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**Use of Different Microporous and Mesoporous Materials
as Catalyst in the Diels Alder and Retro-Diels Alder Reaction
Between Cyclopentadiene and *p*-Benzoquinone. Activity of Al-
, Ti- and Sn-Doped Silica**

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Abstract

Diels Alder cycloaddition between cyclopentadiene and *p*-benzoquinone has been studied using amorphous silica and different ITQ-2 and MCM-41 pure silica and metal containing materials as catalysts. The reaction can afford different products depending on the molecular reacting site, and the possibility of consecutive additions. Structured solid catalysts increase the selectivity to the *endo-endo* isomer. Silanol groups have not enough Brönsted acidity to interact with the carbonyl groups present in the dienophile, to reduce LUMO's energy and provide a better overlap between HOMO and LUMO, according to the frontier molecular orbital theory.

The introduction of transition metal atoms in the framework increases the reaction rate for the Diels-Alder reaction while preserving the selectivity to the *endo-endo* isomer. The presence of more acidic OH groups enhance the retro Diels-Alder reaction increasing the selectivity to the *endo-exo* isomer.

Keywords: Diels Alder reaction; ITQ-2; MCM-41; amorphous silica; Brönsted acid

Introduction

The Diels-Alder is an orbital-controlled pericyclic reaction which is generally carried out with an electron-rich 1,3-diene and an electron-deficient dienophile. Different procedures have been described to increase the reaction rate of Diels-Alder reaction, and involve the use of homogeneous Lewis acids [1], heterogeneous acids [2], high pressures [3] and water as a solvent [4].

Micro and mesoporous molecular sieves can strongly enhance the rate of bimolecular reactions by combining the spatial confinement of the reactants which decrease the reaction frequency factor, and the presence of catalytic active sites which decrease the activation energy [5-6]. Moreover, when these materials are used as catalysts, their pore dimensions and topology can also influence product selectivity. It is then not surprising that molecular sieves have been used as catalysts for Diels-Alder reactions (DAR) [7-14]. However in many cases the activity of microporous molecular sieves for DAR can be strongly limited by the diffusion of reactants, and products.

In this work, we have made use of a delaminated zeolitic materials (ITQ-2) that combine high external surface with the presence of “cup like“ cavities open to the exterior [15], as well as mesoporous molecular sieves to carry out DAR between cyclopentadiene, and *p*-benzoquinone which can generate several reaction products with different shapes and sizes. The reaction has been performed with the pure silica materials, in order to see the effect of the adsorption-concentration on reaction rate, as well as with the same materials containing Lewis or Brønsted acid sites. The results are compared with those obtained under homogeneous conditions by thermal activation.

Experimental Section

Catalyst preparation

Aerosil was supplied by Degussa. ITQ-2 zeolites [pure silica ITQ-2, ITQ-2 (Ti), and ITQ-2 (Al)] were prepared and characterized according to the procedures described in the literature [16-17]. MCM-41 catalysts [pure silica MCM-41 of 40 and 24 Å, MCM-41(Sn), MCM-41(Ti) and MCM-41(Al)] were hydrothermally synthesized and characterized according to the procedures in the literature [18-21], using hexadecyltrimethylammonium bromide as a template, aerosil as silica source, and TiO₄, SnCl₄ or Al₂O₃ as sources of heteroatoms.

Catalytic tests

After being activated under vacuum at 250° C, 250 mg of the corresponding calcined material were introduced in a two necked bottom flask under N₂. Immediately after, 108 mg of *p*-benzoquinone (1.0 mmol) and 10.0 mL of CDCl₃ were added. The mixture was stirred at room temperature for a few minutes and 0.2 mL of freshly distilled cyclopentadiene (3.0 mmol) were added via syringe. Then, it was heated at 60 ° C and samples were taken every hour, being directly analysed by ¹H NMR.

Reaction products were isolated by HPLC using mixtures H₂O:MeOH:MeCN (45:50:5). Identification of these products was carried out by NMR techniques (¹H, ¹³C, DEPT, COSY, HETCOR and NOE) being spectral data fully coincident with literature [22].

Conversion values for *endo-endo* and *endo-exo* products are always referred to conversion to the *endo* adduct.

Results and Discussion

In *Figure 1* the yields to the different products at different levels of conversion are given.

<Figure 1>

The shape of the curves indicate that the primary DAR gives the *endo* isomer that very rapidly reacts with a second molecule of cyclopentadiene to give specially the *endo-endo* isomer. Under our reaction conditions, we have not detected the *exo* isomer neither the secondary *exo-endo* and *exo-exo* products.

From these results, the reaction network given in *Scheme 1* can be written:

<Scheme 1>

It should be remarked that even though the *exo* DA isomer is more stable than the kinetically controlled *endo*, the second was the only one formed, and no any other product was detected by ^1H NMR.

Influence of catalyst adsorption/confinement

As we have seen the DAR between cyclopentadiene and *p*-benzoquinone can take place thermally without requiring a catalyst. However the rate of the reaction could be increased by introducing a high surface area solid which may increase the rate of the reaction by concentrating the reactants on the surface. This effect should be enhanced if the solid has pores and cavities that can confine the reactants and further decrease the entropy of the activated complex, while influencing product selectivity. In order to check that, we have selected three materials:

a) Silica aerosil which has $200\text{ m}^2\text{g}^{-1}$, all corresponding to external surface area and with no confinement effect.

b) A mesoporous molecular sieve of the MCM-41 type with two different pore diameters.

c) A delaminated zeolited material with well structured high external surface area formed by “cup like” cavities of $\sim 0.7 \times 0.8$ nm.

The textural characteristic of these materials are given in *Table 1*.

<Table 1>

Reactivity results after 2 and 3 h reaction time, are given in *Table 2*.

<Table 2>

The results clearly show that the presence of silica does not increase conversion¹, neither has any effect on selectivity conversion is referred here to the second addition of cyclopentadiene, taking as starting material the endo product . On the other hand both pure silica MCM-41 samples increase conversion. Nevertheless, it appears that ITQ-2 gives a higher selectivity to the *endo-exo* isomer than MCM-41 or silica. This effect can be due to the presence of the “cups like” cavities at the external isomers.

At this point, there is another factor which has to be considered when discussing the observed conversion increase with ITQ-2 and MCM-41, and this is the presence of a large number of silanol groups on these materials. Indeed, the Si-OH can act as weak Brönsted acid sites which could interact with the carbonyl groups present in *p*-benzoquinone, reducing the energy of the LUMO and providing a better overlap between HOMO of cyclopentadiene and the LUMO of the benzoquinone. In order to check that possibility IR spectra of aerosil, MCM-41 and ITQ-2 in the 3600–3800 cm^{-1} region have been recorded, after activation in vacuum at 400°C, 10^{-4} Torr during 10 hours. The results given in *Figure 3* show that the intensity of the ~ 3745 cm^{-1} band

¹ Conversion values are referred to the second addition of cyclopentadiene, taking as a starting material the endo product

associated to silanol groups follows the order ITQ-2>MCM-41 (40 Å)>MCM-41 (24 Å)>>Aerosil.

<Figure 2>

From those results and those given in *Table 2* we can not find a direct correlation between the normalized intensity of the silanol groups absorbing at 3745 cm^{-1} , and the catalytic activity, indicating that the main catalytic effect of the pure silica solids should be related with a concentration and confinement effect on the surface of the structured catalysts.

Catalyst recycling was studied with pure silica MCM-41 (40Å). Results in Figure 3 show that some deactivation occurs after repeated recycling. It is worth noting that while conversion decreases, no changes in selectivity were observed.

<Figure 3>

Introduction of Lewis and Brönsted acid sites in the solids

The presence of homogeneous Lewis acids has been shown to catalyze the DAR [1], by modifying the energy levels of the reagents, usually the dienophile, by complexation with the carbonyl group. Thus, we have prepared Ti-ITQ-2 [23], and Ti [21] and Sn [20] MCM-41.

The results presented in *Figures 4 and 5* clearly show the catalytic effect of Ti and Sn, which by being tetrahedrally coordinated in those materials [24] act as Lewis acid sites for the DAR.

<Figure 4a>

<Figure 4b>

<Figure 5a>

<Figure 5b>

While the above results look quite straight forward, an interesting observation can be made from the kinetic curves (see *Figures 4 and 5*) at long reaction times. It can be seen there that the selectivity to the *endo-endo* and *endo-exo* decreases and increases respectively when the reaction is prolonged for longer times, being this effect more notorious with Sn- than with Ti-MCM-41. This effect can be explained by considering that the retro-Diels-Alder reaction (retro-DAR) occurs with Ti-MCM-41 and, specially, with Sn-MCM-41.

The retro-Diels–Alder is a competitive reaction of DAR, and from the point of view of the frontier molecular orbital theory, they both assemble. Thus, the retro-DAR is affected by the same reaction and catalyst variables than DAR. However, Wijnen and Engberts [4b] have shown that H₂O, can promote the retro-DAR with respect to DAR by acting as a hydrogen-bond-donating agent. Taking this into account we speculate that the hydroxyl group in Sn-OH by having a higher positive density on the hydrogen than in Ti-OH or Si-OH, should promote better the retro-DAR. This effect is represented in *Figure 6*.

<Figure 6>

As it can be seen there, initially the *endo* monoadduct isomer formed in the first DAR reacts with a second cyclopentadiene molecule to provide the *endo-endo* isomer (1). This process occurs very fast, even thermally, giving a high yield of the *endo-endo* and a low yield of the *endo-exo* isomer. However when the more acidic Sn-OH group is present, the above step is “reversible” (2) due to the retro-DAR, and consequently the monoadduct is regenerated. Then, even if the formation of the *endo-exo* requires a higher activation energy, the *endo-exo* product is more stable than the *endo-endo*, and consequently the retro-DAR of the *endo-exo* is much slower. This phenomena will result in a selectivity increase of the *endo-exo* isomer with reaction time.

If all the above is true, we should expect that by increasing further the positive density of charge on the hydrogens in OH groups i.e. increasing the Brönsted acidity, the rate of the retro-DAR should increase, increasing therefore the selectivity to the *endo-exo* isomer. As it is well known, stronger Brönsted acid sites can be generated in silicates by introducing aluminium in framework positions. When this was done in ITQ-2 and MCM-41, the results presented in *Figure 4* and *5* show that the Al containing samples not only strongly increase conversion, but the selectivity to the *endo-exo* isomer is much enhanced with reaction time, in agreement with an improvement on the rate of the retro-DAR.

Conclusions

We have shown that while aerosyl does not have any effect on the DAR between cyclopentadiene and *p*-benzoquinone, a pure silica delaminated zeolitic ITQ-2 and structured mesoporous MCM-41 materials strongly increase the reaction rate due to an adsorption-confinement effect of the reactants. Silanol groups appear to play a minor, if any, catalytic role. It is noticeable that by decreasing the pore diameter of the MCM-41 an increase in conversion occurs, which should be due to a further molecular confinement.

Tetrahedrally coordinated Ti and Sn catalyze the DAR, strongly increasing the reaction rate. The presence of Ti and more so Sn, catalyze the retro-DAR resulting in an increase of the selectivity to the *endo-exo* isomer with time. This effect is related with the presence of more acidic Sn-OH groups. Indeed, when stronger Brönsted acid sites were generated by introducing framework Al, the retro-DAR was much faster and the selectivity to the *endo-exo* isomer increased by a factor of four.

Highly accessible delaminated zeolitic and mesoporous molecular sieve materials with either Brönsted or Lewis acid sites are excellent catalysts for DAR.

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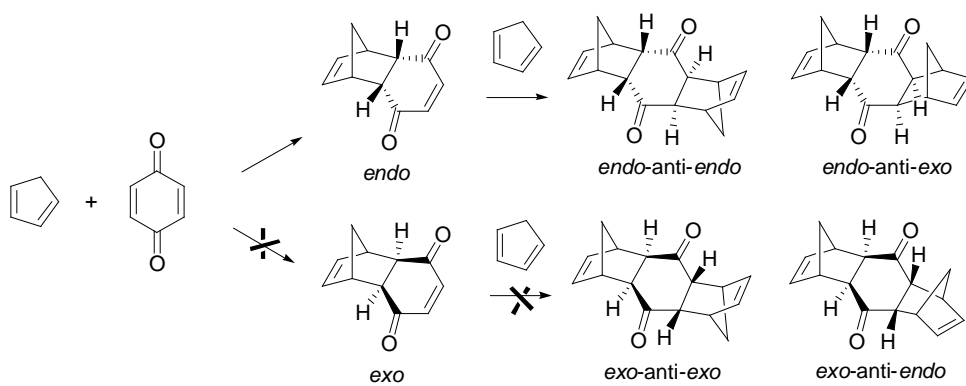
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References

- [1] (a) S. Yamabe, T. Dai, T. Minato, *J. Am. Chem. Soc.* 117, (1995), 10994. (b) C. Cativiela, J. M. Fraile, J.I. Garcia, J.A. Mayoral, E. Pires, A.J. Royo, F. Figueras, L.C. de Menorval, *Tetrahedron*, 49(19), (1993) 4073.
- [2] (a) C. Cativiela, J.M. Fraile, J.I. Garcia, J.A. Mayoral, F. Figueras, L.C. de Menorval, P.J. Alonso, *J. Catal.* 137, (1992), 394. (b) F. Figueras, C. Cativiela, J. M. Fraile, J.I. Garcia, J.A. Mayoral, L.C de Menorval, E. Pires, *Studies in Surface Science and Catálisis 83 (Zeolites and Microporous Crystals)*, (1994), 391.
- [3] G. Isaacs, *Chem. Ber.*, 1987, 47.
- [4] (a) D.C. Rideout, R. Breslow, *J. Am. Chem. Soc.* 102, (1980), 7816. (b) J.W. Wijnen, J.B.F.N. Engberts, *J. Org. Chem.* 62, (1997), 2039.
- [5] A. Corma, *J. Catal.* 216(1-2), (2003), 298.
- [6] A. Corma, H. García, *Chem. Rev.* 103(11), (2003), 4307.
- [7] C. Cativiela, F. Figueras, J.M. Fraile, J.I. Garcia, J.A. Mayoral, L.C. de Menorval, E. Pires, *Appl. Catal. A: General* 101(2), (1993), 253.

- [8] J. Kang, J. Rebeck, *Nature* 50, (1997), 385.
- [9] E. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* 119, (1997), 4117.
- [10] M. Osaka, Y. Ryota, *Chem. Lett.* 1998, 259.
- [11] T. Kugita, M. Ezawa, T. Owada, Y. Tomita, S. Namba, N. Hashimoto, M. Osaka, *Microp. Mesop. Mater.* 44-45, (2001), 531.
- [12] T. Kugita, S.K. Jana, T. Owada, N. Hashimoto, S. Namba, *Appl. Catal. A: General* 245, (2003), 353.
- [13] A. Satsuma, Y. Segawa, H. Yoshida, T. Hattori, *Appl. Catal. A: General* 264, (2004), 229.
- [14] A. Corma, *Catal. Rev. Sci. Eng.* 46(3 & 4), (2004), 369.
- [15] (a) A. Corma, V. Fornes, S.B. Pergher, Th.L.M. Maesen, J.G. Buglass, *Nature (London)* 396(6709), (1998), 353. (b) I. Rodríguez, M.J. Climent, S. Iborra, V. Fornes, A. Corma, *J. Catal.* 192(2), (2000), 441.
- [16] A. Corma, U. Diaz, V. Fornes, J. M. Guil, J. Martinez-Triguero, E. J. Creyghton, *J. Catal.* 191(1), (2000), 218-224.
- [17] A. Corma, U. Diaz, V. Fornes, J. L. Jorda, M. Domine, F. Rey, *Chem. Commun.* 9, (1999), 779.
- [18] A. Corma, Q. Kan, M.T. Navarro, J. Perez-Pariente, F. Rey, *Chem. Mater.* 9(10), (1997), 2123
- [19] A. Corma, J.L. Jorda, M.T. Navarro, J. Perez-Pariente, F. Rey, *Proc. Int. Zeolite Conf.*, 12th 3, (1999), 817.
- [20] A. Corma, M.T. Navarro, L. Nemeth, M. Renz, *Chem. Commun.* 21, (2001), 2190.

- [21] T. Blasco, A. Corma, M.T. Navarro, J. Perez-Pariente, *J. Catal.* 156 (1), (1995), 65.
- [22] P. Yates, K. Switlak, *Can. J. Chem.* 68, (1990), 1894.
- [23] A. Corma, U. Diaz, V. Fornes, J.L. Jorda, M. Domine, F. Rey, *Chem. Comm.* 9, (1999), 779.
- [24] P. Atienzar, A. Corma, H. Garcia, J.C. Scaiano, *Chem. Mat.* 16(6), (2004), 982.



Scheme 1. Distribution of products in the Diels-Alder reaction between cyclopentadiene and *p*-benzoquinone

Table 1. Textural characteristic of the studied all silica materials.

<i>Catalyst</i>	<i>Area (m²g⁻¹)</i>	<i>Pore Volume (cm³g⁻¹)</i>	<i>Pore Diameter (Å)</i>
<i>Aerosil</i>	200	-	-
<i>ITQ-2</i>	884	0.5957	-
<i>MCM-41 (40 Å)</i>	960	0.92	40
<i>MCM-41 (24 Å)</i>	1216	0.64	24

Table 2. Conversion and selectivities for all silica materials at times 2 and 3 h. Those values are referred to the *endo* isomer as starting material (*exo* isomer in not detected).

<i>Catalyst</i>	<i>Reaction Time (h)</i>					
	2			3		
	<i>Conversion</i> (%)	<i>Selectivity (%)</i>		<i>Conversion</i> (%)	<i>Selectivity (%)</i>	
		<i>endo-endo</i>	<i>endo-exo</i>		<i>endo-endo</i>	<i>endo-exo</i>
<i>Thermal</i>	61.9	88.0	11.9	70.0	91.4	8.6
<i>Aerosil</i>	52.1	88.7	11.3	65.19	90.6	9.3
<i>ITQ-2</i>	85.8	87.0	13.0	91.0	86.4	13.5
<i>MCM-41 (40 Å)</i>	83.7	90.8	9.0	92.0	92.6	7.4
<i>MCM-41 (24 Å)</i>	83.3	90.8	9.0	90.0	91.4	8.6

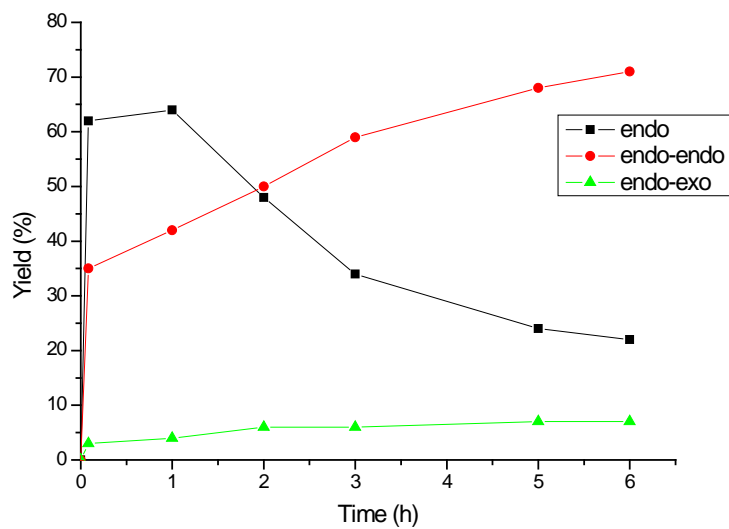


Figure 1. Product distribution when reaction is carried out in homogeneous phase.

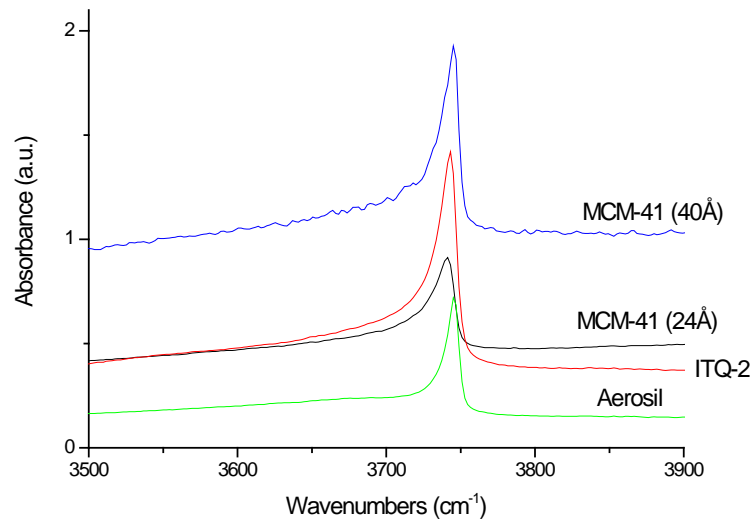


Figure 2. Intensity of silanol band in the IR spectra for used materials.

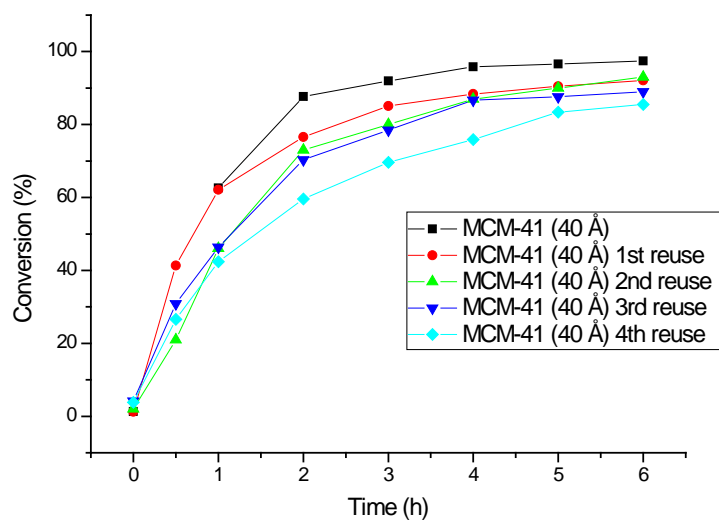
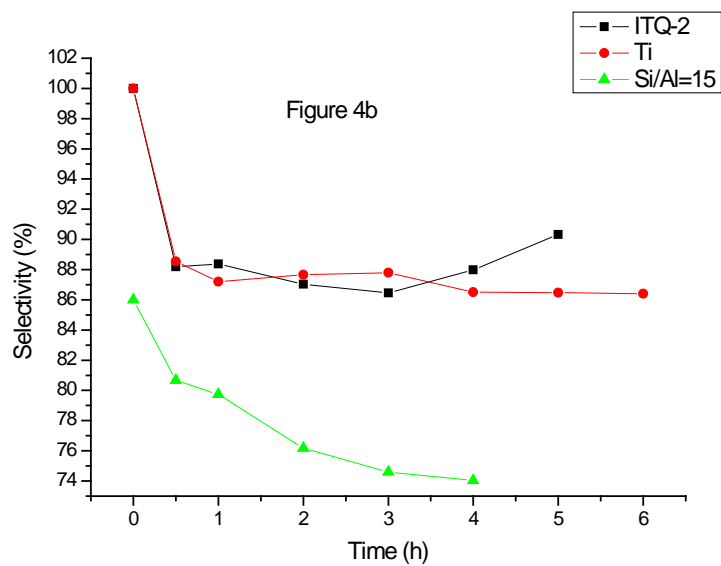
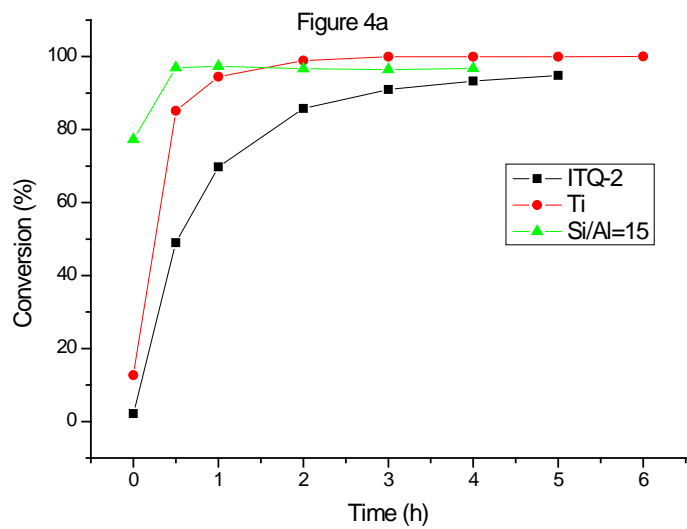
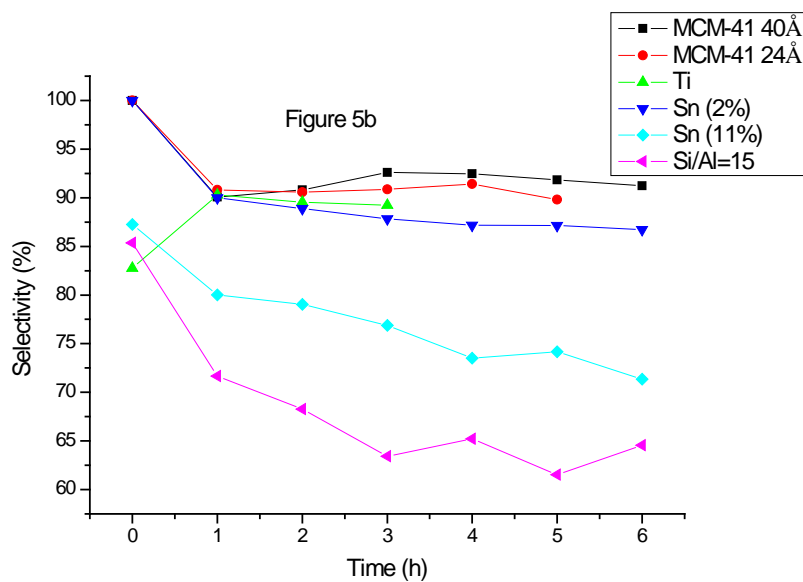
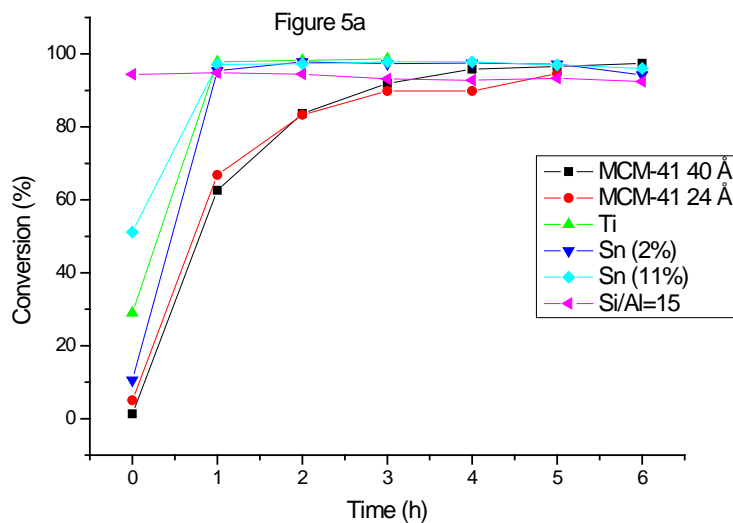


Figure 3. Study of catalyst deactivation with of MCM-41 (40Å).





Figures 4 (a and b) and 5 (a and b). Conversion and selectivity to *endo-endo* isomer for different ITQ-2 and MCM-41 materials.

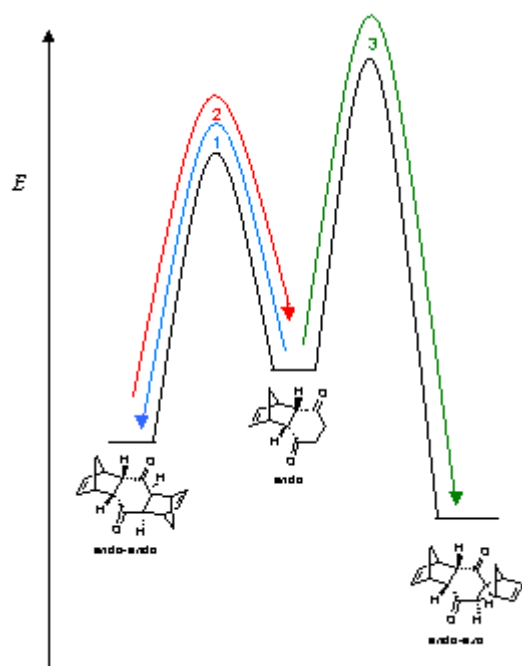


Figure 6. Diagram's energy for the retro-DAR effect.