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Retained Product from Reaction of 1-Hexene on SAPO-34: Formation of Adamantanes

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Treatment of the microporous silico-alumino-phosphate SAPO-34 (similar in structure to chabazite) with 1-hexene at 513 K generates retained reaction product in which adamantanes (adamantane, 1-methyl, dimethyl, ethyl derivatives) are major constituents, together with cyclopentadienes, alkanes, and some alkylbenzenes. No adamantanes could be detected in the evolved gaseous products. Adamantanes are maximized at intermediate treatment times (4–28 h), while products related to naphthalene and anthracene/phenanthrene become important at very long times or higher temperatures. Evidence suggests that adamantanes are formed by acid-catalyzed reactions passing from cyclopentadienes (CPDs) via CPDs-dimer and tetrahydro-CPDs-dimer, while products in the naphthalene and anthracene/phenanthrene systems are produced by alternative acid-catalyzed pathways from CPDs and CPDs-dimer. Evidence shows that adamantanes are formed within the SAPO-34 cages, which appear to be uniquely active for this reaction for reasons possibly related to size/shape coincidence between host cage and transition state guest (analogous, it is suggested, to enzyme–substrate (transition state) complementarity in enzyme chemistry).

1. INTRODUCTION

Both the microporous silico-alumino-phosphate SAPO-34 (*1*) and the structurally similar zeolite chabazite are subject to rapid deactivation by the deposition of retained organic residue during conversion of methanol (*2, 3*). The present paper explores the nature and the mechanism of formation of the retained residue from the treatment of SAPO-34 with 1-hexene, a reactant chosen for ease of comparison with a previous study using H-ZSM5 zeolite (*4*), and also because olefins are probable intermediates (or end products) in the conversion of methanol (*1, 5, 6*) over solid acid catalysts.

A striking result from the treatment of SAPO-34 with 1-hexene was the generation, under a specific range of reaction conditions, of a substantial proportion of diamondoid hydrocarbons (adamantane and alkyladamantanes) in the product retained by the catalyst: no evidence for them could be found in the products returned to the gas phase.

The acid-catalyzed isomerization of the tricylic tetrahydrodicyclopentadiene into adamantane is well known; Friedel–Crafts catalysts such as aluminum chloride have been extensively used (reviews (*7, 8*)). The reaction has also been reported using an acidic LaY-zeolite catalyst (*9*), while a number of acid-catalyzed isomerization reactions are known by which adamantane or an alkyladamantane is formed from a tricyclic hydrocarbon precursor other than a tetrahydrodicyclopentadiene (*7, 8, 10–12*). However, we know of no previous work which has identified the formation of substantial amounts of adamantanes from a simple aliphatic reactant such as 1-hexene. The channel structure in a microporous solid can allow reaction chemistry to be controlled by size/shape selectivity effects, and effects of this sort appear to be evident in the present reactions with SAPO-34.

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2. EXPERIMENTAL

The experimental methods used in the present work for the treatment of the SAPO-34 catalyst with 1-hexene vapor and for product analysis were similar to those recently described (*4*). Briefly, treatments were carried out using 1.0 g of SAPO-34 supported as a thin (ca. 3 mm) bed in a down-flow reactor. The carrier gas was high-purity nitrogen (≤10 ppm impurity), and the catalyst sample was first pretreated *in situ* at 773 K for 2 h in an oxygen stream (20 cm^3 min^{-1}), then flushed in a nitrogen stream at 773 K for 2 h, and cooled to reaction temperature in nitrogen. The reactant (1-hexene) was delivered from a motor-driven syringe (0.27 cm^3 h^{-1}, liq.) into the carrier gas stream (20 cm^3 min^{-1}) in a heated vaporizer. At the end of the treatment time the sample was cooled to room temperature in the nitrogen flow.

The reaction product retained with and within the SAPO-34 catalyst was analyzed by dissolution of the SAPO-34 in dilute HF (4 *M*) with simultaneous solvent extraction (CH_2Cl_2) of the organic components (*13*) (273 K, 3–5 min), followed by removal of much of the CH_2Cl_2 by evaporation at room temperature. The recovered residue and the gaseous reaction products were analyzed by GC and GC–MS.

The total organic content of the treated SAPO-34 was estimated by oxidative burn-off as previously described (*4*).

Exhaustive exchange (350 h) of the SAPO-34 (Union Carbide Corp. (*33*)) with 1 *M* $NaNO_3$ solution at room temperature followed by titration of the liberated acid gave the estimated total acidity as 75.0 mmol/100 g. 1-Hexene was from Sigma and reference adamantane from BDH. Literature methods were used for the preparation of reference amounts of 1-methyladamantane (*14*) and 1,3-dimethyladamantane (*15, 16*).

Adamantane, 1-methyladamantane, 1,3-dimethyladamantane, and 1-ethyladamantane were identified from mass spectra and retention times. Adamantane—(*m/e*), intensity [found/authentic sample/literature (*18*)]—(136), [100/100/100]; (135), [39/31/26]; (121), [17/11/9]; (107), [17/12/10]; (95), [21/17/17]; (94), [31/25/24]; (93), [47/42/47]; (92), [18/10/7]; (91), [22/12/8]; (81), [25/16/19]; (80), [36/31/35]; (79), [56/49/46]; (67), [25/28/26]; (41), [31/34/38]—retention time—found, 21.7 min; authentic sample, 21.7 min. 1-Methyladamantane—(*m/e*), intensity [found/authentic sample/literature (*17*)]—(150), [16/15/15]; (136), [10/11/12]; (135), [100/100/100]; (107), [10/12/11]; (93), [29/23/37]; (91), [10/17/8]; (79), [19/18/25]; (41), [19/17/12]—retention time—found, 22.3 min; authentic sample, 22.3 min. 1-Ethyladamantane—(*m/e*), intensity [found/literature (*17*)]—(164), [14/5]; (136), [13/10]; (135), [100/100]; (107), [14/8]; (93), [14/17]; (91), [8/6]; (79), [22/23]; (41), [11/12]—retention time—found, 26.2 min. 1,3-Dimethyladamantane—(*m/e*), intensity [found/authentic sample/literature[2] (18, 19)]—(164), [20/22/14]; (150, [14/20/18]; (149), [100/100/100]; (107), [21/28/30]; (93), [24/44/48]; (91), [13/16/14]; (79), [14/16/16]—retention time—found, 22.8 min; authentic sample, 22.8 min. Four other dimethyladamantane isomers were found at longer retention times with mass spectra generally similar to that of the 1,3-isomer. A total of five dimethyladamantane isomers is possible. Another ethyladamantane with a mass spectrum generally similar to that of 1-ethyladamantane was found at a longer retention time and assigned as the 2-isomer. Trimethyladamantanes were assigned from observed mass spectra: four components with similar mass spectra were observed ((*m/e*)/intensity: (178)/17; (163)/100; (121)/14; (107)/42; (93)/11; (41)/17).

3. RESULTS

Treatments of SAPO-34 with 1-hexene were carried out at temperatures in the range 459–673 K and at treatment times in

[2] The mass spectrum for 1,3-dimethyladamantane given in Ref. (*18*) contains a spurious peak at *m/e* = 151 which is not recorded in Ref. (*19*).

TABLE 1

Products from SAPO-34 Treated with 1-Hexene at 513 K

Component	Treatment time:	Composition (wt%) 1 h	4 h	28 h	165 h[a]
Alkanes/olefins[b]		R,[c] 27 (5–11)[d] G,[c] 22 (6–8)	R, 10 (7–11)	R, 3 (7–10) G, 13 (6–12)	R, —
Alkylbenzenes		R, 11 (7–10) G, 61 (6–8)	R, 29 (7–10)	R, 41 (8–10) G, 84 (6–11)	R, small (7–10)
Alkylcyclopentadienes		R, 42 (8–11) G, —	R, 22 (9–11)	R, 6 (9–10) G, —	R, —
Alkylindanes/indenes		R, 4 (9) G, 17 (10)	R, —	R, 2 (11) G, 3 (9)	R, small (10–11)
Alkylnaphthalenes		R, — G, —	R, —	R, — G, —	R, medium (11–15)
Alkyldi-, tetra-, octa-hydronaphthalenes		R, 8 (12–13) G, —	R, —	R, — G, —	R, medium (11–13)
Alkylphenanthrenes/anthracenes		R, — G, —	R, —	R, — G, —	R, small (14–19)
Adamantane		R, — G, —	R, 1	R, 2 G, —	R, small
1-Methyladamantane		R, 5 G, —	R, 9	R, 10 G, —	R, medium[e]
Dimethyladamantanes					
1,3-isomer		R, 3; G, —	R, 9	R, 10; G, —	R, medium
four other isomers		R, 3; G, —	R, 8	R, 11; G, —	R, medium
Ethyladamantanes[g]					
1-isomer		R, —; G, —	R, 2	R, 2; G, —	R, —
2-isomer		R, —; G, —	R, 1	R, 1; G, —	R, —
Trimethyladamantanes[h]		R, — G, —	R, 6	R, 6 G, —	R, small
Other components		R, — G, —	R, 2[i]	R, 3[i] G, —	R, small[j]
Unknown		R, — G, —	R, 1[f]	R, 3[k] G, —	R, small[l]

[a] In addition to the products shown, some black insoluble residue was obtained from the acid dissolution/solvent extraction process.

[b] Including some cyclo compounds.

[c] R, residue; G, gas.

[d] Total carbon number range in parentheses.

[e] Including some 2-isomer assigned with the longer retention time.

[f] Two components.

[g] Mass spectra of isomers are similar, 2-isomer assigned with the longer retention time.

[h] Four isomers with similar mass spectra.

[i] Tricyclo[4.3.1.1^{3,8}] undecane from mass spectrum.

[j] Acenaphthalene from mass spectrum.

[k] Three components.

[l] Substantial number of small unidentified components in residue with complex chromatogram.

the range 1–164 h. Adamantanes were most prominent in the retained products for reactions at 513 K (cf Table 1), being of relatively small proportion for a treatment time of 1 h and increasing at 4 and 28 h. However, a large further increase in treatment time (164 h) caused a substantial increase in the proportion of higher hydrocarbons re-

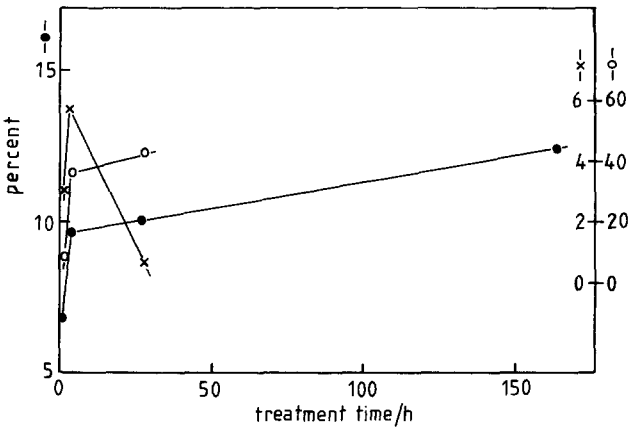


FIG. 1. Dependence on treatment time of SAPO-34 by 1-hexene at 513 K of: total residue content/wt% (●); fraction of adamantanes in residue/wt% (○); fraction of total 1-hexene converted to adamantanes/wt% (×).

lated to naphthalene and phenanthrene/anthracene, and a relative reduction in adamantanes. (The GC–MS/GC results at 164 h were very complex so that compositional data could be obtained only on an approximate indicative basin; cf. Table 1.)

At a treatment time of 4 h, increasing the 1-hexene treatment temperature to 673 K resulted in increased proportions of higher hydrocarbons, and only trace amounts of 1-methyladamantane and dimethyladamantane could be detected (indicative composition from a complex chromatogram: alkylbenzenes, medium; alkylindanes/indenes, medium; alkyldi- and tetrahydronaphthalenes, medium; alkylnaphthalenes, large; di- and tetrahydrophenanthrene/anthracene, small; alkylphenanthrenes/anthracenes, small; miscellaneous, small (alkylfluorenes, acenaphthene, acenaphthalene, alkylpyrenes); some black insoluble residue was also found).

With a treatment of 453 K/2 h only small amounts of 1-methyladamantane and dimethyladamantane could be detected. The GC–MS/GC results were very complex; the main product classes were (cyclo)alkanes/olefins, alkybenzenes, alkylcyclopentadienes, and very small amounts of various alkylhydronaphthalenes and alkylnaphthalenes.

Table 1 also contains data for the composition of evolved gaseous products obtained at 513 K/1 h and 513 K/28 h. Alkylbenzenes and (cyclo)alkanes/olefins were the main products and, in particular, no adamantanes were detectable in the gas phase.

The total residue content of the treated SAPO-34 increased with increasing treatment time, and Fig. 1 gives the data for treatment at 513 K.

4. DISCUSSION

Reaction Location and General Nature

The data for reaction at 513 K (Table 1, Fig. 1) show that the proportion of adamantanes in the retained residue increased rapidly from ca. 8 wt% of the residue for 1 h treatment time to ca. 36 wt% at 4 h, and thereafter increasing more slowly to ca. 42 wt% at 28 h, consistent with the adamantanes being nonprimary products and also consistent with the most probable reaction pathway (vide infra).

From data for the residue content of treated SAPO-34, the 1-hexene feed rate (0.27 $cm^3\ h^{-1}$, liq.; 0.18 $g\ h^{-1}$) and the quantity of SAPO-34 catalyst used per experiment (1 g), the fraction of total 1-hexene feed converted to admantanes may be calculated (Fig. 1). The values pass through a

maximum at an intermediate treatment time (4 h) at which there is also a discontinuity in the rate of increase in total residue content and a sharp reduction in the rate of increase in the proportion of adamantanes in the residue with treatment time (Fig. 1).

With an estimated average residue density of ca. 0.85 g cm^{-3}, the residue content at 513 K/4 h (9.7 wt%) corresponds to a residue volume of ca. 0.083 cm^3(g SAPO)$^{-1}$, which is ca. 26% of the total pore volume (0.32 cm^3 g^{-1}; O_2 physisorption (*1*)), so that ca. 74% of the total pore volume should have been free of residue. Nevertheless, N_2 physisorption measurements on 1-hexene-treated SAPO-34 gave values for the accessible fraction of total pore volume of only 34% (513 K/1 h) and 25% (513 K/28 h). Thus, although under these conditions the entire pore volume is not filled with residue, the latter is so located as to block access to much (ca. 2/3 for 513 K/28 h) of the nominally free pore volume.

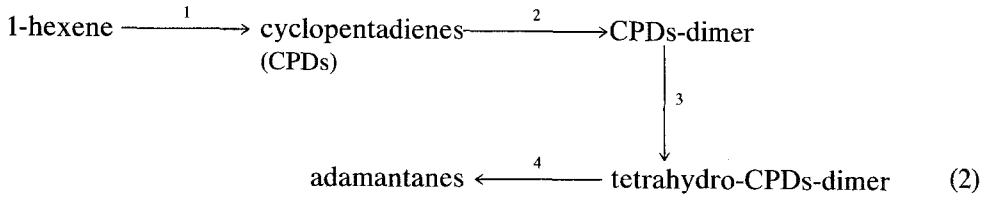
From the considerations outlined above we conclude that most or all of the adamantanes were formed from reactant which had entered the pores of the SAPO-34. While one cannot entirely rule out the possibility that some adamantanes may be formed at the external surface, the data suggest that this proportion cannot be large since the rate of increase of residue content with treatment time in the region <4 h was about ×60 that in the region >4 h.

Reaction Pathway

Tetrahydrodicyclopentadiene (endo) (*1*) is the standard precursor from which adamantane (*2*) is readily formed by acid-catalyzed isomerization (the adamantane position numbers are shown):

(1) (2) (1)

The isomerization reaction is a complex multistep process which has been elaborated mechanistically in considerable detail (*7, 8, 20*). Since (alkyl)cyclopentadienes have been identified as a substantial product class in the residue-forming reaction of 1-hexene on SAPO-34 (Table 1), it is reasonable to propose the generalized pathway



(2)

Using the formation of dimethyladamantane ($C_{12}H_{20}$) as an example, the overall reaction requires the loss of four hydrogens per dimethyladamantane formed. If 1-hexene is itself the hydrogen acceptor, the overall conversion is

$$4C_6H_{12} \rightarrow C_{12}H_{20} + 2C_6H_{14}. \quad (3)$$

From literature thermodynamic data (*21–23*), ΔG_f^0 for adamantane at 513 K is 433 kJ mol^{-1}, which leads to an estimated ΔG_f^0 at 513 K for dimethyladamantane of ca. 460 ± 10 kJ mol^{-1} and ΔG^0 at 513 K for reaction (3) of ca. −28 ± 10 kJ mol^{-1}.

We note that step 1 of reaction (2) (formation of cyclopentadienes from 1-hexene) is a process known to occur on at least some acidic zeolites (e.g., a major residue product class with H-ZSM5 at 453, 513 K (*4*)). The likely mechanism, involving cyclization from an alkylpentadienyl carbocation, has been discussed previously (*4*). Step 1 requires the formation of hydrogen acceptor coproducts and would contribute

to the alkanes which are found in both residue and gaseous products.

Following facile dimerization (step 2), the hydrogenation in step 3 is most reasonably represented by a Brønsted acid-mediated hydrogen donor/acceptor process of standard type involving hydride and proton transfers (*24*) (the two double bonds in the CPDs-dimer would be expected to be hydrogenated independently). Hydrogen donor products would be necessarily coproduced (e.g., alkylbenzenes).

With the mechanism proposed in reaction (2), the substituents on the product adamantanes relate directly to those on the alkylcyclopentadiene-dimer and tetrahydroalkylcyclopentadiene-dimer precursors. The alkyladamantane substituents are, in fact, limited to methyl and ethyl (monomethyl and dimethyl dominant), despite the expected presence of a wide spectrum of potential alkylating agents derived from olefins (1-hexene with its oligomerization/cracking products). Although alkylcyclopentadienes with 3–6 carbon atoms in alkyl substituents are abundant in the retained residue, only 1–3 carbon atoms in alkyl substituents are carried through into the adamantanes. We suggest that this limitation is size/shape selective in origin.

Size/Shape Selectivity Effects

SAPO-34 has a structure closely similar to that of chabazite zeolite (*1*), and a comparison of X-ray data (*25*) shows that *d*-values for the main diffraction peaks for SAPO-34 are smaller than those of chabazite by an average of only 0.74%. The free intercage window diameter in SAPO-34 is estimated at 0.43 nm from the use of molecular probes (*1*), while in chabazite the value is reported at ca. 0.4 nm (*7, 8, 26*).

As reported for chabazite (*26–29*), the main pore structure consists of elongated cages linked via the eight-ring intercage windows, there being six windows per cage. The cage is roughly circular in cross section, slightly waisted toward the middle, and with free internal dimensions of length

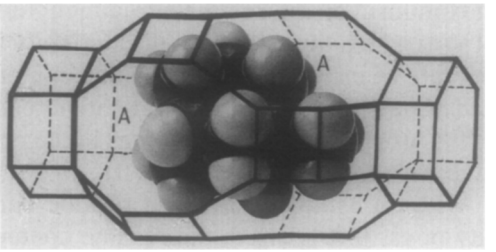


FIG. 2. Molecule of 1-methyladamantane in cage of SAPO-34. The cage outline represents the free internal dimensions which have been taken to be the same as those of chabazite (*29*), and the molecule is on the same scale. Two of the six intercage windows are marked A.

ca. 1.0 nm and minimum diameter (at the waist) of 0.66 nm (cf. Fig. 2). The relatively small windows allow the passage of straight-chain hydrocarbons, but not those with chain branching or cyclic structure. On the other hand, the cage size is large enough for fairly bulky molecules to be accommodated. The cage can thus function as an ultramicroreactor into which a straight-chain hydrocarbon reactant can enter but from which any non-straight-chain product cannot escape. We suggest that this very long effective residence time assists in the occurrence of the complex sequence of reactions which ultimately lead to the adamantanes.

All of the methyl-, dimethyl-, and ethyladamantane isomers we have observed have dimensions which allow one such molecule (but not more than one) to fit into a cage. We have estimated van der Waals molecular dimensions from measurements on Catalin models, applying a small flat correction (reduction) of 0.04 nm to the measured values (this correction was obtained as the difference between Catalin measurements and known molecular kinetic diameters (*30*) for a series of alkylbenzenes). On this basis, with the molecule in the most favorable orientation for accommodation in the cage, molecular dimensions were obtained as the maximum values in three orthogonal directions (the direction for the

largest dimension lying in the direction of the cage length). The following values were obtained (cf. the adamantane structure in reaction (1) for position numbering): adamantane, 0.62 × 0.60 × 0.56 nm; 1-methyl, 0.71 × 0.60 × 0.56 nm; 2-methyl, 0.73 × 0.56 × 0.56 nm; 1,3-dimethyl, 0.74 × 0.60 × 0.58 nm; 1,2-dimethyl, 0.72 × 0.62 × 0.58 nm; 1,4-dimethyl, 0.76 × 0.65 × 0.60 nm; 1,4′-dimethyl, 0.84 × 0.60 × 0.57 nm; 2,2′-dimethyl, 0.71 × 0.56 × 0.56 nm; 1-ethyl, 0.82 × 0.60 × 0.56 nm; 2-ethyl, 0.79 × 0.61 × 0.56. Examination of molecular models also shows that the likely reaction intermediates and transition states involved in the formation of adamantane and its methyl and dimethyl derivatives (*11, 20*) can be accommodated in SAPO-34 cages. There is a very large number of possible trimethyladamantane isomers. We have not enumerated all of them, but it is clear that some will fit into a cage (e.g., 1,2,4′-trimethyl, 0.78 × 0.60 × 0.57 nm; 1,2,6′-trimethyl, 0.77 × 0.60 × 0.60 nm) while some will not fit (e.g., 1,3,5-trimethyl, 0.77 × 0.72 × 0.60 nm). It is reasonable to assume that the four observed trimethyl isomers (Table 1) could have had dimensions allowing their existence inside the cages.

We turn now to the formation of products related to the naphthalene and phenanthrene/anthracene systems. Although these products were absent at 513 K/4 h and 513 K/28 h, they occurred at significant levels for 513 K/164 h and 673 K/4 h. Some of these species could readily fit within the SAPO-34 cages (e.g., 2-methylnaphthalene, 2,6-dimethylnaphthalene) but some others of larger size could not (e.g., alkyl derivatives of phenanthrene and anthracene—the parent hydrocarbons are marginal cases). We therefore suggest that while much of this product probably occurred within the cages, some of the larger molecular species may have been formed on the external surface. The latter were, in any case, relatively minor constituents (cf. Table 1).

As recently demonstrated in detail for the reaction of 1-hexene on H-ZSM5 (*4*), Brønsted acid-catalyzed pathways leading to fused ring aromatics can be initiated from (alkyl)cyclopentadiene and from its dimer. Thus, both these intermediates which occur in reaction (2) could potentially lead to fused ring aromatics. Furthermore, the overall process (reaction (4)) for the formation of, for instance, dimethylnaphthalene ($C_{12}H_{12}$) from 1-hexene,

$$8C_6H_{12} \rightarrow C_{12}H_{12} + 6C_6H_{14}, \qquad (4)$$

where 1-hexene also functions as a hydrogen acceptor, is much more favorable than reaction (3) for the formation of dimethyladamantane ($C_{12}H_{20}$) (at 513 K: ΔG^0 reaction (4), -416 ± 10 kJ mol^{-1}; ΔG^0 reaction (3), -28 ± 10 kJ mol^{-1}).

Thus, two basically different reaction pathways are available to (alkyl)cyclopentadiene and its dimer: one path leads via the dimer and its tetrahydro derivative to adamantanes; the other leads to fused ring aromatics (with mechanistically distinct paths proceeding in parallel from monomer and dimer (*4*)). Clearly, pathway selection (fused ring aromatics vs adamantanes) is kinetically not thermodynamically controlled, with fused ring aromatic formation presumably having a considerably higher activation energy than that for adamantanes, so the former become significant products only at higher temperatures (e.g., 673 K), or at lower temperature and very long reaction time (e.g., 513 K/164 h).

Finally, we address the question of the apparent specificity of SAPO-34 (and by inference possibly chabazite itself) for the formation of adamantanes. (Alkyl)cyclopentadienes were dominant residue components from the treatment of H-ZSM5 with 1-hexene at 453 K/30 min and 513 K/30 min (*4*), but no evidence for adamantanes could be found under these conditions, nor at 513 K/3 h and 673 K/2 h (*31*), although at ≥593 K fused ring aromatics were formed, mainly on the external surface. Furthermore, no adamantanes could be detected in the retained residue from the treatment of

ultrastable Y-zeolite with 1-hexene at 513–673 K (*31*).

Adamantane and its monomethyl, dimethyl, and ethyl derivatives are small enough to be accommodated in the channels of H-ZSM5, particularly at channel intersections, and examination of molecular models shows that this is also true for the likely reaction intermediates (*11, 20*) and probably true for the transition states. Thus, in comparison with the ready formation of adamantanes from (alkyl)cyclopentadienes in SAPO-34 cages at 513 K, (i) why were none formed within H-ZSM5 channels at 513 K and (ii) even if the formation of the adamantanes was sterically inhibited in the H-ZSM5 channels, why were none formed at the external surface of H-ZSM5 or in the large cages of ultrastable Y-zeolite, where size/shape selectivity factors would not operate?

It is very improbable that the enhanced activity of SAPO-34 for the formation of admantanes is an acidic strength effect, since the acidic strength of SAPO-34 is somewhat lower than that of H-ZSM5 (*1, 32*). Even so, the acidity of SAPO-34 is sufficient to convert methanol to lower olefins (*3, 33*), and the present work has shown that it is also capable of some conversion of olefins to aromatics: both of these reactions are well known for H-ZSM5.

We suggest that the exhanced activity of SAPO-34 cages for formation of adamantanes lies with size/shape coincidence between the host environment (i.e., the SAPO-34 cage) and the guest molecule. Adamantanes are very compact molecules. Those of present interest are of roughly ellipsoidal shape, and there is a striking spacial coincidence between guest and host (Fig. 2). We propose that this very close host/guest (product) spacial coincidence also operates to a sufficient extent when the guest is the transition state for the rate-controlling step, for the energy of the transition state to be lowered enough for considerable rate enhancement to occur.

In effect, this proposal is an application of the concept of enzyme–substrate (transition state) complementarity which is well accepted in enzyme chemistry (*34, 35*). However, we believe this is the first case in which there is reasonably plausible evidence for its applicability to a nonenzymatic catalytic system.

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