyl adamantane (1,3,5-TriMA), together with very minor amounts of higher boiling adamantanes. Table 1 provides specific reaction conditions.

These adamantanes were apparently present in the HDC heavy naphtha, as shown by subsequent experiments in which 10% decalin and 10% methyl decalins were added to the feed. (Decalin and methyl decalins are the C10 + polycyclic hydrocarbons likely to be found in the boiling range of this feed.) No new adamantane was formed. In keeping with the 210°C endpoint of heavy naphtha feed, only the lowest boiling of the methyl adamantanes were present. (1,3,5-TriMA has a boiling point of 199°C [2].)

Since methyl adamantanes boil between 190 and 250°C, the HDC recycle stream (boiling range 175–260°C) would be expected to contain substantially more adamantanes. It did, as shown by the product depicted in Fig. 3. In an effort to keep the reaction gas-phase at low reactor temperature (256°C), a 1:1 blend of HDC heavy naphtha and HDC recycle was chosen as the feed. The product, boiling above 190°C, contained a full complement of methyl adamantane isomers. When corrected for adamantanes in the heavy naphtha, the compounds shown in Fig. 3 represented approximately 11 wt% of the 175–260°C HDC recycle stream.

Table 1
Reaction conditions for isolating adamantanes

Feedstream	Catalyst	Temperature (°C)	WHSV (1/h)	Conversion [a] (wt%)	Adamantanes (wt%)
Heavy naphtha	HiAct-Beta	255	1.8	91	0.8
Heavy naphtha	HiAct-Beta	254	0.9	97	0.6
Blend [b]	HiAct-Beta	256	1.9	88	5.7
Kerosene	HiAct-Beta	261	2.0	96	0.4
Blend [c]	HiAct-Beta	266	1.8	96	0.9
Heavy naphtha	LoAct-Beta	289	1.5	72	0.8
Heavy naphtha	LoAct-Beta	312	2.0	94	0.5
HDC recycle	LoAct-Beta	303	1.9	90	8.9
HDC recycle	LoAct-Beta	319	1.7	93	7.2
Heavy naphtha	USY	289	1.7	72	0.5
HDC recycle	USY	347	1.9	91	2.2

[a] Of feed hydrocarbon boiling above 150°C to lower boiling hydrocarbon.
[b] 1:1 HDC heavy naphtha:HDC recycle from a heavy crude refinery.
[c] 1:1 HDC heavy naphtha:HDC recycle from a light crude refinery.

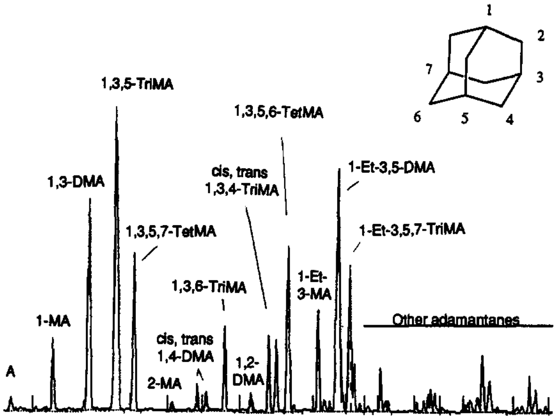

Fig. 3. GC trace of adamantanes isolated from the HDC recycle with "high-activity" Beta. Peak assignments are based on [2], [5], and [16] and on GC–MS. Abbreviations are the same as those used in Fig. 2, extended to include ethyl (Et) and tetramethyl (TetM) species.

It is believed that the adamantanes were formed in considerable part in the HDC (and possibly FCC) units, but that some portion entered the refinery with the crude. Support for adamantanes in the crude was found in an experiment with hydrotreated kerosene (boiling between 120 and 240°C), a stream which had never contacted a zeolite catalyst, but a stream which, given its boiling range, should contain any adamantanes in the crude. When processed over HiAct-Beta, a full complement of methyl adamantanes was again observed, but with a yield corresponding to 0.4% of the kerosene, as shown in Table 1. It remains to be shown that these adamantanes were not formed during the processing over HiAct-Beta.

Before exploring possible adamantane formation over HiAct-Beta, it is important to note that the high adamantane content in the above HDC recycle stream was specific to a refinery operating on heavy crude. When the experiment was repeated with the HDC recycle stream from a refinery operating on light, conventional crudes, only about 1% adamantanes were found. The adamantane isomer distribution was very similar to that shown in Fig. 3 except that 1,3-DMA, rather than 1,3,5-TriMA, was the major species.

3.1.2. *Formation of adamantanes*

A model compound was used to probe possible conversion of tricyclic naphthenes to adamantanes over Beta catalysts under mild hydrocracking conditions. Based on the literature [7], perhydrofluorene (PHF) was selected for most of the experiments. It boils at 253°C, and it should convert to 1,3,5-TriMA.

Conversion of PHF to 1,3,5-TriMA was largely absent with zeolite Beta, for reasons which will be discussed below. Dissolved at 10% in HDC heavy naphtha and processed over HiAct-Beta at 305°C and 2 WHSV, the yield of adamantanes based on PHF was only 3%. (The PHF was 100% converted.) What few adamantanes were produced appeared to have methyl (or ethyl) groups on non-bridgehead carbons, and little or none of the expected endproduct, 1,3,5-TriMA, was formed. A similarly low adamantane yield was obtained with phenanthrene, a molecule which might be expected to hydrogenate and isomerize to 1,3,5,7-TetMA over a noble metal/zeolite catalyst. Thus, HiAct-Beta was ineffective in converting tricyclic hydrocarbons into adamantanes.

3.1.3. *Conversion of adamantanes*

The stability of adamantane in the presence of acid is well recognized [19]. Thus, that adamantanes would be among the least reactive of the hydrocarbons present under these process conditions was not surprising. Surprising was the observation that only certain of the adamantanes could be converted over zeolite Beta under mild hydrocracking conditions. As shown at the bottom of Fig. 2, the smallest of the adamantanes, A and 1-MA, were converted as reaction severity was increased. The larger molecules, 1,3-DMA and 1,3,5-TriMA, were much less reactive.

3.1.4. *Size-selective exclusion*

Exclusion of all but the smallest adamantanes from the pore system of HiAct-Beta is believed to be the explanation. Unsubstituted adamantane is a spherical molecule with a Van der Waals diameter of 7.4 Å, known to penetrate the pore of zeolite Y [14]. While the Y pore has a reported free diameter of 7.4 Å, that of Beta is more constrained. It is elliptical, with a critical free diameter of 6.4 Å [20].

Size-exclusion from the HiAct-Beta pore system explains both the lack of conversion of most adamantanes in these experiments and the ineffectiveness of HiAct-Beta in isomerizing PHF into 1,3,5-TriMA.

3.2. *Low-activity Beta*

3.2.1. *Effect of reaction temperature*

In order to compare HiAct-Beta behavior with that of the USY sample, it was important to eliminate intrinsic catalyst activity, i.e. reaction temperature, as a variable. Thus, a dealuminated, "low-activity" Beta (LoAct-Beta) catalyst was prepared and tested. Whereas a temperature of 250°C was sufficient with HiAct-Beta to convert 90% of the 150°C + HDC heavy naphtha (at 2 WHSV) and isolate the adamantanes, approximately 310°C was required with the "LoAct" sample. Little or no difference in adamantane yield or conversion behavior was observed at the higher temperature, as will be discussed below.

Table 2
Adamantanes obtained from processing HDC recycle oil in a heavy crude refinery

Catalyst	HiAct-Beta	LoAct-Beta	LoAct-Beta	USY
Temperature (°C)	256	303	319	347
Conversion [a] (%)	88	90	93	91
Total adamantanes (%)	10.7 [b]	8.9	7.2	2.2
A	0.8	0.5	0.2	1.5
1-MA	3.5	3.1	1.5	5.4
1,3-DMA	12.1	12.4	11.0	13.7
1,3,5-TriMA	17.2	18.8	23.2	26.0
1,3,5,7-TetMA	6.7	7.0	8.8	19.2
2-MA	0.7	0.3	0.1	0.9
1,4-DMAs	2.3	1.7	0.7	2.5
1,2-DMA	0.9	0.7	0.3	0.7
1,3,6-TriMA	3.9	3.7	3.1	2.2
1,3,4-TriMAs	5.8	5.1	3.4	2.3
1,3,5,6-TetMA	6.8	6.9	8.0	3.2
1-Et-3-MA	4.9	5.0	3.0	1.2
1-Et-3,5-DMA	12.9	13.3	16.2	3.2
1-Et-3,5,7-TriMA	6.3	6.5	8.2	13.3
Others	14.6	15.1	12.3	4.7

[a] Of feed hydrocarbon boiling above 150°C.
[b] After correction for adamantanes in the heavy naphtha.

Higher temperature afforded the opportunity to process the 175–260°C portion of the HDC recycle stream alone and thus to compare LoAct-Beta and USY more directly in their ability to isolate a full complement of adamantanes. When processed at 300 and 320°C over LoAct-Beta, adamantane yields were 8.9 and 7.2%, respectively. In both cases, the fraction boiling above 150°C was essentially all adamantanes. As shown by the two LoAct-Beta runs in Table 2, (a) the smallest of the adamantanes reacted preferentially, and (b) there was large similarity in isomer distribution between the adamantanes obtained with HiAct- and LoAct-Beta, despite the substantial differences in reaction temperature.

4. Zeolite USY

4.1. *Demonstration of adamantanes*

Like LoAct-Beta, USY was also able to isolate adamantanes from the 135–210°C HDC heavy naphtha, but it afforded a lower yield and a different distribution of methyl adamantanes from those obtained with Beta. With USY, at 290°C and 72% conversion of 150°C + material, the adamantane yield was approximately half that obtained with LoAct-Beta. And with USY, the two larger adamantanes, 1,3-DMA and 1,3,5-TriMA, were reduced in concentration relative to the smaller compounds, A and 1-MA. The (A + MA)/(DMA + TriMA) ratio was 1.2 with USY, vs. 0.8 with Beta. No formation of 1,3,5,7-TetMA was observed.

The greater ability of USY to convert adamantanes was readily apparent in the behavior of the 175–260°C portion of the HDC recy-

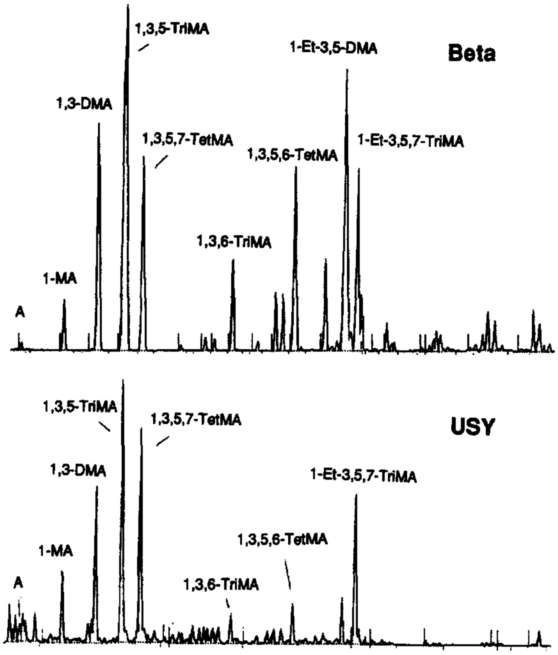

Fig. 4. A GC comparison of adamantanes isolated from HDC recycle using ''low-activity'' Beta and USY zeolites. All peaks in the Beta sample are adamantanes.

cle stream, a stream known from the Beta experiments to contain approximately 11% adamantanes. On processing this stream over USY at 347°C, the adamantanes shown in Fig. 4 were obtained, with a yield of 2.2% based on total feed. Shown for comparison is the product obtained with LoAct-Beta, at a similar conversion of 150°C + material. The adamantane yield in this Beta experiment was 7.2%.

Analysis of the data in Fig. 4 shows that USY preferentially converted all adamantanes containing alkyl groups on bridging carbons. Migration of such groups to bridgehead carbons is a commonly accepted intermediate reaction in the chemical synthesis of methyl adamantanes. Noteworthy, however, was the special robustness of the two adamantanes in which all four bridgehead carbons contain alkyl groups, 1,3,5,7-TetMA and 1-Et-3,5,7-TriMA. Detailed data are in Table 2. The robustness of these two unique tetra-alkyl adamantanes is consistent with their inability to form a tertiary carbenium ion, i.e. a 1-adamantyl cation, which is presumed to be the prime intermediate in adamantane conversion [19].

4.2. Formation of adamantanes

Though better able to convert adamantanes, USY was also better able to generate them, from tricyclic naphthenes. When the 10% PHF in HDC heavy naphtha experiment with Beta was repeated with USY, at 320°C and 1.7 WHSV, the product contained 3.5% adamantanes which, when corrected for the heavy naphtha contribution, represented a 27% yield based on PHF. The yield with Beta was only 3%. PHF, a C13 molecule, was again 100% converted, and GC–MS showed four new non-bridgehead C13 adamantanes. 1,3,5-TriMA, also a C13 molecule, was enhanced in concentration relative to the other bridgehead isomers.

5. Conclusions

These experiments demonstrate (a) that adamantanes can be formed under HDC conditions over certain noble metal/zeolite catalysts, particularly USY, (b) that these molecules currently exist in refinery HDC recycle streams, occasionally at very significant concentrations, and (c) that, due to their relative inertness and their large size, they can be isolated quite effectively by mild hydrocracking over selected metal/zeolite catalysts, notably zeolite Beta.

The absolute amount of adamantane in a refinery depends on crude source, catalyst, unit configuration, and operating conditions. As shown by the heavy crude example, a level of some 10% can be found in the 175–260°C portion of an HDC recycle stream. Heavy crudes are particularly desirable for adamantane synthesis and recovery because they are depleted in paraffin and enriched in polycyclic alkanes, relative to light, conventional crudes.

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References

[1] S. Landa and V. Machacek, Coll. Czech. Chem. Commun., 5 (1933) 1.
[2] W.S. Wingert, Fuel, 71 (1992) 37.
[3] S. Landa and J. Vanek, Coll. Czech. Chem. Commun., 35 (1970) 3733.
[4] Z.V. Yakubson, O.A. Aref'ev and A.A. Petrov, Neftekhimiya, 13 (1973) 345; Chem. Abstr., 79, 116756.
[5] A.A. Petrov, Petroleum hydrocarbons, Springer-Verlag, Berlin, 1984, pp. 93–99.
[6] P. von R. Schleyer, J. Am. Chem. Soc., 79 (1957) 3292.
[7] A. Schneider, R.W. Warren and E.J. Janoski, J. Am. Chem. Soc., 86 (1964) 5365.
[8] A. Schneider, R.W. Warren and E.J. Janoski, J. Org. Chem., 31 (1966) 1617.
[9] D.E. Johnston, M.A. McKervey and J.J. Rooney, J. Am. Chem. Soc., 93 (1971) 2798.
[10] A.F. Plate, Z.K. Nikitina and T.A. Burtseva, Neftekhimiya, 1 (1961) 599.
[11] E.I. Bagry and P.I. Sanin, US Pat., 3 637 876 (1972).
[12] S. Landa and V. Podrouzhkova, Neftekhimiya, 14 (1974) 551.
[13] K. Honna, N. Shimizu and K. Kurisaki, US Pat., 3 944 626 (1976) to Idemitsu.
[14] G.C. Lau and W.F. Maier, Langmuir, 3 (1987) 164.
[15] Z. Gao and X.-B. Yang, Chinese J. Chem., 12 (1994) 52.
[16] L.D. Rollmann, L.A. Green, R.A. Bradway and H.C. Timken, Prepr. Div. Fuel Chem., 40 (1995) 1013.
[17] R.L. Wadlinger, G.T. Kerr and E.J. Rosinski, US Pat., 3 308 069 (1967) to Mobil.
[18] D.W. Breck, Zeolite molecular sieves, Wiley, New York, 1974.
[19] G. Olah, Cage hydrocarbons, Wiley, New York, 1990, p. 110.
[20] W.M. Meier and D.H. Olson, Zeolites, 12 (1992) 1.