

# Selective synthesis of 2,5-dimethyl-2,4-hexadiene by condensation of *iso*-butyl aldehyde with *tert*-butyl alcohol over molecular sieve catalysts

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## Abstract

Several molecular sieve catalysts have been investigated for Prins condensation of *iso*-butyl aldehyde with *tert*-butyl alcohol in a liquid phase reaction. The results demonstrate that acidic molecular sieves are effective catalysts for the condensation reaction, and HZSM-5 molecular sieves possessed strong enough acidity and proper channel systems exhibit high activity and selectivity. Up to 78.6% *iso*-butyl aldehyde conversion is obtained with a 57.8% 2,5-dimethyl-2,4-hexadiene yield over HZSM-5 with Si/Al of 39 after 8 h at 160 °C, which provides a useful and economical potential industrial application way on a large scale to manufacture 2,5-dimethyl-2,4-hexadiene.

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## 1. Introduction

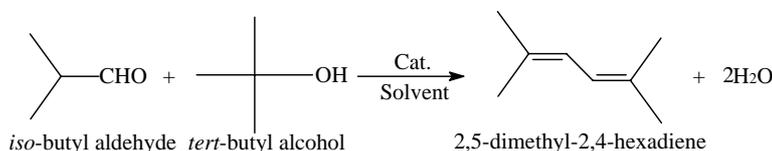
The Prins condensation of olefins with aldehydes is considered to be an important organic reaction, since it allows one to obtain various unsaturated alcohols, glycols, acetals, and other valuable compounds. This reaction is typically catalyzed by strong mineral acids such as H<sub>2</sub>SO<sub>4</sub> in homogeneous catalysis [1], but in some cases, such as the synthesis of isoprene, an increasing interest in heterogeneous catalysis must be noted [2–4].

2,5-Dimethyl-2,4-hexadiene (octadiene, OCD) is an important intermediate in the synthesis of esters of chrysanthemic acids, which are pyrethroid insecticides widely used in agriculture and domestic hygiene with less toxicity and more efficiency [5]. The Prins condensation of isobutylene (or/and *tert*-butyl alcohol) with *iso*-butyl aldehyde (IBA) is a valuable and economical way of synthesis OCD (Scheme 1). Like most of the

Prins reaction, this reaction is also catalyzed by liquid acids in homogeneous medium [6] with relative low yield of OCD (less than 40%) and formation of large number of by-products. Furthermore, this method would also cause corrosion and separation problems. In order to convert the homogeneous catalytic processes into heterogeneous ones, niobic acid was used to catalyze the condensation of isobutylene with IBA in a vapor phase [7–9], in which the catalytic performance of niobic acid could be closely related to its acidic properties. However, as reported by Iizuka and coworkers [10,11], niobic acid would change its acidic properties, such as acid strength, number of acid sites and kind of acid types (Lewis or Bronsted acid) by calcination, which could not be recovered by rehydration treatment. This means that niobic acid catalyst would lose its activity during reaction and could not be regenerated easily. In the present research, we try to use molecular sieve catalysts testing the condensation reaction in a liquid phase. In addition, instead of isobutylene, *tert*-butyl alcohol (TBOH) is used as reagents. It is proved that HZSM-5 molecular sieve exhibits high activity and selectivity toward the formation of OCD.

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Scheme 1. Synthesis of 2,5-dimethyl-2,4-hexadiene by condensation of *iso*-butyl aldehyde with *tert*-butyl alcohol.

## 2. Experimental

Typical condensation reactions were carried out in an autoclave (200 ml) equipped with a temperature controller. For each test, IBA (5 ml), TBOH (20 ml) and fresh molecular sieve catalysts (3 g) were loaded in the autoclave containing 25 ml 1,4-dioxane as solvent. The reaction was operated at 160 °C and under autogenous pressure. After reaction (8 h), the autoclave was cooled to room temperature, and the liquid products were analyzed on a Varian CP-3800 gas chromatograph equipped with an SE-30 capillary column (50 m) and an FID detector. Toluene was used as internal standard to evaluate the amount of OCD and IBA in the liquid. GC-MS,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR techniques were used to identify products. HY, H-mordenite (HM) and H- $\beta$  molecular sieves were obtained from Fushun Petrochemical Corp., PetroChina. SAPO-5 and HZSM-5 with varying Si/Al ratios were synthesized in our laboratory by the reported methods [12,13].

## 3. Results and discussion

The properties of these catalysts and the typical reaction results over different molecular sieve catalysts are shown in Table 1.

The activities of the different molecular sieves used here decrease in the order H- $\beta$  > HZSM-5 > HY > SAPO-5 > HM. This may be attributed to the acidity and the channel systems required for the condensation reaction. H- $\beta$  and HZSM-5 possess much higher acid strength than HY and SAPO-5 catalysts, so they exhibit high activity for the acid-catalyzed condensation reaction. For HM molecular sieve, the 8-ring channel (0.26 × 0.57 nm) is too small for the reactants and the

products, so only the 12-ring straight channel (0.65 × 0.70 nm) is effective for the reactants (and/or products) diffusion, which is unfavorable compared with the diffusion over molecular sieves with more than mono-channel, such as HY, H- $\beta$  and HZSM-5. This may result in the low activity over HM. For its weak acidity, HY exhibits lower activity than HZSM-5. SAPO-5 molecular sieve shows little activity in the reaction for its weak acidity and mono-channel system.

The HZSM-5 catalyst shows much higher selectivity than HY and H- $\beta$ , though all of them possess 3-dimensional channels. This may be attributed to the different acid strength and framework structure of different molecular sieves. In the reaction on H- $\beta$ , the selectivity is much lower and the product distribution is completely different from that on HZSM-5; that is, the major product is not OCD but polybutylene compounds. This may be attributed to the unusual channel system of  $\beta$  molecular sieve. For  $\beta$ -zeolite, it possesses relative bigger size of pore open (0.66 × 0.67 nm ↔ 0.56 × 0.56 nm) than ZSM-5 (0.53 × 0.56 nm ↔ 0.51 × 0.55 nm), which may be favorable to the formation of polymers. For HY, the supercages dampen free diffusion of the reactants, and the relative weak acidity is disadvantageous for the formation of OCD, so it exhibits lower activity and selectivity. HZSM-5 molecular sieves possessed strong enough acidity and unusual straight channel systems show much higher activity and shape-selective effect than the other molecular sieve catalysts investigated.

Except the acidity and channel system, the hydrophobicity/hydrophilicity of the catalysts would also affect the condensation reaction. The catalysts adsorbed proper amount of hydrophilic IBA and oleophilic *iso*-butylene would show optimum catalytic performance.

Table 1  
Properties and catalytic performance of molecular sieve catalysts

Catalyst	Si/Al (mol)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore size (nm) [14]	Dimension	IBA con. (%)	OCD sel. (%)	Yield (%)
SAPO-5	–	243	0.73 × 0.73	1	30.5	1.6	0.5
HM	7.5	397	0.65 × 0.70	1	22.1	1.4	0.3
HY	3.0	561	0.74 × 0.74	3	57.3	23.6	13.5
H- $\beta$	46.2	538	0.66 × 0.67	3	88.8	11.9	10.6
			0.56 × 0.56				
HZSM-5	38.8	329	0.51 × 0.55	3	78.6	73.5	57.8
			0.53 × 0.56				

The mole ratios of SAPO-5 is Al<sub>0.50</sub>P<sub>0.44</sub>Si<sub>0.06</sub>O<sub>2</sub>.

Table 2  
Reaction results of condensation of IBA with TBOH over HZSM-5 with different Si/Al

Catalyst	Si/Al (mol)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	IBA con. (%)	OCD sel. (%)	Yield (%)
HZSM-5 (25)	24.9	349	72.8	49.2	35.8
HZSM-5 (30)	30.0	320	74.5	62.8	46.8
HZSM-5 (39)	38.8	329	78.6	73.5	57.8
HZSM-5 (62)	61.7	333	72.1	65.9	47.5
HZSM-5 (89)	88.7	347	66.5	60.8	40.4

The reaction conditions are the same as in Table 1.

Detailed studies are thus focused on HZSM-5 molecular sieves with varying Si/Al ratios. As can be seen from Table 2, up to 78.6% IBA conversion is obtained on HZSM-5(39) with a 57.8% OCD yield after 8 h at 160 °C. This is the first observation of such a high OCD yield by condensation of IBA with TBOH over molecular sieve catalysts in a liquid phase.

For the HZSM-5 catalysts used here possess same channel systems and approximate acidity, we deduce primarily that it is the aluminum concentration of the molecular sieves that results in the differences in the catalytic performance. HZSM-5 molecular sieves with lower Si/Al will adsorb large number of polar species (such as IBA and H<sub>2</sub>O) in the pores of the catalysts due to its high density of acid sites and the hydrophilicity, which would influence the adsorption of isobutylene formed by dehydration of *tert*-butyl alcohol as one of condensation steps. On the other hand, the higher Si/Al ratio of the catalyst results in a decrease in the number of acid sites of the HZSM-5, and this may cause a decline in the reaction rate. Moreover, the adsorption and conversion of large amount of IBA on weak or mild strong acid sites will cause an increasing of decomposition and disproportionation of IBA, which will decrease the selectivity of the condensation reaction. Hence, the catalytic synthesis of OCD by condensation of IBA with TBOH is controlled by the competition between the condensation reaction and the side reactions, such as polymerization, decomposition and disproportionation, and the HZSM-5 catalyst with an optimum Si/Al ratio that adsorbs proper amount of isobutylene and IBA in the pores at the same time exhibits the highest activity and selectivity.

The same HZSM-5 catalyst was recovered and renewed by calcinations for eight times, and no obvious variety of activity and selectivity is observed. This indicates that the catalyst can be used repeatedly.

The liquid products were analyzed with GC-MS. About 50 kinds of compounds were formed in the system. They can be divided into three groups: small molecule group, 8-carbon atoms group, and 12-carbon atoms group. In the small molecule group, the main products are the unreacted reactants (including IBA and TBOH), *iso*-butylene, isobutanol, *sec*-butyl alcohol, and isobutyric acid. In the 8-carbon atoms group, besides the desired product OCD, there are more than 20 kinds of

octenes with one or two double carbon bonds. Small amount of 2,2,5,5-tetramethyltetrahydrofuran, unsaturated octanol, and *iso*-butyl *sec*-butyl ether were also observed at the same time. In the 12-carbon atoms group, there are more than 10 kinds of compounds formed by addition of various octenes with IBA or TBOH.

#### 4. Conclusion

Overall, this is the first report on the catalytic synthesis of OCD by Prins condensation of IBA with TBOH over molecular sieve catalysts in a liquid phase. The results discussed above demonstrate that acidic molecular sieves are effective catalysts for the condensation reaction, and only the molecular sieve catalysts with strong enough acidity and proper channel systems exhibit high activity and selectivity. Up to 78.6% IBA conversion is obtained with a 57.8% OCD yield over HZSM-5 with Si/Al of 39 after 8 h at 160 °C, which provides a useful and economical potential industrial application way on a large scale to manufacture OCD.

#### References

- [1] C.R. Noller, Chemistry of Organic Compounds, third ed., W.B. Saunders, Philadelphia/London, 1965.
- [2] W. Hölderich, M. Hesse, F. Näumann, Angew. Chem. Int. Ed. 27 (1988) 226.
- [3] T.M. Jyothi, M.L. Kaliya, M.V. Landau, Angew. Chem. Int. Ed. 40 (2001) 2881.
- [4] T.M. Jyothi, M.L. Kaliya, M. Herskowitz, M.V. Landau, Chem. Commun. (2001) 992.
- [5] S.H. Harper, H.W.B. Reed, R.A. Thompson, J. Sci. Food Agric. 2 (1951) 94.
- [6] K. Takagi, M. Murakami, K. Manabe, Ger. Offen. (1973) 2243701.
- [7] T. Yamaguchi, C. Nishimichi, Catal. Today 16 (1993) 555.
- [8] Y. Higashio, K. Takahashi, EP (1987) 0215567.
- [9] T. Yamaguchi, C. Nishimichi, A. Kubota, Prepr. Am. Chem. Soc., Div. Pet. Chem. 36 (1991) 640.
- [10] T. Iizuka, K. Ogasawara, K. Tanabe, Bull. Chem. Soc. Jpn. 56 (1983) 2927.
- [11] K. Ogasawara, T. Iizuka, K. Tanabe, Chem. Lett. (1984) 645.
- [12] D. Young, M.E. Davis, Zeolites 11 (1991) 277.
- [13] R.J. Argauer, G.R. Landolt, US Patent (1972) 3702886.
- [14] C. Baerlocher, W.M. Meier, D.H. Olson, Atlas of Zeolite Framework Types, Elsevier, The Netherlands, 2001.