

Catalysis of Diels–Alder Reactions by Zeolites

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The Diels–Alder cyclodimerization of buta-1,3-diene to 4-vinylcyclohexene was found to be catalysed by non-acidic zeolites, especially large-pore zeolites such as Na-ZSM-20, Na- β , and Na-Y, and also by carbon molecular sieves.

The report on the acceleration of Diels–Alder reactions by cyclodextrins¹ and the more recent observation of catalysis by zeolitic electron acceptors² prompt us to present some of our results on the catalysis of Diels–Alder reactions by non-acidic crystalline zeolites. The Diels–Alder cyclodimerization of buta-1,3-diene to 4-vinylcyclohexene is a well-known, thermally-initiated electrocyclic reaction,³ kinetically second-order in butadiene.⁴ Neither acidic nor basic catalysis has been observed for this reaction.

At 250 °C and atmospheric pressure, the thermal uncatalysed conversion of butadiene to 4-vinylcyclohexene in a Vycor-filled glass reactor at a flow rate of $15 \times 10^{-3} \text{ dm}^3 \text{ min}^{-1}$ was less than 0.1%. However, when the Vycor chips were replaced with various zeolites in their non-acidic sodium ion-exchanged forms, substantial catalysis was observed

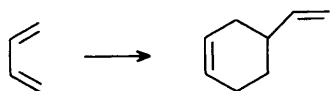


Table 1. Catalysis of butadiene cyclodimerization.

Catalyst (g used)	% Conversion at 250 °C
None	<0.1
Na-ZSM-20 (9)	>20
Na- β (5)	>10
Na-Y (10)	4
Na-ZSM-12 (6)	0.5
Na-ZSM-5 (8)	0.2
Cu-ZSM-12 (0.5)	20
Cu-ZSM-5 (0.5)	0.3
Carbon mol. sieve (5)	>30
Silica gel (5)	1

(Table 1). This catalysis was especially noteworthy when large pore zeolites,⁵ such as Na-Y, Na- β , and Na-ZSM-20, were employed. Na-ZSM-12 and Na-ZSM-5 were substantially less effective as catalysts for butadiene cyclodimerization.

The catalytic role of zeolites in the Diels–Alder reaction can be understood on the basis of the ability of zeolites to concentrate hydrocarbons within their cavities.⁶ By increasing the butadiene concentration inside the zeolitic pores relative to that in the external gas phase, zeolites can dramatically enhance the rates of bimolecular reactions such as the Diels–Alder reaction. The effect of zeolites is, in this regard, comparable with the use of elevated pressures. This specific effect for the Diels–Alder reaction is in addition to the increase in effective residence time produced by substrate sorption within the zeolites.

The substrate concentrating ability of the zeolites has been inferred from rate accelerations and product distribution changes observed for reactions conducted over non-acidic zeolite catalysts.⁶ We have been able to measure directly the concentrating ability of these zeolites at high temperatures (Table 2), and find that indeed the concentration enhancement can be several orders of magnitude at temperatures as high as 400–500 °C. Concentration enhancement is defined as the hydrocarbon concentration inside the zeolite (in molecules $\times 10^3$ per dm^3 of void volume) relative to the hydrocarbon concentration in the external gas phase.

From Table 2, it is clear that the greater effectiveness of large pore zeolites in catalysing the Diels–Alder reaction of butadiene is not due entirely to any superiority in their ability to concentrate substrates, but is in part due to the greater space available within their cavities for the proper alignment of the reactant molecules. The high temperature sorption capability of zeolites is a necessary but not sufficient condition for catalysis of bimolecular reactions.

Table 2. Reversible high temperature sorption of hydrocarbons on non-acidic zeolites.

Zeolite	Cs-Y	Cs-Y	Cs-ZSM-5	Na- β	Na-ZM-20	Na-ZSM-12						
Hydrocarbon	Hexane	Decane	Hexane	Hexane	Hexane	Hexane						
Partial pressure in He/Torr	83	0.8	83	83	83	83						
Gas phase conc./ g dm^{-3} at 25 °C	0.42	0.0067	0.42	0.42	0.42	0.42						
Zeolite capacity/ $10^{-3} \text{ dm}^3 \text{ g}^{-1}$	0.252	0.252	0.166	0.20	0.261	0.131						
Temp./°C	Sorp. ^a	Enhance. ^b	Sorp.	Enhance.	Sorp.	Enhance.	Sorp.	Enhance.	Sorp.	Enhance.	Sorp.	Enhance.
300	27	490	26	7500	4	110	22.6	520	16.8	290	14.7	520
350	12	240	12	3800	1.2	35	10.0	250	7.3	140	6.6	250
400	5	110	2.0	680	0.4	14	3.8	100	2.7	56	2.0	84
450	2.7	63	0.75	270			1.2	34				
500	1.2	31	0.19	75			0.27	8				

^a Sorption in mg per g ash. ^b Enhancement relative to external gas phase, corrected for high temperature expansion.

Since catalysis of the Diels–Alder reaction by zeolites is predominantly physical in nature rather than chemical, in that they concentrate reactants internally, other substances capable of sorbing substrates at high temperatures should be equally effective as catalysts. To test this concept, the catalytic activity of a highly porous chromatographic grade carbon (Carbosphere, from Alltech Associates, having a surface area of about $1000 \text{ m}^2 \text{ g}^{-1}$, with a pore size of about 13 \AA) was examined. As expected, this carbon catalyst was highly effective in catalysing the cyclodimerization of butadiene to 4-vinylcyclohexene. In fact, even amorphous silica gel had some catalytic activity, although to a considerably reduced extent (Table 1).

The smaller pore zeolites, ZSM-12 and ZSM-5, exhibited only a relatively minor catalytic effect in the cyclodimerization of butadiene. Copper incorporation into these zeolites, however, had a substantial beneficial effect in the case of ZSM-12, but no enhanced catalysis was obtained with Cu-ZSM-5 (see Table 1). Copper ion catalysis of a Diels–Alder reaction has been reported for X- and Y-zeolites⁷ and hydrated glasses,⁸ probably owing to co-ordination of butadiene with the copper(II) ion. The failure to observe substantial catalysis with ZSM-5, even when copper-exchanged, may be due to steric inhibition in the transition state caused by the relatively narrow channels of this zeolite.

The use of solid sorbents, such as zeolites, provides a convenient laboratory synthesis of Diels–Alder adducts and obviates the need for sealed tubes or high pressure reactors. Furthermore, the possibility of influencing product distributions due to stereochemical effects induced by the geometry of the zeolitic cavities could prove most intriguing.

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