Molecular recognition of geometrical isomers in montmorillonite [☆]

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cis-alkenes are hydrogenated preferentially followed by trans-alkenes sequentially from the mixture of geometrical isomers by the montmorillonitebipyridylpalladium(II) acetate catalyst. Such molecular recognition in montmorillonite is unusual and remarkable, and forms an advanced model to enzymes.

Keywords: Molecular recognition; montmorillonite catalyst; molecular recognition by clay catalysts

1. Introduction

Enzymes display the highest substrate selectivity recognising one chemical species in presence of hundreds of other similar species [1]. Search for new materials that can impart molecular recognition reminiscent of enzymes resulted into the discovery of many synthetic materials such as cyclodextrins [2], cyclophanes [3], macrocyclic ethers [4], zeolites [5], etc. A recent success of preferential substrate selectivity towards *n*-octane in presence of cyclohexane in the supercages of zeolites induced and catalysed by Pd–Fe system is the highlight of molecular recognition applied to catalysis [5]. However, enzymes or enzyme mimics are not known to display sequential and preferential molecular recognition of isomers, a desirable quality that allows use of a mixture of isomers in place of pure components in chemical reactions, which has larger industrial bearing. Our recent discovery on molecular recognition of ortho/para isomers in arylation of acrylates [6], stereo and regiomers in oxidation of alcohols [7] and various acrylates and cyclic olefins in hydrogenation [8] reactions sequentially and preferentially in montmorillonite

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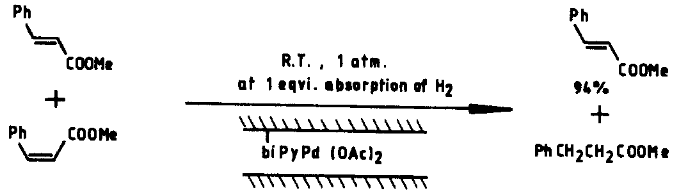


Scheme 1. Molecular recognition in hydrogenation of geometrical isomers.

have prompted many of the researchers to carry out their research in this specialized area. For example, Laszlo's report of similar sequential and preferential molecular recognition in the Friedel–Craft's alkylation [9] reactions has further widened the scope of this field. We report in this letter molecular recognition of geometrical isomers for the first time in the interlayers of montmorillonite induced and catalyzed by montmorillonitebipyridylpalladium system (scheme 1).

2. Experimental

2.1. PREPARATION OF THE CATALYST

The catalyst is prepared as described earlier [10]. H-montmorillonite, prepared from commercial montmorillonite K10 (Fluka, surface area 232 $m^2 g^{-1}$, mesh size <200), was allowed to react with excess $SOCl_2$ in dry benzene under reflux for 24 h to give chloromontmorillonite. The chloromontmorillonite (5 g) was suspended in dry THF and cooled to −80°C and excess *n*-butyl lithium (6.25 mL, 10 mmol, 1.6 M in hexane) was added to the stirred suspension. The solution was stirred at 0°C for 4 h and then allowed to warm to room temperature. After the solution was stirred for 1 h at room temperature, 2,2-bipyridine (3 g, 19 mmol) was added as a solid and the solution was brought to reflux for 4 h. The reaction mixture turned purple during refluxing. It was allowed to cool to room temperature and air was bubbled through the solution until the entire solution had become yellow. The resulting montmorillonite bipyridine was thoroughly washed with THF, ethylacetate, and benzene and was subjected to soxhlet extraction for 24 h with THF to remove any adhering bipyridine. Reaction with $Pd(OAc)_2$ (0.11 g, 0.5 mmol) in benzene under stirring for 6 h gave the catalyst, which was thoroughly washed with benzene and THF (nitrogen content, 0.4 mmol g^{-1}; Pd 0.2 mmol g^{-1}; surface area, 10.7 $m^2 g^{-1}$; mesh size, 200).

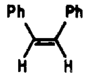
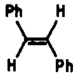
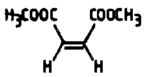
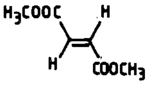
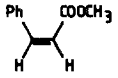
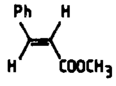
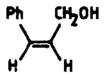
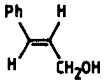
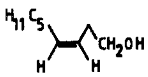
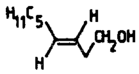
2.2. GENERAL PROCEDURE FOR COMPETITIVE HYDROGENATION

A weighed amount of the catalyst (100 mg, 0.02 mmol Pd) was introduced into a 100 ml two-necked round-bottomed flask which was attached to the classical hydrogenation apparatus. To this 10 ml of dry THF was added and the whole system was evacuated and flushed three times with pure hydrogen gas. The mixture was shaken for 30 min in presence of hydrogen gas (pretreatment). A mixture of 1.0 mmol of substrate S_1 and 1 mmol of substrate S_2 was injected through the septum. Reaction was followed by measuring the volume of hydrogen gas absorbed. Reactions were terminated after the absorption of one equivalent of hydrogen gas. The products were characterized by gas chromatography (CIC, India, 10% carbowax 20 M TPA on chrom-W 60–80 mesh) and ^{1}H NMR. On prolonged hydrogenation, totally hydrogenated products were obtained.

2.3. GENERAL PROCEDURE FOR INDIVIDUAL HYDROGENATION

The individual hydrogenation reaction was similarly conducted as described for the competitive reaction except by taking a substrate (1 mmol only). The relative rate of hydrogenation of each substrate in the individual reaction can be seen in table 1.

Table 1
Molecular recognition of geometrical isomers by montmorillonite bipyridine palladium catalyst

Entry	Substrate S1	Substrate S2	Relative initial rates of S1 / S2 in individual reactions	Product ratio of S1 : S2 in competitive reaction at 1 eqvi. absorption of H_2
1			4.1 / 3.2	80 : 20
2			3.9 / 3.0	72 : 28
3			3.2 / 2.6	94 : 6
4			3.0 / 2.4	96 : 4
5			2.6 / 2.1	96 : 4

3. Results and discussion

In the competitive reactions of alkenes, cis-isomers are hydrogenated preferentially followed by trans-isomers sequentially from the mixture of geometrical isomers by the montmorillonitebipyridylpalladium catalyst (table 1) and the highest substrate selectivity is achieved with the polar geometrical isomers of larger dimensions.

Fig. 1, which compares the rate of hydrogenation in competitive reaction with individual reactions, provides evidence for the preferential molecular recognition of cis-cinnamyl alcohol over trans-cinnamyl alcohol (96 : 4) by Pd catalyst intercalated in montmorillonite unambiguously. Further, the reaction rate is enhanced in competitive reaction when compared with the individual reaction, which is attributed to the synergistic effect and in good agreement with earlier results [6,9]. When identical studies were undertaken with different palladium catalytic systems, viz., Pd/C, polymer anchored palladium catalyst and Lindlar catalyst with a same amount of palladium content, only montmorillonitebipyridylpalladium catalyst displayed molecular recognition as is evident from fig. 2. The other intercalated catalyst, montmorillonitediphenylphosphinepalladium complex [11] also displayed similar molecular recognition of geometrical isomers in the competitive reaction for entries 1 and 2 of table 1.

ORIGIN OF SUBSTRATE SELECTIVITY

The substrate selectivity shown by the present catalytic system can be due to either diffusion in, diffusion out or transition state selectivity. The diffusion out

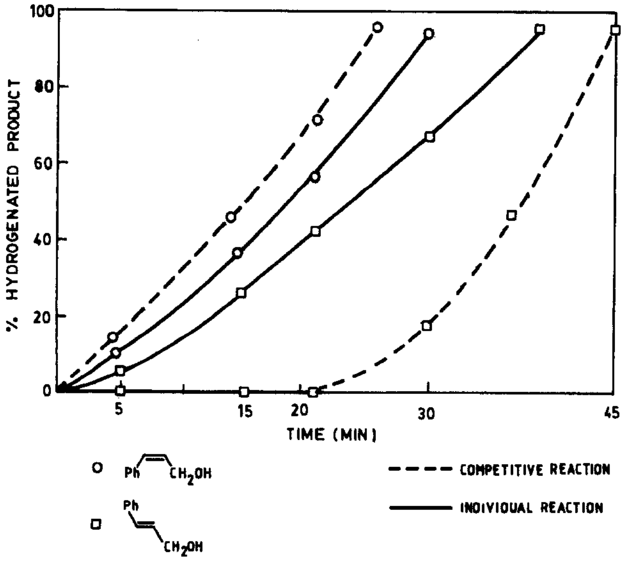


Fig. 1. Molecular recognition of geometrical isomers.

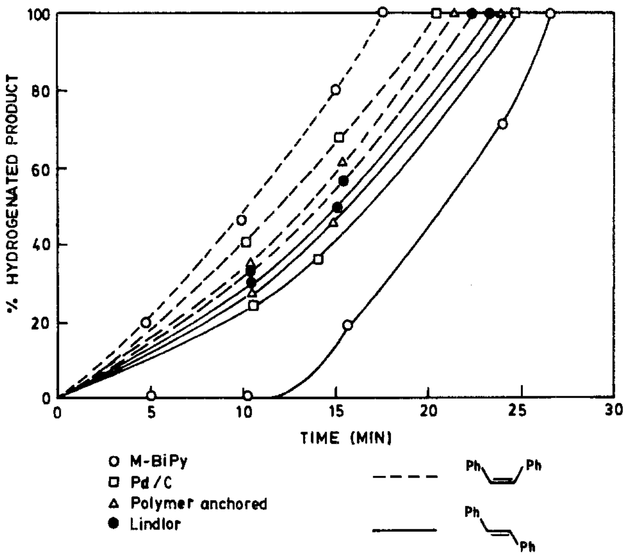


Fig. 2. Comparision of molecular recognition with various catalytic systems.

problem can be ruled out straightaway since the product formed from either of geometrical isomers in the hydrogen reaction is the same. It was observed in the solid phase reactions that cis-alkenes were selectively diffused into the swellable interlayers of montmorillonite [12]. When the same absorption studies were conducted on montmorillonite/montmorillonitebipyridylpalladium complex in THF in the present work no such selective absorption/complexation respectively were seen in the absence of hydrogen, because the swellability of montmorillonite interlayers in THF is too large to accommodate both isomers [13]. These results indicate the selective hydrogen transfer by a transition species; hydrido palladium bipyridyl complex formed in situ with the cis-alkenes is preferred over trans-alkenes as can be seen in fig. 3, since the basal oxygens of the support exercise more repulsions towards trans adducts.

Thus the potentiality of sequential and preferential molecular recognition is widened with the present application for geometrical isomers by modified montmorillonites.

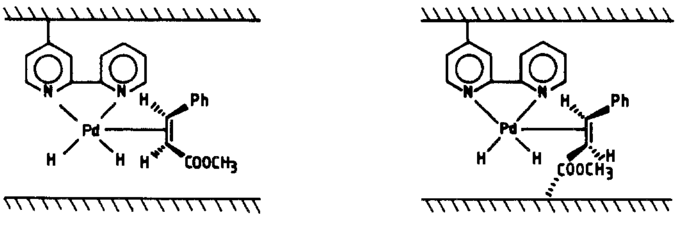


Fig. 3. Palladium complexes of geometrical isomers in the interlayers of montmorillonite.

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