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Diels-Alder Reaction between Isoprene and Methyl Acrylate over Different Zeolites: Influence of Pore Topology and Acidity

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In memory of Detlef Schröder

The Diels–Alder reaction between isoprene and methyl acrylate over several zeolites was thoroughly investigated. ZSM-5 zeolites provided the highest productivity in methyl 4-methylcy-clohex-3-enecarboxylate isomer, achieving 0.219 mmol product per mmol H^+ in 1 hour. In addition, this study highlights the

influence of ZSM-5 zeolite's Brønsted acidity and crystal size on its performance in the Diels–Alder reaction. An optimal configuration between the two reactants within the medium-poresized ZSM-5 framework is obtained, thus suggesting the presence of a confinement effect.

Introduction

The Diels-Alder reaction, a cycloaddition between an olefin and a diene,^[1] is commonly used to synthesise six-memberedring compounds in fine chemistry and total synthesis of natural products.^[1b,2] Cycloadducts are usually obtained with high regio- and stereoselectivities with complete atom economy. High pressures,^[1b,3] high temperatures,^[1b,4] ultrasonication^[1b,5] or microwave activation^[1b,6] are sometimes used to enhance reaction rates and/or selectivities, but non-conventional media proved beneficial as well: ionic liquids,^[1b,7] water^[1b,8] and supercritical CO2.^[1b,9] However, most Diels-Alder reactions are accelerated and more selective upon acid activation. Such activations are usually performed by Lewis acids,^[10] such as AICl₃^[11] or LiClO4,^[12] often used in (sur)stoichiometric amount and thus generating hazardous wastes, but also by protic acids, such as triflic acid^[13] or phosphonic acids,^[14] also leading to safety and waste concerns.

To avoid and minimise these problems, the replacement of homogeneous acids by easily separable and recyclable heterogeneous solid acids in Diels–Alder reactions has been extensively investigated. In earlier studies, numerous solid acid catalysts, such as zeolites, clays, alumina and silica, have been reported.^[15]

Zeolites, which belong to the class of tectosilicates, offer many advantages with respect to their homogeneous homologues: they are non-corrosive, non-toxic, easy to handle and recoverable, as well as having high thermal, mechanical and

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chemical stabilities.^[16] Furthermore, their porous structures exhibit confined nanospaces, which favour contact between the reactants and the zeolite active sites, often related to the acidic properties. Though zeolites possess two types of acidity, Brønsted and Lewis,^[17] with strength close to superacidity, they also render possible peculiar molecular diffusion, adsorption and reactivity thanks to the so-called confinement effect. Introduced by Derouane in 1986,^[18] this concept explains how each molecule present within the pores is affected by the zeolite. Indeed, non-covalent interactions between zeolite and substrate are formed, guided by the presence of non-equivalent adsorption sites, surface curvature and pore topologies. These interactions induce modifications in the conformational landscape of molecules to raise substrate/zeolite interactions.[19] The adsorption energy of one molecule on the zeolite surface is therefore strongly enhanced, by about eight times, with respect to a planar surface.^[20] In addition, it has been shown that Lennard-Jones interactions are favoured if the molecular size fits the pore aperture.^[21,22]

The aim of the present study is to highlight the influence of the zeolite framework and acidity in the Diels–Alder reaction between isoprene 1 and methyl acrylate 2 (Scheme 1). These



Scheme 1. Diels-Alder reaction between isoprene and methyl acrylate.

two substrates were chosen on the basis of their limited reactivity and for comparison purposes. Indeed, Onaka et al.^[23] conducted this reaction at -1 °C for 18 hours in hexane in the presence of hexagonal mesoporous silica materials with high

Al content. They achieved the formation of adducts **3** and **4** in a regioisomeric ratio of 97:3 but with yields depending on the solvent (94% in hexane, 73% in toluene and 65% in dichloromethane). Meanwhile, in dichloromethane heated at reflux as solvent and in the presence of BEA zeolite, Carlson et al. achieved a 99% selectivity toward **3**.^[24] Using other kinds of zeolites (ZSM-5, mordenite, Y), they observed regioisomeric ratios in the range 4:96–0:100 but associated with low yields (11–48%). Nevertheless, no relationships between physico-chemical properties of the solid acids and conversion or selectivity have been provided.

Hence, the outcome of this study would be to settle a relationship between the zeolite structure (pore and acidity), the size of the crystals and the activity/selectivity in the Diels– Alder reaction.

Results and Discussion

To evaluate the role and activity of zeolites in the Diels–Alder reaction, commercial as well as specifically designed zeolites were used as catalysts for the isoprene–methyl acrylate reaction as model (Scheme 1). With the goal of having zeolites of different crystal sizes, porosities and acidities, three H-ZSM-5 samples, named N1, N2 and N3, were prepared according to our previously reported procedure involving sugar-cane bagasse residues.^[25] Two other MFI-type samples, named G1 and G2, have also been obtained by performing the zeolite syntheses at neutral pH through the non-conventional fluoride route, which led to large zeolite crystals.^[26–29] For comparison purposes, an H-Y zeolite, named Y1, was synthesised according to a slightly modified reported procedure^[30] (see the Supporting Information for details).

Preliminary Diels-Alder experiments

To optimise the reaction conditions, preliminary Diels–Alder reactions between isoprene 1 and methyl acrylate 2 (Scheme 1) were performed at different temperatures with commercial H-ZSM-5 zeolite (CBV5020, Zeolyst) as catalyst. The methyl acrylate conversion rose gradually with the temperature, achieving nearly 60% at 90°C (with nearly complete isoprene conversion), whereas the selectivity toward regioisomer 3 decreased slightly above 40°C (Figure 1). It appears that a compromise between high conversion and appreciable selectivity toward the cycloadduct 3 was obtained at 75°C. Indeed, 95% of isoprene was incorporated into the cycloadducts by reacting with methyl acrylate, with nearly 90% selectivity in 3 achieved at this temperature.

Besides the major regioisomer **3**, several products were also detected by GC (Figure S3 in the Supporting Information) and identified by GC–MS or by injection of reference compounds. Diprene was observed as the major by-product (see mass spectrum in Figure S2). It is worth mentioning here that it has been shown that the cycloadducts could react further with isoprene.^[23]

To select the more suitable zeolite catalyst, two experiments (repeated twice) were performed at $75 \degree C$ in *n*-heptane with



Figure 1. Selectivity in isomer 3 and methyl acrylate conversion as a function of temperature.



Figure 2. Degree of methyl acrylate conversion and selectivity in 3 as a function of time for H-ZSM-5 and H-USY zeolites.

commercial H-ZSM-5 and H-USY catalysts at iso-site conditions. The results (Figure 2) revealed both a higher activity and selectivity in regioisomer **3** on performing the reaction in the presence of the ZSM-5 zeolite.

A further refinement of the influence of the pore topology was attempted by evaluating different commercial zeolite structures and other solid acids in the reaction. Table 1 presents those results and further highlights the best performance of the ZSM-5 zeolite structure (94% selectivity in **3** and 95% estimated isoprene conversion; Table 1, entry 6). It appears that the trend in the catalyst performance did not follow the

Table 1. Screening of commercial zeolites and other solid acids for Diels-Alder reaction (Scheme 1) at 75 $^\circ$ C for 24 hours.

Entry	Pore size [Å]	Catalyst	Selectivity in methyl 4-methylcyclohex-3- enecarboxylate 3 [%] ^[a]	3/4	Estimated isoprene conversion [%]	Methyl acrylate conversion [%]	
1	7.4	H-Y	90	100:0	86	52	
2	7.4	H-USY	90	100:0	88	53	
3	7	H-MOR	58	91:9	90	54	
4	5.6/7.7	H-BEA	81	100:0	96	58	
5	5.4	FER	88	100:0	85	51	
6	5.5	H-ZSM5	94	96:4	95	57	
7	-	-	87	100:0	55	33	
8	30	nafion	2	-	70 ^[b]	42 ^[b]	
9	-	SnO ₂ /SO ₄ ²⁻	24	94:6	98 ^[b]	59 ^[b]	
10	-	SiO ₂ /Al ₂ O ₃	83	100:0	96	58	
11	-	$Cs_3HSiW_{12}O_{40}$	-	-	0 ^[c]	0 ^[c]	
[a] The selectivity is defined by the ratio between moles of product 3 formed divided							

[a] The selectivity is defined by the ratio between moles of product **3** formed divided by the molar total amount of all products formed. [b] Polymerisation occurred. [c] No reaction occurred.

specific surface area (SSA) of the different zeolites (SSA values given in the Experimental Section). Indeed, ZSM-5 zeolite exhibits roughly two-thirds of the SSA of FAU zeolites (Y or USY). It is therefore sound to investigate parameters other than the BET area.

The highest methyl acrylate conversion was achieved over H-BEA zeolite (58%) as already reported by Eklund et al.,^[24] but at the expense of selectivity (Table 1, entry 4). Furthermore, the screening of zeolites and related solid acids tends to demonstrate the importance of acid catalysts possessing a highly organised microporous network in performing the Diels-Alder reaction. Indeed, the two regioisomers could barely be obtained, neither over strongly acidic Keggin-type heteropolyacid (Table 1, entry 11) nor over Nafion-H grafted on MCM-41 mesoporous silica (Table 1, entry 8). Likewise, the activity of highly acidic sulfated tin oxide^[31] also remained limited (Table 1, entry 9). In contrast, amorphous silica-alumina, which also exhibits strong acidity, led to good methyl acrylate conversion (58%, Table 1, entry 10). However, its selectivity toward isomer 3 remained lower than that obtained with mediumpore-sized ZSM-5 zeolite.

To summarise, these preliminary experiments have demonstrated the importance of using a solid acid catalyst. However, this is a necessary but non-sufficient condition because other solid acids, heteropolyacids for instance, were rather inactive. The microporous architecture of zeolites seems therefore to be required, since perfluorinated Nafion-H grafted on mesoporous silica led to 42% methyl acrylate conversion but with almost no formation of the Diels–Alder products. With the latter catalyst, the diffusion of the reactants throughout the mesoporous network is a priori accelerated with respect to zeolites.^[32,33] It does, however, seem to have a detrimental effect on the reaction. A compromise has therefore to be found between the size of the reactants and the pore aperture. Hence, zeolite can be regarded as a solid solvent, which possibly induces a confinement effect facilitating the reactant interaction.^[34–38] Commercial ZSM-5 zeolite provided the best results, maximising the selectivity toward regioisomer **3** at a high degree of methyl acrylate conversion, so therefore it is worth investigating our as-prepared MFI-type zeolites that exhibit different crystal morphologies and Brønsted acid site densities, to further attempt to establish structure and activity/selectivity relationships.

Material study

X-ray diffraction (XRD) was used to assess the structures of as-prepared zeolites. Fingerprints of both MFI and FAU structures could be evidenced for all assynthesised materials from their XRD pattern, as shown for N1, G1 and Y1 zeolites in Figure 3 and Figure 4, respectively. Notably, the different as-synthesised ZSM-5 zeolites (N1–N3, G1 and G2) differed significantly in their respective Si/Al ratio, but dis-



Figure 3. XRD pattern of N1 and G1 zeolites (MFI structure).

played the same porosity and SSA values of $320-370 \text{ m}^2\text{g}^{-1}$.

Notably, these zeolites exhibit a high crystallinity. To distinguish the morphological effects related to crystal size on the catalyst performances, these materials were observed by SEM. Figures 5-7 present the micrographs for N1-N3, G1 and G2, and Y1 samples, respectively. By varying the synthesis duration, different morphologies and sizes were obtained for the ZSM-5 samples (Figure 5). A micrometre-sized N1 material (nearly 4-5 µm) was formed by the growth of several nanoplates nearly 100 nm in width and hundreds of nanometres in length (Figure 5 a). In contrast, N2 and N3 samples exhibit a rather spherical morphology of several micrometres (6-8 µm), and are formed by the assembly of French fries-shaped nanocrystals as already reported elsewhere.^[25] These materials exhibit a high roughness, which indicates the presence of a high level of mesoporosity.^[32,33] Energy-dispersive X-ray (EDX) analysis coupled with the SEM chamber confirmed the homogeneous distribution of Al, O and Si elements, with Si/Al ratios ranging from 25 to 47 for these MFI materials (Table 2).

G1 and G2 samples exhibit the classical prismatic morphology of MFI crystals, being highly elongated with sizes of approx-

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Figure 4. XRD pattern of Y1 sample (FAU structure).

imately 35 and 25 μ m, respectively (Figure 6). These two MFI zeolites can be considered as giant crystals. Figure 7 shows the pyramidal FAU-type crystals of sample Y1, which have a size comprised between 300 and 500 nm. For the latter, a high density of aluminium, Si/AI=2.1, was confirmed by elemental analysis.

Acidity measurements were conducted according to the isotope exchange of OH/OD groups from the zeolite surface, thus allowing the quantification of all the Brønsted sites present in

Table 2. Crystal sizes, elemental composition and Brønsted acidity of as- prepared zeolites.								
Catalyst	Crystal size building block [µm] ^[a]	Si/Al ^[b]	Number of Brønsted acid sites [mmol g ⁻¹] ^[c]					
N1	0.1–0.2	31	1.07					
N2	0.3-0.4	25	1.33					
N3	0.3-0.4	47	0.73					
G1	35–40	100	0.38					
G2	25	90	0.42					
Y1	0.3	2.1	5.31					
[a] Building block refers to individual crystals. [b] Measured by EDX analy- sis. [c] H/D isotope exchange technique.								

the material.^[39,40] Table 2 summarises these values along with the Si/Al ratio and the crystal sizes of the different zeolites. Note that all MFI crystals and FAU nanocrystals exhibit acidity in line with the Si/Al ratio. The two MFI zeolites in the form of giant crystals possess nearly the same acidities: 0.38 and 0.42 mmol H^+g^{-1} for G1 and G2, respectively. The lower density of Brønsted sites in the latter two MFI zeolites has already been reported for the fluoride-mediated route.^[41,42] Surprisingly, N1, N2 and N3 materials exhibit rather different amounts of Brønsted acid sites. The non-conventional sugar-mediated route probably allowed different interactions and arrangements between Al species from the zeolite precursors and OH groups from the sugars during the crystal growth process.^[28,43] However, all these zeolites are highly crystalline and exhibit the sole MFI topology.

Optimisation: rational design of MFI zeolite

All our as-synthesised zeolites proved to be very active for the Diels–Alder reaction optimised previously (75 °C for 24 h). The selectivity in favour of regioisomer **3** was always between 87 and 91% for the five ZSM-5 materials and the Y1 sample, whereas variations in methyl acrylate conversion were observed depending on the nature of the zeolite (Figure 8). The highest conversions were again achieved over ZSM-5 zeolites (\geq 52%), except for the N3 sample, which gave a slightly lower conversion (48%).

Despite its high number of Brønsted acid sites (5.3 mmol H⁺ g⁻¹), the Y1 sample only led to a 46% methyl acrylate conversion, in turn confirming that acidity alone is a non-sufficient parameter. Among the zeolites N1–N3 prepared with sugarcane residues, it nevertheless appears that the conversion was enhanced in line with an increase in the density of Brønsted acid sites as follows: N3 < N1 < N2. In contrast, G1 zeolite with approximately half of the acid sites (0.42 mmol H⁺ g⁻¹) led to an unexpected 55% conversion in view of its low acid site density. Such anomalous behaviour might be linked (at least partially) to the larger crystal size and also to a higher crystallinity of this zeolite prepared by the fluoride-mediated route.^[27]

To go further and try to better understand and rationalise the performances of MFI zeolites, we defined a site time yield (STY) as the moles of produced adduct **3** relative to the number of catalyst Brønsted sites per time unit. Figure 9 shows these productivity data for the five ZSM-5 samples. The values for the N2 and N3 catalysts are in the range of the commercial ZSM-5 zeolite (H-ZSM5 C) used in the preliminary experiments. Interestingly, a roughly 50% higher productivity rel-

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Figure 5. SEM images of (a) N1 ZSM-5 obtained after 1 day of synthesis, (b) N2 ZSM-5 obtained after 2 days of synthesis and (c) N3 ZSM-5 obtained after 6 days of synthesis.

ative to N2 and N3 was achieved over N1 catalyst, possibly owing to the formation of higher-quality crystals (Figure 5a). More interestingly, a nearly four times higher productivity was observed for the G1 sample (three times higher for G2) with respect to N2 and N3 materials.

The outstanding performance demonstrated by G1 and G2 is probably and mainly a result of the extremely long diffusion length for the reactants throughout the porous network. It is worth reminding ourselves here that G1 crystals are approximately six times larger than N1 crystals. However, the reduced acid site density (three to four times) may also play an important role. In addition, the quantity of Brønsted acid sites of the former is roughly three times lower than that of the latter. One may therefore expect a high dispersion of these sites within the giant MFI crystal.

In contrast, the re-adsorption probability should be facilitated in N1 zeolite, with the risk to perform consecutive reactions,

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Figure 6. SEM images of (a) ZSM-5 G1 crystals and (b) ZSM-5 G2 crystals.



Figure 7. SEM image of FAU-type zeolite crystals (Y1).



Figure 8. Methyl acrylate conversion over home-made zeolites. The experiments were conducted under iso-mass conditions.



Figure 9. Productivity in regioisomer 3 expressed in mmol per number of Brønsted acid sites per hour.

or inhibit the proper geometrical organisation of the two reactants in the vicinity of one or two acid-site neighbours.

Although not fully understood yet, it seems that peculiar conditions are brought together within giant MFI crystals to maximise the interactions between the reagents and the catalyst surface (possibly through long-distance non-covalent van der Waals bonding). This is in line with the so-called confinement effect favoured in large zeolite crystals. In parallel, it has been recently shown by FTIR spectroscopy that these giant MFI crystals exhibit few silanol defects in comparison with conventional ZSM-5 samples.^[44,45]

Confinement effects^[34-38] in the pores as a result of the longrange electrostatic field should permit the absorption of reactant molecules in the solid solvent and guide them towards the strong Brønsted acid sites. Intra-zeolite void volumes surrounding those sites ensure the required "activation volume" and therefore a tight fit between the reactants and the zeolite framework.^[46]

The catalytic data presented herein revealed that a confinement effect may occur in the MFI framework for this Diels-Alder reaction. However, it appears that a compromise has to be found between the diffusion length within the crystal and a proper density of Brønsted acid sites. Hence, a proper Al pairing in the zeolite framework has to be tailored to optimise the adsorption/desorption phenomena on the surface. Quantum chemical calculations and statistical studies have demonstrated the high probability for having a second Al atom in the next-nearest-neighbour coordination spheres of one Al atom in MFI zeolites with Si/AI ratios below 50.[47-49] One may therefore expect a drastically reduced probability in giant crystals (G1 and G2) to possess two Brønsted sites in the vicinity of the reactants, since their Si/Al ratios approach or equal 100 (Table 1). An optimum seems to have been found in these giant crystals possessing fewer sites to allow a higher productivity in the Diels-Alder reaction. It is therefore shown that a special configuration, along with a tight fit in sizes between methyl acrylate and isoprene within the MFI pores, occurred.

Conclusion

Several commercial and specifically designed zeolites have been studied as catalysts in the isoprene-methyl acrylate Diels-Alder reaction. Correlations between crystal sizes, porosities and acidities of the different zeolites examined have been observed, which led to unexpected but interesting results. ZSM-5 proved to be the best catalyst, but the synthesis procedure seems critical. Indeed, ZSM-5 exhibiting giant crystal size combined with a low density of acid sites led to a four times higher productivity into cycloadduct.

Further studies are in progress to investigate the influence of the MFI zeolite intrinsic properties on its performance in other Diels–Alder reactions.

Experimental Section

Catalyst design

Commercial zeolites H-Y (Aldrich, SSA = 655 m²g⁻¹), H-USY (Zeolyst, CBV500, 621 m²g⁻¹), H-MOR (Zeolyst, CBV20A, 558 m²g⁻¹), H-ZSM5 (Zeolyst, CBV5020, 425 m²g⁻¹), H-BEA (Zeochem, 620 m²g⁻¹), H-FER (Petrobras, 400 m²g⁻¹) and Nafion-H (Aldrich, 200–250 m²g⁻¹) were used in their H-form. Prior to use, these catalysts were activated in an air atmosphere at 550 °C during 15 h.

H-Y zeolite (Y1) was synthesised according to a slightly modified procedure (see the Supporting Information).^[29] In addition, several H-ZSM-5 zeolites were prepared with different crystal sizes, porosities and acidities. Three MFI-type samples were prepared according to our previously reported procedure involving biomass residues (see the Supporting Information).^[25] The samples N1, N2 and N3 were obtained after hydrothermal synthesis in an autoclave at 170 °C for 24, 48 and 144 hours, respectively. To investigate the influence of the crystal size, we also prepared zeolites (G1 and G2) at neutral pH by the non-conventional fluoride route (see the Supporting Information).^[26,42,50-52]

Material characterisation

XRD (Figures 3 and 4), SEM (Figures 5–7) and EDX analysis (see Table 2) were used to characterise the as-prepared materials. An evaluation of the Brønsted acidity of the different catalysts was performed through H/D isotope exchange according to the method developed by Louis et al.^[39,40,44,53] (see Table 2 and the Supporting Information).

Diels-Alder procedure

Catalytic experiments were performed under iso-Brønsted acid site conditions by adjusting the catalyst mass, according to the same procedure applied with each catalyst (see the Supporting Information). Under an argon atmosphere, H-USY zeolite (62 mg, 0.24 mmol H⁺), previously activated at 550 °C during 15 h, was poured into dry heptane (3 mL; or dry cyclohexane) under stirring at room temperature. Methyl acrylate (0.375 mL) in dry heptane (2 mL; or dry cyclohexane) was added to the former mixture containing the catalyst. Finally, isoprene (0.25 mL) was slowly added separately to dry heptane (1 mL; or dry cyclohexane) and the mixture was stirred at 20–90 °C for 24 hours (see Figure 1). The catalyst was then isolated by filtration over a Millipore membrane and the filtrate was analysed by gas chromatography.

The non-limiting reagent, methyl acrylate, was used to determine the conversion. As the isoprene signal was quite close to heptane in the chromatograms, we decided to focus on methyl acrylate concentration. The degree of conversion was therefore determined based on the quantity of methyl acrylate reacted. In addition, an extrapolated isoprene conversion is given, assuming its sole reaction with the acrylate.

The selectivity toward the regioisomer **3** was calculated as the ratio of its amount formed divided by the whole quantity of products formed (taking into account the GC response factor through the use of an external standard). Methyl 4-methylcyclohex-3-ene-carboxylate **3** appeared as the major product along with regioisomer **4** obtained in lower amount. The yield of isolated **3** obtained under optimised conditions (75 °C, 24 h of reaction time) was very low, in the range of 7% (1–94% reported in the literature).^[24] The experiment was repeated three times but the high volatility of the product drastically hindered the purification steps. The main by-product was identified as the isoprene dimer, diprene.^[54]

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