Isomerization of cyclohexane and hexane over silica- embedded triflate derivatives catalysts

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Abstract

Isomerization of cyclohexane and hexane over silica-embedded tert-butyldimethyl-silyltrifluoromethanesulfonate and lanthanum triflate is reported. Immobilization of these triflate derivatives was found to give materials exhibiting at least similar catalytic performances to the free molecules. Using these catalysts, the reactions occured at considerably lower temperatures than those prevailing in industrial processes. The catalysts could be recovered and reused. Traces of water had a favorable influence on the reaction, but led to more cracking to isobutane. Larger amounts of water caused catalyst deactivation.

Keywords: Isomerization, cyclohexane, hexane, silica-embedded triflate, catalyst

Introduction

The use of strong acid catalysts in organic synthesis was introduced by the work of Friedel and Crafts[1] in alkylation of aromatic hydrocarbons. Afterwards, Nenitzescu[2] was the first who reported the isomerization of paraffins over the same kind of catalysts. He showed that aluminum chloride was able to isomerize hexane in the presence of traces of water.

Since then, isomerization of n- and cyclo-paraffins has found an increased interest because of practical applications mainly in the refinery and petrochemical industry, but also for the

synthesis of fine chemicals. Most interesting to industry are the processes, which lead to the formation of the more highly branched, higher octane and dimethylbutane isomers. The development of the process followed two directions, the one in heterogeneous catalysis and the other one in homogeneous catalysis. Because these reactions are favored at low temperatures, catalysts active at low temperatures are desirable. In heterogeneous catalysis, bifunctional Pd/ or Pt/zeolite catalysts are known to give high isomerization selectivities at medium conversions and are the most common n-alkane hydroconversion catalysts.[3-5] Pt supported on mesoporous aluminosilicate MCM-41 materials were also found to exhibit catalytic activity in this reaction.[6]

More recently, other new solid acid materials have been reported to be active catalysts in this reaction even at temperatures lower than 520 K, which is typical for Pt/zeolites. Sulfated zirconias have been investigated mainly as catalysts for the acid catalyzed isomerization of light alkanes at relatively low temperatures.[7,8] The most active catalyst in this family is sulfated zirconia doped with Fe and Mn oxides. This catalyst is able to operate n-butane isomerization above room temperature,[9,10] but it quickly deactivates. Addition of Pt to sulfated zirconia increases the time stability.[11] Bifunctional Pt/WO_3-ZrO_2 and Mo carbides were also reported as selective catalysts for isomerization of paraffins.[12-15]

In homogeneous catalysis, the liquid superacids based on HF are very effective catalysts, able to carry out selectively this reaction at room temperature.[16, 17] Trifluoromethanesulfonic acid was also reported as an efficient homogeneous catalyst for this reaction. It was tested in butane,[18] isobutane,[19] and 3-methylpentane[20] isomerization.

Both kinds of processes have some inconveniences. Heterogeneous catalysts require rather high temperatures while most of the homogeneous catalysts are active even at low temperature but they are very corrosive and not easily recoverable. Therefore, a logical solution might reside in some hybrid catalysts resulting from the immobilization of these active compounds. But the insertion of solid superacids such as SbF_5 into graphite[21] or its deposition on SiO_2[22] led to catalysts which easily deactivate.

The aim of this paper is to present results of the isomerization of hexane and cyclohexane on new hybrid catalysts resulting from the embedding of triflate derivatives in silica using a sol-gel procedure.

Results and Discussion

Figure 1 shows the conversion of cyclohexane over silica-embedded tert-butyldimethylsilyltrifluoromethanesulfonate catalysts (BDMSTFMS) (series A1-A4) after 2 h of reaction as a function of temperature. An increase of temperature leads to an increase of conversion. The selectivity was 100%, no other reaction products than methylcyclopentane being identified. The dependence of the yield on the reaction time is in concordance with the thermodynamics of the system. A similar dependence was determined for the silica-embedded

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lanthanum triflates (series B1-B4), except that these catalysts were less active than the similarly prepared BDMSTFMS catalysts (Figure 2).

The conversion-time curves of Figure 3 show that, even after 4 h of reaction, the conversions stay quite low. In the absence of boundary layer and inter- and intraparticle diffusional influences, the conversion of cyclohexane, determined for levels smaller than 12%, indicates that the isomerization of cyclohexane over these catalysts followed the requirements of Bassett-Habgood[23] kinetic treatment for first order reaction rate kinetic processes in which the rate-determining step is the surface reaction. The pores of these materials are large enough (about 2 nm) as to cause any mass transfer limitation. Table 1 gives the calculated apparent rate constants.
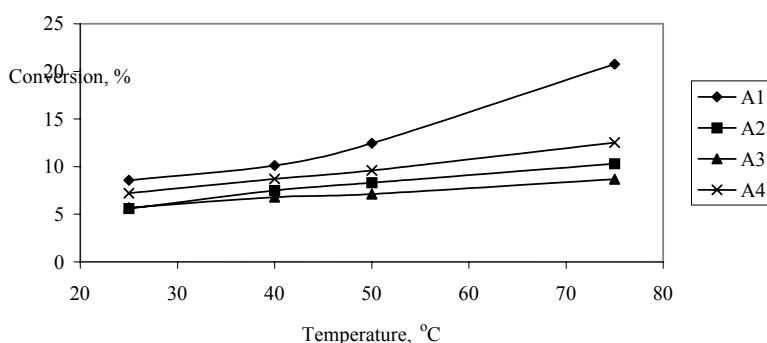
Figure 1. Variation of the conversion of cyclohexane with reaction temperature (30 mg catalyst, 10.1 g cyclohexane, 2 h, 800 rpm).

Table 1. Apparent rate constant (k_a) at 300 K

Catalyst	Apparent rate constant ($k_a \times 10^5$ h^{-1}) at 300 K	
	Series A	Series B
1	8.23	4.86
2	4.54	1.70
3	3.75	2.44
4	6.05	3.12
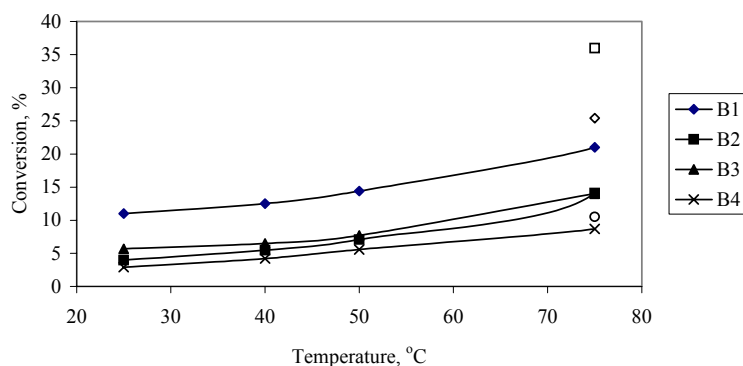
Figure 2. Variation of the conversion of cyclohexane with reaction temperature (30 mg catalyst, 10.1 g cyclohexane, 4 h, 800 rpm; ◊-B1, □-B2, and o-B4 catalysts with 90 mg H_2O).

Separate catalytic tests were carried out in homogeneous conditions over pure triflate derivatives, using the same amount of triflate as in embedded catalysts. They exhibit a different catalytic behavior, intermediate between the catalysts 1 and 2-4. For pure BDMSTFMS at 25 $^{\circ}$C and after 2 h of reaction, the conversion was about 5% in the absence of water, and 8.7% in the presence of 90 mg water. It is worth to note that in the presence of water, cracking to isobutane amounted to 4.7%, in perfect agreement with previous data obtained over silica-supported aluminum chloride.[24] At 75 $^{\circ}$C, the conversion increased at 12.9% in the absence of water and at 22.4% in the presence of 90 mg H_2O. Lanthanum triflate was less active. At 75 $^{\circ}$C and after 4 h, the conversion was about 16% but in the presence of 90 mg water. At room temperature, no conversion of cyclohexane was detected on this catalyst.

The behavior of the immobilized catalysts was a heterogeneous one. The liquor separated after 4 h reaction remained untransformed for another 4 h reaction.
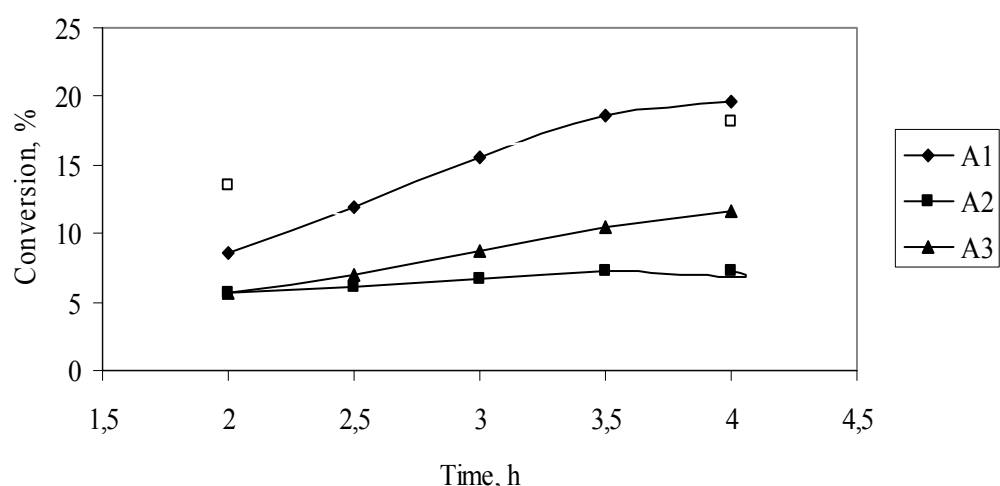
Figure 3. Variation of the conversion of cyclohexane with reaction time (30 mg catalyst, 10.1 g cyclohexane, 25 $^{\circ}$C, 800 rpm, -catalyst A2 with 90 mg H_2O).

As shown above, the addition of a very small amount of water (90 mg) had a positive effect on the reaction. The conversion of cyclohexane to methylcyclopentane was improved, irrespective of the reaction conditions used (Figures 2 and 3). For pure lanthanum triflate derivatives, the increase of the conversion caused by the addition of water was very small, cca. 1%. It is worth to note that the embedded catalysts were not altered by the addition of a small amount of water. Reuse of the catalysts gave the same catalytic performances. NH_3-FTIR spectra indicated the presence of Lewis acid sites as inferred from a band at 1611 cm^{-1}, but also of Brønsted acid sites (bands in the range 1460-1490 cm^{-1}). The bands at 1784-1782 and 1750-1747 cm^{-1} are assigned to imine groups resulting from the same ammonia chemisorption (Figure 4). The band at 1460-1490 cm^{-1} may indicate that a limited part of the triflate-derivative is hydrolyzed, leading to chemisorbed triflate. The sensibility of triflates to moisture is well known.[25] An increase of the water content to 10 mmoles caused the catalysts deactivation.
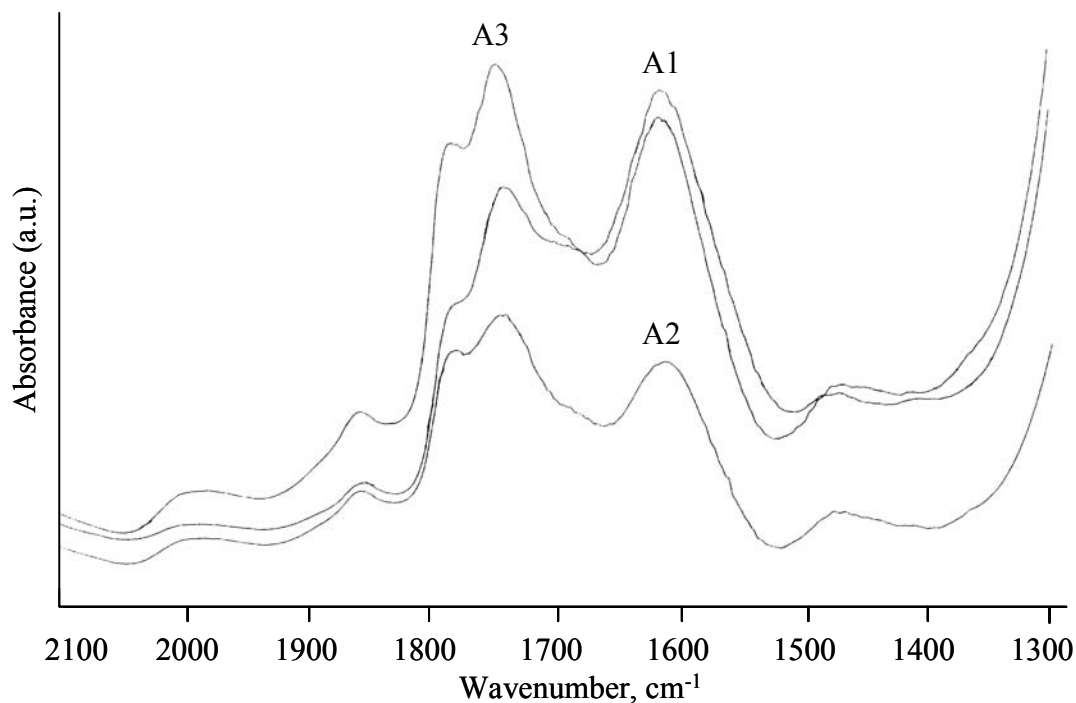
Figure 4. NH$_3$-FTIR spectra of A catalysts at 100 ^{o}C.

    The catalytic tests using catalysts pre-calcined at 300 ^{o}C to remove the surfactant indicated a slightly lower activity than the non-calcined catalysts. This temperature was chosen according to results obtained from thermogravimetric analysis. Figure 5 illustrates such a behavior for B catalysts. The addition of water also improved the catalytic activity. The structural investigation using FTIR, ^{13}C-NMR and XPS suggested that the triflate derivatives were not decomposed under these conditions (Table 2). *The* XPS F/S ratio was near 3 in all the investigated embedded-triflates, which is in a perfect agreement with those obtained by chemical analysis. The binding energies of sulfur and fluorine slightly increased in each series indicating more oxidized species. ^{13}C-CP/MAS NMR signals due to CF$_3$ were found <u>at</u> the same positions as for the pure triflates. The decrease of the conversion must be associated with some textural modifications caused by the surfactant decomposition. The calcined samples had surface areas about 15% smaller compared to the values given in Table 2, which might suggest that some pores were blocked by the surfactant decomposition.

Table 2. XPS, CP/MAS NMR and surface area characteristics of the investigated catalysts

Sample	Binding energy, eV			XPS F/S ratio	^{13}C-CP/MAS NMR signals due to CF$_3$, ppm	Surface area, m^2/g
	S$_{2p}$	F$_{1s}$	Si$_{2p}$			
A1	168.9	688.4	103.4	3.01	118, 123	483
A2	169.2	688.7	103.7	3.00	118, 123	461
A3	170.0	688.9	103.8	3.00	118, 123	412
A4	170.3	689.2	103.9	2.95	118, 123	572
B1	168.6	687.3	103.5	2.97	118, 123	421
B2	168.9	688.1	103.7	2.95	118, 123	357
B3	169.5	688.5	103.6	2.96	118, 123	312
B4	169.5	688.6	103.7	2.97	118, 123	468

As it was stressed above, an additional increase of the amount of water to 90 mg was not effective also for the calcined catalysts. Under such conditions a second aqueous phase started to be formed and the conversion was drastically decreased.
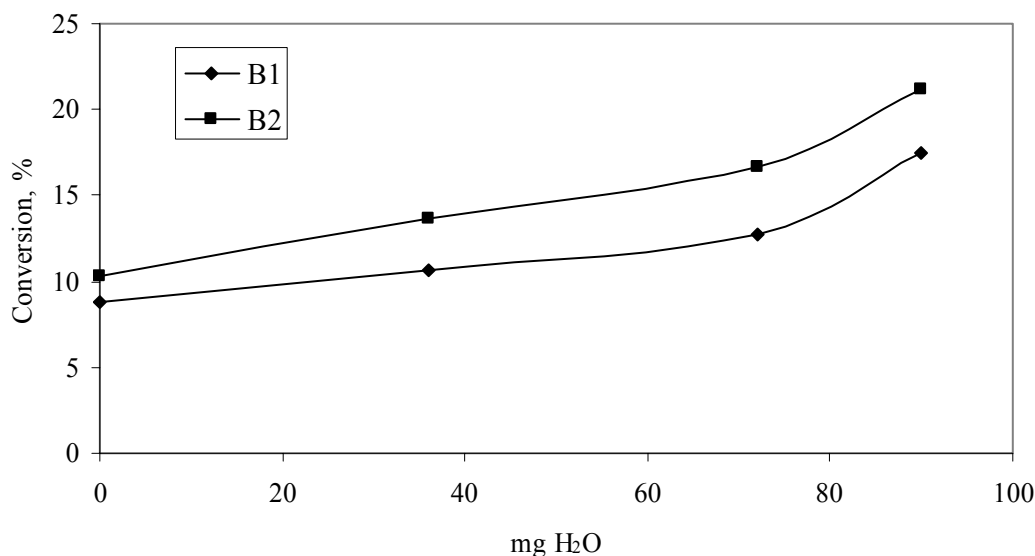
Figure 5. Variation of the conversion of cyclohexane as a function of water content for calcined catalysts (30 mg catalyst, 10.1 g cyclohexane, 4 h, 75 ^{o}C, 800 rpm).

Similar experiments were carried out using n-hexane. Isomerisation of hexane to 2- and 3-methylpentanes ocurreded only over the A catalysts, and in the range of temperatures used, the conversions were smaller than 5%, irrespective of the reaction conditions. For A1, the selectivities were as follows: 10.5% to 2-methylpentane, 6%-to 3-methylpentane, 42% to methylcyclopentane, and 41% to cyclohexane.

These data may account for a different reaction mechanism according to the molecule which is reacted. Schemes 1 and 2 describe the reaction pathways which may correspond to the reaction of cyclohexane and hexane on the investigated embbed triflates.

Scheme 1. The reaction mechanism in isomerization of cyclohexane.

For n-hexane, the ionic-radical mechanism[26] is more plausible (Scheme 2). Summarizing, the immobilization of triflate derivative catalysts on silica led to systems able to catalyze the skeletal isomerization of cyclohexane at temperatures much lower than reported for zeolites.[27] The system is comparable with silica-supported aluminum chloride[24] but it is environmentally more friendly. The difference of the catalytic reactivity between cyclohexane and n-hexane is not a thermodynamical one because the free Gibbs energies of the reactions are similar, about -1 kcal/mol in both cases. The reason of the reactivity might be related, as suggested by the reaction mechanism, to the different ionization potential of the two molecules. On the investigated catalysts, only cyclohexane is able to surpass this barrier, leading to reasonable conversions.

The differences among the investigated catalysts result from the nature of the triflate and its accesibility. It is worth to note that the conditions in which the immobilization is carried out may lead to higher performances than free triflate derivatives (see A1 and B1 catalysts). Traces of water improve the performances, reediting Nenitzescu chemistry.[2] Water was found to adsorb on these catalysts without altering the acid character. As proposed by Kobe at al. [28] for the isomerization of butane over sulfated zirconia catalysts, water may lower the energy barrier through which the catalytic cycle must proceed. Excessive catalyst hydration leads to the suppression of the catalytic activity very probably because of an extensive hydrogen bonding at the active sites.

Scheme 2. The reaction mechanism in isomerization of hexane.

Experimental Section

General Procedures. The analysis of the reaction products was made using a HP gas chromatograph, model 5890, series II equipped with a Chrompack capillary column. FTIR (Fourier Transform-Infrared Spectroscopy) spectra were recorded with a Bruker Equinox 55 instrument, equipped with KBr optics and a DTGS detector. Pure samples (15 mg) were pressed and placed inside a commercial temperature-controlled environmental chamber and evacuated at 10^{-5} bar. Ammonia was introduced in this chamber at 50 mbar and the spectra were recorded at room temperature, 100, 250 and, 300 °C. The XPS (X-ray Photoelectron Spectroscopy) spectra were obtained with a SSI X probe FISONS spectrometer (SSX -100/ 206) with monochromated Al-Kα radiation. The spectrometer energy scale was calibrated using the $Au_{4f_{7/2}}$ peak (binding energy of 84.0 eV). For the calculation of the binding energies, the C_{1s} peak of the C-(C,H) component at 284.8 eV of adventitious carbon was used as an internal standard. The composite peaks were decomposed by a fitting routine included in the ESCA 8,3 D software. The surface

composition of the investigated samples was determined using the same software. The F_{1s}, S_{2s}, Si_{2p}, La_{3d}, and O_{1s} peaks were investigated. Solid-state ^{13}C CP/MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer, equipped with a double-bearing probe. The rotor (7 mm internal diameter) was charged with the samples and sealed by a Kel-F inset. The optimal contact time for ^{13}C cross-polarization was 2-3 ms. The spinning rate was between 2 and 4 kHz. The external standard for ^{13}C NMR was adamantane [δ (CH$_2$)= 38.40, relative to tetramethylsilane]. Thermal curves were recorded using a SETARAM TGA 92.16.18 equipment. The samples in an amount of 40 mg were heated in a high purity helium stream (Air Liquide) from room temperature to 500 ^{o}C at a heating rate of 5 ^{o}C min^{-1}.

Materials. Tert-butyldimethylsilyltrifluoromethanesulfonate was of Gelest quality, while all others materials (products, chemicals) had Aldrich quality.

Reaction procedure. Standard experiments were carried out between room temperature and 75°C using 30 mg catalyst and 120 mmoles cyclohexane, for reaction times up to 4 h. Water was added in some experiments in amounts up to 10 mmoles. The experiments were carried out in a 25 ml round-bottom flask with an attached condenser, where the mixture was vigorously stirred (800 rpm). After the test, the catalyst was separated and the solution was kept under reaction conditions for another 4 h. The separated catalyst was reused in a new reaction. Conversion was expressed as total percent isomerization of cyclohexane and hexane.

Catalysts A. Tert-butyldimethylsilyltrifluoro-methanesulfonate (BDMSTFMS) is only soluble in carbon tetrachloride and triethylamine. The sol-gel synthesis was carried out in inert atmosphere (Ar), using an adapted route in which the silica sol was obtained by acid hydrolysis of a solution of tetraethoxyorthosilicate (TEOS). Water was then added to the acidic solution in a TEOS : H$_2$O molar ratio of 1:10 (samples A1 and A2) or 1:4 (sample A3), and the mixture was refluxed at 70°C for 2 h. After cooling the silica sol solution at room temperature, the silyl-triflate derivative was added under vigorous stirring as a 0.3 M solution in CCl$_4$ (samples A1 and A3) or as such (sample A2). Hexadecyltrimethylammonium bromide (as a surfactant) was then introduced and the gelation was carried out at 90 ^{o}C for two days in a teflon cylinder within an autoclave (samples A2 and A3), or at room temperature for 6 days (sample A1). The resulting gel was dried under vacuum, first at room temperature for 24 h and then at 100 ^{o}C for 6 h. Sample A4 was obtained following the same procedure as for A1 except for the fact that no surfactant was added. Samples with 15 wt% BDMSTFMS were obtained.

Catalysts B. The immobilization of lanthanum triflate (LaT) was made in the same way, except that the solvent was ethanol (samples B). Samples with 15 wt% LaT were prepared.

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