



Features of formation transition states of 1,3-dioxanes by Prins reaction in the pores of synthetic zeolites A and carbon nanotubes

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ABSTRACT

We have theoretically studied the possibility of change stage of formation of new materials by using principles of molecular imprinting on the choice of compliance parameters of transition states (TS) to the parameters of existing porous materials. Geometric parameters TS of 1,3-dioxanes formed by Prins reaction between alkenes and formaldehyde dimer has been studied in MP2(fc)/6-31G(d,p) approximation. Energetic parameters and features interaction of these TS with zeolites A and carbon nanotubes (CNT) studied with molecular dynamics method. The highest level of interaction TS of 1,3-dioxane with zeolite A $\text{Ca}_x[\text{Al}_{2x}\text{Si}_y\text{O}_z]\cdot n\text{H}_2\text{O}$ being observed if the pore size is 5,1–5,4 Å. The highest level of this interaction being observed for pore size 9,4–10,9 Å by using CNT. Such a relationship of the interaction TS 1,3-dioxane and pore sizes of zeolites A and CNT suggest the possibility of exchange stage synthesis a new material by using a principles of molecular imprinting. In this case we can choose existing material if size its pore does conform to the investigated TS.

1. Introduction

One of the important area of research the development a new catalysts is the using principles of molecular imprinting [1]. By this way the molecule should be chosen that have a shape with compliance geometric parameters to TS of investigated reaction. Then polymeric 3d structure with molecular fingerprint is formed and this material can be used as a catalyst. Our idea is that instead of formation material with fingerprint we offer its choosing from existing porous material (zeolites, nanotubes and etc). Quantum-chemical modeling allowed to use as a fingerprint the transition state itself. Obviously the finding criteria of choosing porous materials are important in this case. We believe that the sufficient criterion is the degree of interaction in system TS – pore depending from its diameter. Thus our approach involves investigation geometric parameters of TS and identifying features its formation in pores of zeolites A and CNT. A similar approach to the analysis of catalytic activity was used in Refs. [2–4] researches. The data obtained by the authors show that the theoretical estimate is an agreement with the experimental results. When mechanism of reaction is unknown it is possible to use more sophisticated approach, which consider interaction between reagents, products and zeolite's channels [5–7]. However, this approach also can provide good explanation of experimental data.

We used formerly investigated by us Prins reaction as an object for

studying [8–16]. We had shown that the Prins reaction have more complex mechanism which don't described as simple addition of formaldehyde to double bond. The typically mechanism specified by Price doesn't consider the role of formaldehyde's oligomeres in 1,3-dioxane formation. In our previous researches we had demonstrated that all products in the Prins reaction are formed by their own mechanism and degree of formaldehyde polymerization is the “selector” which defines a reaction pathway [16,22]. E.g. 1,3-dioxane becomes major product in Prins reaction when formaldehyde is present in reaction media as oligomers [17,18,24]. Also we had shown that 1,3-dioxanes are “kinetically controlled” products [23] instead of hydrogenated pyrans, which are “thermodynamically controlled” products formed by reactions between alkenes and two monomers of formaldehyde. Thus selectivity of 1,3-dioxane formation can be increased by addition of specific catalyst, which will stabilize TS only of this reaction. We suppose that materials with specific pore size (CNT and zeolites) close to TS dimension will show high catalytic activity in this reaction.

2. Computation methods

We had carried out search of transition states using MP2(fc)/6-31G(d,p) and recalculating of Hessian on every step during geometry optimization in Firefly v. 8.0.0 [19]. Structure found TS was checked by

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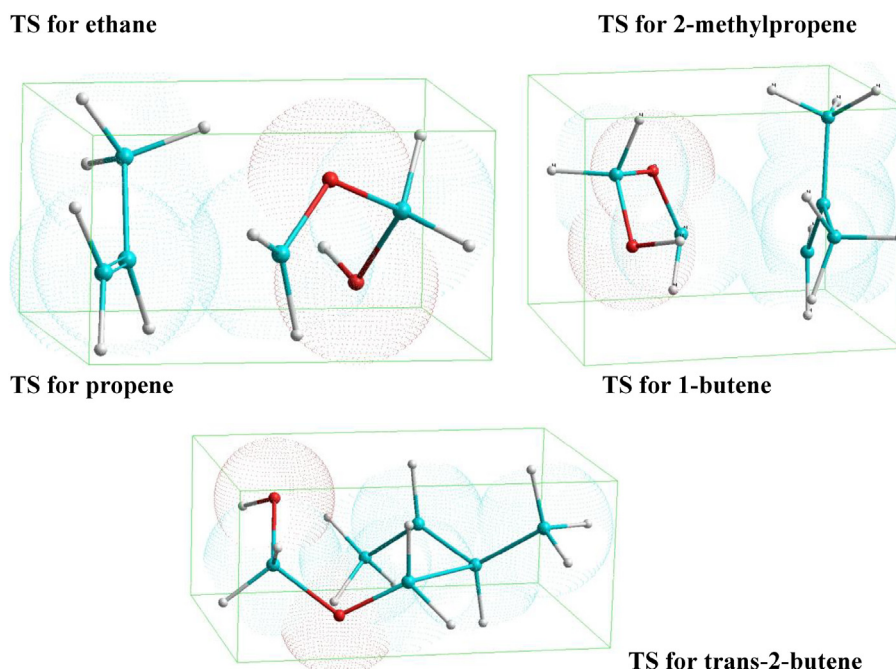


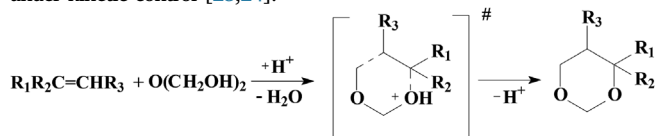
Fig. 1. Shapes of TS for formation of 1,3-dioxanes from alkenes and formaldehyde dimer.

using the procedure IRC [20] (Supplementary data, Appendix A). We determined feature the interaction and energy stabilization of TS on a zeolites A (Supplementary data, Appendix B) and on a CNT (Supplementary data, Appendix C) using “Adsorption module Locator” in the program Accelrys Material Studio 6.0 [21]. TS formed from ethylene (1), propene (2), 2-methylpropene (3), 1-butene (4) and trans-2-butene (5) has been used as the model of TS. We used synthetic zeolites ANA, NAT, BEA, STI, GIS, YUG, PAR (IZA-code) [25] and single-walled CNT as porous materials.

3. Results and discussion

3.1. Identification of transition states for the formation of 1,3-dioxanes

Formerly we had shown [22] that 1,3-dioxanes is formed by Prins reaction as a one-step addition of formaldehyde oligomers to double bond under kinetic control [23,24].



Below are the calculated values geometric parameters of TS for 1,3-dioxanes formation from formaldehyde dimer and alkenes (Fig. 1, Table 1).

As follows from the presented data, considering TS can be inscribed

Table 1

Linear dimensions of TS for 1,3-dioxanes formation from alkenes and formaldehyde dimer, Å

Alkene	x	y	z
Ethene	3.84	2.59	5.08
Propene	4.59	2.97	5.25
1-Butene	3.98	3.77	5.92
2-Methylbutene	4.37	4.02	5.35
trans-2-Butene	4.52	2.94	6.59

in a parallelepiped with sides x,y,z. They have tendency to increase when increase a molecular mass of alkene. The structural isomers have different values x, y, z but full volume of parallelepiped doesn't change. It's important that the minimum size of the pore, where the investigated transition states can be formed, must be 4–5 Å depending from alkene.

3.2. The interaction of TS with zeolites A

Subject to the foregoing, convenient models with pores of the desired size are zeolites. So we investigated the interaction TS and some zeolites A with the same chemical composition, but different size of pores. The results of the calculations of interaction TS with used zeolites given in Table 2 and Fig. 2. Structure of the TS during the molecular dynamic calculations has been frozen.

In accordance with the data presented in Table 2 and Fig. 2, zeolites with pores 5.1–5.4 Å are the preferred porous material for the stabilization of the investigated TS. Obviously that in this case transition state can fit into the pore of zeolite and stabilize due to the intermolecular interaction with inner surface of pore. If the pore diameter is less than 5 Å, then the transition state does not fit into the pore and can be stabilized due to the outer surface of zeolite. In the case of zeolites with bigger size of pore the interaction is realized by part of inner or outer surface of pore.

Table 2

The dependence of the adsorption energy of transition state from the pores diameter of zeolites, KJ/mol.

Zeolite	d, Å	Ethene	Propene	1-Butene	2-Methylpropene	trans-2-Butene
ANA	3.8	−49.5	−57.6	−59.2	−56.9	−63.8
NAT	4.0	−49.6	−60.2	−53.6	−52.1	−62.6
BEA	5.1	−107.3	−121.3	−140.3	−139.2	−140.1
STI	5.4	−90.6	−98.1	−134.6	−96.6	−137.3
GIS	5.8	−63.0	−72.6	−68.6	−77.9	−73.8
YUG	6.2	−52.6	−59.9	−65.3	−66.1	−70.2
PAR	6.6	−49.5	−57.6	−59.2	−56.9	−63.8

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