

Liquid-phase catalytic synthesis of 2,5-dimethyl-2,4-hexadiene by condensation of *iso*-butyl aldehyde with *tert*-butyl alcohol over solid acidic catalysts

Hua Wang, Zhongmin Liu*, Chenglin Sun, Gongwei Wang

Natural Gas Utilization & Applied Catalysis Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457#, Zhongshan Road, Dalian 116023, PR China

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Abstract

Several solid acidic catalysts have been investigated for the 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 catalytic performance. Solvent polarity and solvent–active site interaction would significantly affect the aldehyde conversion and the 2,5-dimethyl-2,4-hexadiene selectivity. The *iso*-butyl aldehyde to *tert*-BuOH ratio, catalyst amount, solvent amount, reaction temperature, reaction time, Si/Al ratio of HZSM-5 molecular sieves, catalytic performance of different solid acids, and side-reactions in the system are studied. 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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Keywords: 2,5-Dimethyl-2,4-hexadiene; HZSM-5 molecular sieve; *iso*-Butyl aldehyde; Liquid-phase; Prins reaction; *tert*-Butyl alcohol

1. Introduction

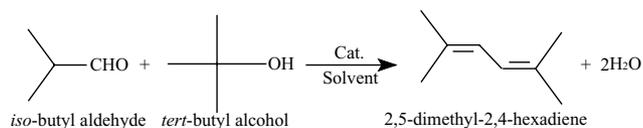
The Prins condensation of olefins with aldehydes is considered to be an important organic reaction, since it allows one to obtain various unsaturated alcohols, glycols, acetals, and other valuable compounds. This reaction is typically catalyzed by strong mineral acids such as H₂SO₄ in homogeneous catalysis [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 a significant intermediate [5] 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. 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 reactions, this reaction is also catalyzed by liquid acids in homogeneous medium [6] with relative low OCD yield (less than 40%) and large number of by-products formation. 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 co-workers [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 work, solid acidic catalysts were tested in a liquid-phase condensation reaction. In addition, instead of isobutylene, *tert*-butyl alcohol (TBOH) was used as reagent. It was proved that HZSM-5 molecular sieves exhibit high activity and selectivity toward the OCD formation.

* Corresponding author. Tel.: +86 411 4685510; fax: +86 411 4691570.
E-mail address: liuzm@dicp.ac.cn (Z. Liu).



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

2. Experimental

2.1. Catalysts and materials

The HY, H-mordenite (HM) and H-beta molecular sieves were obtained from Fushun Petrochemical Corp. PetroChina. $\text{ZrO}_2\text{-SO}_4^{2-}$, SAPO-5 and HZSM-5 with varying Si/Al ratios were synthesized in our laboratory by the reported methods [12–14]. Nb_2O_5 was used without further pre-treatment. HNbO_3 was prepared by calcination 5 g Nb_2O_5 with 20 g KOH in air at 600 °C for 1 h, then the sample was dissolved in water and pretreated by adding nitric acid until pH = 4. The deposit was separated from the aqueous solution by filtration, and dried at 100 °C for 6 h after washing with water for five times.

The compositions of molecular sieves catalysts were determined by X-ray fluorescence spectroscopy using a Philips Magix 601 apparatus. X-ray power diffraction patterns were recorded on a RIGAKU D/max-rb instrument using Cu K α radiation with a nickel filter to ensure that the molecular sieves samples were in high crystallinity.

Analytical grade *tert*-butyl alcohol, *iso*-butyl aldehyde, methanol, ethanol, tetrahydrofuran (THF), cyclohexane, and 1,4-dioxane were used without further purification.

2.2. Catalytic runs

Typical condensation reactions were carried out in an autoclave (200 ml) equipped with a temperature controller. For each test, IBA, TBOH and fresh catalysts were loaded in the autoclave containing proper amount of solvent. The autoclave was sealed, flushed with N_2 for several times to replace the air. The standard temperature was set according to the reaction experiments. For all runs, the pressure was autogenous. Detailed reaction conditions are shown in tables or figures.

2.3. Product analysis and identification

After reaction, the autoclave was cooled to room temperature, and liquid products were analysed 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, ^1H NMR and ^{13}C NMR techniques were used to identify products.

The conversion was calculated on the basis of the amount of IBA converted.

Table 1

The results of Prins condensation of IBA with TBOH over various solid acidic catalysts in a liquid-phase^a

Catalyst	Si/Al (mol)	Conversion of IBA (%)	Yield of OCD (%)
H-beta	46.2	80.4	4.4
HY	3.0	38.3	0.4
HNbO_3	–	64.2	0.3
HZSM-5	25.0	70.1	3.1
HM	7.5	28.8	3.1
Nb_2O_5	–	49.0	0.4
$\text{ZrO}_2\text{-SO}_4^{2-}$	–	93.6	3.5

^a Reaction conditions: catalyst 4 g, IBA 5 ml, TBOH 20 ml, ethanol (solvent) 30 ml, temperature 200 °C, time 8 h.

3. Results and discussion

3.1. Catalysts selection

Table 1 shows the results of Prins condensation of IBA with TBOH over various solid acidic catalysts in a liquid-phase reaction. The results clearly demonstrate that all the catalysts investigated are effective for the condensation reaction, although the OCD yields are very low over some of them. The catalysts possessed higher acidity, such as H-beta, HZSM-5, HM, and $\text{ZrO}_2\text{-SO}_4^{2-}$ perform higher activity for the OCD formation. This indicates that strong enough acidity is needed for the liquid-phase Prins reaction. Considering the mono-channel system of HM and the unsteadiness of $\text{ZrO}_2\text{-SO}_4^{2-}$ catalyst, we pay our attention to H-beta and HZSM-5 zeolites.

3.2. Effect of solvent polarity on the condensation reaction

The solvent effect of condensation reaction over H-beta and HZSM-5 is shown in Table 2. The results clearly demonstrate that different kind of solvents influence the condensation reaction differently. Decreasing polarity of the solvent

Table 2

Solvent effect of condensation of IBA with TBOH over H-beta and HZSM-5^a

Solvent	Catalyst	Conversion of IBA (%)	Yield of OCD (%)
H_2O	H-beta	99.7	13.5
H_2O	HZSM-5	91.0	17.9
$\text{H}_2\text{O} + 1,4\text{-dioxane}^b$	H-beta	92.5	9.2
$\text{H}_2\text{O} + 1,4\text{-dioxane}^b$	HZSM-5	86.2	20.8
Ethanol	H-beta	80.4	4.4
Ethanol	HZSM-5	70.1	3.1
1,4-Dioxane	H-beta	73.6	9.8
1,4-Dioxane	HZSM-5	69.5	25.5
THF	H-beta	65.3	6.2
THF	HZSM-5	59.0	13.5
Cyclohexane	H-beta	62.1	5.3
Cyclohexane	HZSM-5	54.8	6.1

^a Reaction conditions are the same in Table 1.

^b H_2O 15 ml and 1,4-dioxane 15 ml were mixed as solvent.

causes a dramatic decrease of the IBA conversion over both of the catalysts. The conversion reached almost 100% over H-beta zeolite when the most polar solvent-H₂O was used. This may be attributed to the favoured formation of polar intermediate in polar solvents. According to the mechanism of Prins reaction [15], the cation (RC⁺(H)OH) obtained by the attack of an electrophile (H⁺) to the oxygen atom of IBA forms firstly in the system, and then the cation attacks the double bond of isobutylene. We understand that polar cation is more stable and easy of formation in polar solvents, which would improve the IBA conversion.

In almost all kinds of solvent, the OCD yield over HZSM-5 zeolite is higher than that over H-beta catalyst. These results indicate that HZSM-5 performance higher selectivity than H-beta for the OCD formation.

3.3. Influence of IBA/TBOH ratio

As HZSM-5 zeolites show high activity and selectivity for the OCD formation, the effect of initial ratios between reagents were investigated by using HZSM-5 (Si/Al = 25) sample. The reaction results are shown in Fig. 1.

Increasing the amount of TBOH would increase both the IBA conversion and the OCD yield. The maximum OCD yield is obtained at IBA/TBOH ratio = 1/4 (vol. ratio). Further increasing the amount of TBOH almost hardly affects the IBA conversion, but decreases the formation of OCD. We believe that this is because most of the strong acid sites participate in the polymerization of isobutene when too much TBOH is added, which will not only affect the adsorption of IBA, but also decrease the number of effective acid sites for the Prins reaction.

3.4. Effect of catalyst weight

Data in Fig. 2 show the effect of catalyst weight on the condensation of IBA with TBOH over HZSM-5 (25). The

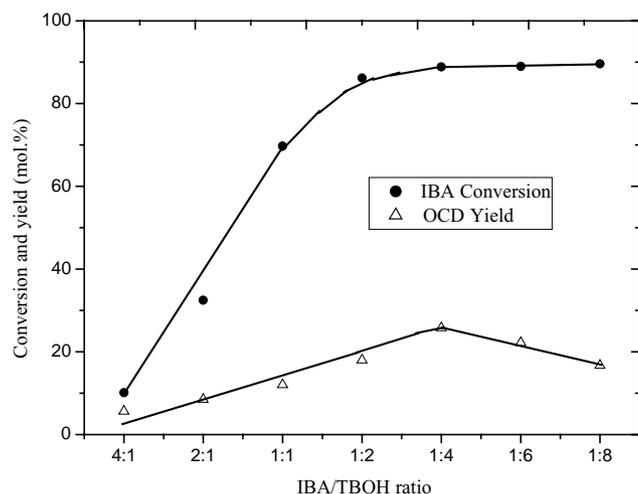


Fig. 1. Effect of IBA/TBOH on the formation of OCD over HZSM-5 (Si/Al = 25). Reaction conditions: catalyst 3 g, IBA 5 ml, 1,4-dioxane 15 ml, temperature 200 °C, time 10 h.

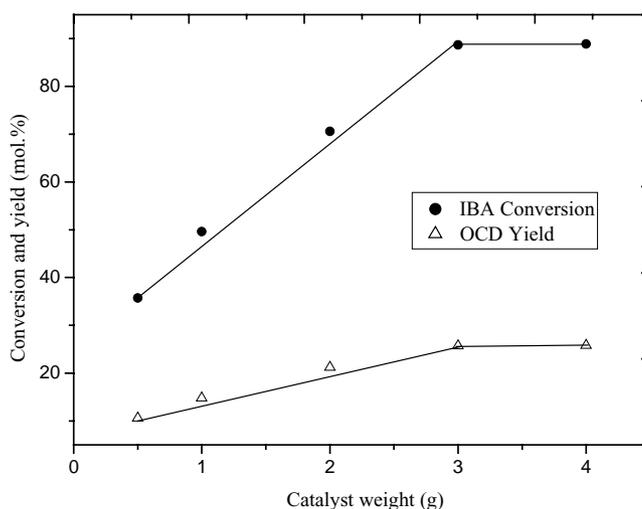


Fig. 2. Conversion of IBA and yield of OCD as a function of catalyst weight. Reaction conditions: TBOH 20 ml, IBA 5 ml, 1,4-dioxane 20 ml, temperature 200 °C, time 10 h.

IBA conversion increases with catalyst weight, and reaches nearly 90% at catalyst/IBA ratio of 3/5 (g/ml). The OCD yield increases also with catalyst weight, and reaches at 26% at the highest IBA conversion. Further increasing the amount of catalysts affects hardly the conversion and the yield.

3.5. Effect of reagents concentration

The changes of IBA conversion and OCD yield with solvent amount are shown in Fig. 3.

Increasing solvent amount causes a linear decrease of IBA conversion. This may be attributed to the decreasing of the reaction rate for diminishing the reactants concentration in the liquid-phase. The maximum OCD yield is obtained when

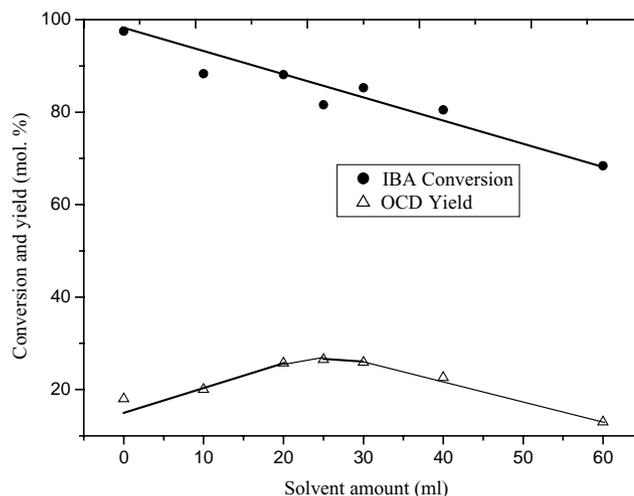


Fig. 3. IBA conversion and OCD yield as a function of solvent amount. Reaction conditions: catalyst 3 g, TBOH 20 ml, IBA 5 ml, temperature 200 °C, time 10 h.

proper amount solvent (solvent/IBA = 5/1 vol. ratio) is added.

3.6. Influence of reaction temperature

Fig. 4 shows the effect of reaction temperature on the condensation of IBA with TBOH over HZSM-5 zeolite. Increasing the reaction temperature causes a dramatic increase of IBA conversion and OCD yield. A maximum OCD yield is obtained at 160 °C and a maximum IBA conversion at about 180–220 °C. These may be attributed to the competition between the condensation reaction and the side-reactions, such as decomposition and disproportionation of IBA. We understand that both the condensation reaction and the side-reactions could be improved by increasing the temperature, which results in the enhancing of IBA conversion and OCD yield. When the reaction temperature reaches at 160 °C, the condensation reaction conquers the other reactions, and the highest OCD yield is obtained. Further increasing the temperature would enhance the side-reactions more than the Prins reaction, which results in the increasing of the IBA conversion but decreasing OCD selectivity. When the temperature is over 220 °C, most of the strong acid sites participate in the side-reactions (including decomposition and disproportionation of IBA and polymerization of isobutylene), and causes the deactivation of the acidic catalysts, which would result in the decreasing of IBA conversion.

3.7. Effect of reaction time

To investigate the effect of reaction time on the condensation reaction, the liquid-phase samples were withdrawn periodically from the autoclave and analysed on a GC. The results are shown in Fig. 5. It is interesting to note that IBA decreased about 40% in the liquid-phase as soon as the auto-

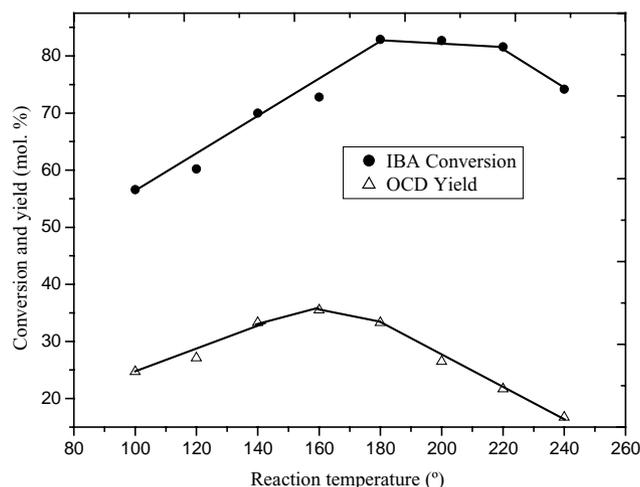


Fig. 4. The effect of temperature on the condensation of IBA with TBOH over HZSM-5 (25). Reaction conditions: catalyst 3 g, IBA 5 ml, TBOH 20 ml, 1,4-dioxane 25 ml.

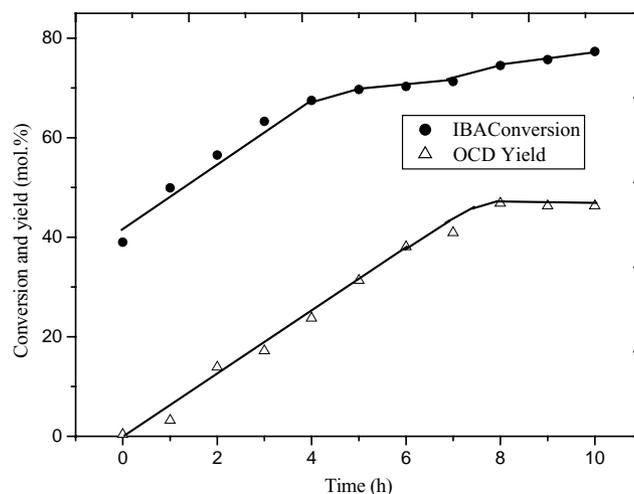


Fig. 5. Conversion of IBA and yield of OCD as a function of reaction time. Reaction conditions: HZSM-5 (30) 3 g, IBA 5 ml, TBOH 20 ml, 1,4-dioxane 25 ml, and temperature 160 °C.

clave was heated to the desired temperature (reaction time = 0). This may be accounted for the fact that part of IBA vaporizes to the gas-phase under the reaction temperature, which would result in the decreasing of IBA concentration in the liquid-phase. At the initial period, the IBA conversion and the OCD yield increase linearly with reaction time. The maximum OCD yield is obtained at about 8 h, which is hardly affected by prolonging the reaction time, but the IBA conversion increases with the reaction time, even though no more OCD was formed.

3.8. Effect of Si/Al ratio of HZSM-5 catalysts

Detailed studies are thus focused on HZSM-5 molecular sieves with varying Si/Al ratios. The results of the condensation reaction are shown in Table 3.

The data in Table 3 show that the Si/Al ratio of HZSM-5 catalysts affect significantly the catalytic performance, and the highest OCD yield (57.8%) was obtained over HZSM-5 with Si/Al = 39. 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 could adsorb large number of polar species (such as IBA and H₂O) 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 TBOH 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 would cause an increasing of decomposition and disproportionation of IBA, which would decrease the selectivity of the condensation reaction. Hence, the catalytic

Table 3
Condensation of IBA with TBOH over HZSM-5 with different Si/Al ratio^a

Catalyst	Si/Al (mol)	Surface area (m ² g ⁻¹)	IBA conversion (%)	OCD selectivity (%)	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

^a Reaction conditions are the same in Fig. 5, but reaction time = 8 h.

synthesis of OCD by condensation of IBA with TBOH is controlled by the competition between 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 optimum reaction conditions for the Prins condensation of IBA with TBOH in a liquid-phase reaction are HZSM-5 (Si/Al = 39) 3 g, IBA 5 ml, TBOH 20 ml, 1,4-dioxane 25 ml, reaction temperature 160 °C, and time 8 h. Up to 78.6% IBA conversion is obtained with a 57.8% OCD yield. 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 reaction. Only a preliminary short note from our group has been reported till date [16]. The same catalyst sample was recovered and regenerated by calcination in air for eight times, and no obvious variety of activity and selectivity is observed. This indicates that the catalyst can be used repeatedly.

3.9. Effect of catalyst type

Typical reaction results for different molecular sieve catalysts in the condensation of IBA with TBOH under optimum reaction conditions are shown in Table 4. 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 molecular sieve catalysts, so they exhibit high activity for the acid-catalyzed condensation reaction. However, HM, which should have enough acidity for the condensation re-

action to occur as it does with H-beta and HZSM-5, shows little activity under the same operation conditions. This suggests that this reaction is not only controlled by acid strength of the catalysts, but also closely connected with pore sizes and channel systems of the molecular sieves. For HM molecular sieve, its topological structure is composed of two pore systems: 8-ring channel of 0.26 nm × 0.57 nm and 12-ring straight channel of 0.65 nm × 0.70 nm. For this reaction, the 8-ring channel is too small to allow the reactants to enter, so only the 12-ring channel is effective for the reactants diffusion, which is unfavourable compared with the diffusion over molecular sieves with multi-dimensional pore structure, such as HY, H-beta and HZSM-5. This may result in the low activity over HM. For HY, though the reactants and products can diffuse easily in the 3-dimensional channels, its acidity is not strong enough to catalyse the condensation reaction effectively under the testing conditions, so it exhibits lower activity than HZSM-5. For its weak acidity and mono-channel system, SAPO-5 molecular sieve shows little activity in the condensation reaction.

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 with the 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 opening (0.66 nm × 0.67 nm ↔ 0.56 nm × 0.56 nm) than ZSM-5 (0.53 nm × 0.56 nm ↔ 0.51 nm × 0.55 nm), which may be favourable to the formation of isomers. For HY, the existing of the supercages dampens the free diffusion of the

Table 4
Properties and catalytic performance of molecular sieve catalysts

Catalyst	Si/Al (mol)	BET surface area (m ² g ⁻¹)	Pore size (nm) [17]	Dimension	IBA conversion (%)	OCD selectivity (%)	Yield (%)
SAPO-5	— ^a	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; 0.56 × 0.56	3	88.8	11.9	10.6
HZSM-5	38.8	329	0.51 × 0.55; 0.53 × 0.56	3	78.6	73.5	57.8

^a The mole ratio of SAPO-5 is Al_{0.50}P_{0.44}Si_{0.06}O₂.

reactants, and the relative weak acidity is disadvantageous for the formation of OCD, so it exhibits lower activity and selectivity. We understand that HZSM-5 molecular sieves possess strong enough acidity for the condensation reaction, and the unusual straight channel systems make the reactants and products diffusing easily, so HZSM-5 shows much higher activity and shape-selective effect than the other molecular sieve catalysts investigated.

Besides the acidity and channel system, the hydrophobicity/hydrophilicity of the catalysts would also affect the condensation reaction. The catalyst adsorbed proper amount of hydrophilic IBA and oleophilic isobutylene would show optimum catalytic performance.

3.10. Side-reactions in the system

One of the main side-reactions is the polymerization of isobutylene, which could be proved by detecting the dimers formation in the liquid-phase.

IBA could be decomposed to propene, CO and H₂ under some reaction conditions [18]. To investigate the IBA decomposition reaction, several blank experiments were carried. Twenty grams of IBA was added into the autoclave with fresh catalysts (4 g), and the autoclave was heated at 160 °C for 8 h. The reaction results are shown in Table 5.

From Table 5, no IBA conversion is observed in the case that catalysts are absent, which indicates that IBA is stable thermodynamically at 160 °C. In the cases that no solvent was added, about 25% IBA conversion is observed over both HZSM-5 and NaZSM-5 catalysts, and the main components in the gaseous are propene, CO and H₂. This result suggests that the IBA decomposition could be catalyzed by both strong and weak acid sites (The NH₃-TPD results show that the strong acid sites have dismissed from NaZSM-5 catalyst), and the main side-reaction is the decomposition of IBA.

In the absence of solvent, the HZSM-5 catalyst possessed both strong acid sites and weak acid sites shows the same catalytic performance as NaZSM-5 does for the decomposition of IBA. Adding 1,4-dioxane (solvent) to the system would significantly increase the IBA conversion (about 55.3%). This may be attributed to the different diffusion and adsorption of the reactants and solvents over acid sites. We under-

stand that IBA is a polar molecule that could adsorb strongly on the strong acid sites, and the strong interaction between IBA and acid sites makes it difficult to release the active centres, which would further affect the IBA conversion over the strong acid sites. In the case that proper solvent presents, the solvent–strong acid site interaction would decrease the adsorption of IBA, and the activated IBA could be desorbed or converted to products. However, different kind of solvents has different interaction degree with the acid sites, which would further affect the reaction differently.

The solvent effect is also observed in the cases that methanol, ethanol, cyclohexane, tetrahydrofuran (THF), and H₂O were used as solvent. However, they do not show the same performance as 1,4-dioxane does. This result further indicates that the solvents in the system not only dissolve and disperse the reactants, but also interacts with the reactive sites, which would further affect the condensation reaction.

The liquid products were analysed with GC–MS. About 50 compounds were formed in the system. They could be divided into three groups: small molecular group, 8-carbon atoms group, and 12-carbon atoms group. In the small molecular group, the main products are the unreacted reactants (including IBA and TBOH), isobutylene, 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 octene 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

Some molecular sieves are effective catalysts to replace strong mineral acids for the Prins condensation of IBA with TBOH in a liquid-phase reaction. The molecular sieve catalysts (specially, HZSM-5) with strong enough acidity and proper channel systems exhibit high activity and selectivity. The catalytic synthesis of OCD is controlled by the competition between the condensation reaction and the side-reactions, and the HZSM-5 catalyst with an optimum Si/Al ratio and proper hydrophobicity/hydrophilicity adsorbed IBA and isobutylene at the same time exhibits the highest activity and selectivity. The main side-reaction related to IBA is the decomposition of IBA to propene, CO and H₂, which could be catalyzed by both strong acid sites and weak acid sites. The solvent–active site interaction would significantly affect the condensation reaction. Only the solvent that not only dissolves both the aqueous and organic phases, but also possesses proper adsorption ability on the active sites shows optimum solvent effect. 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,

Table 5
Effect of different acid sites on the decomposition of IBA

Catalyst	Solvent	Conversion of IBA (%)
HZSM-5 (30)	1,4-Dioxane ^a	55.3
HZSM-5 (30)	No	23.3
NaZSM-5 (30) ^b	No	25.0
No	No	0

^a Thirty grams of 1,4-dioxane was added.

^b NaZSM-5 was prepared by ion-exchanging the HZSM-5 with 0.1 M NaNO₃ at 90 °C for four times, and calcined at 550 °C for 3 h under air.

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, 3rd ed., W.B. Saunders, Philadelphia/London, 1965.
- [2] W. Hölderich, M. Hesse, F. Nümann, *Angew. Chem. Int. Ed.* 27 (1988) 226–246.
- [3] T.M. Jyothi, M.L. Kaliya, M.V. Landau, *Angew. Chem. Int. Ed.* 40 (2001) 2881–2884.
- [4] T.M. Jyothi, M.L. Kaliya, M. Herskowitz, M.V. Landau, *Chem. Commun.* (2001) 992–993.
- [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.* 2 243 701 (1973).
- [7] T. Yamaguchi, C. Nishimichi, *Catal. Today* 16 (1993) 555.
- [8] Y. Higashio, K. Takahashi, *EP* 0 215 567 (1987).
- [9] T. Yamaguchi, C. Nishimichi, A. Kubota, *Prepr. Am. Chem. Soc. Div. Pet. Chem.* 36 (1991) 640–649.
- [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] T. Yamaguchi, *Appl. Catal.* 61 (1990) 1–25.
- [13] D. Young, M.E. Davis, *Zeolites* 11 (1991) 277–281.
- [14] R.J. Argauer, G.R. Landolt, *US Patent* 3 702 886 (1972).
- [15] E. Dumitriu, D. Trong On, S. Kaliaguine, *J. Catal.* 170 (1997) 150–160.
- [16] H. Wang, Z. Liu, C. Sun, G. Wang, *Catal. Commun.* 5 (2004) 41–43.
- [17] C. Baerlocher, W.M. Meier, D.H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, The Netherlands, 2001.
- [18] A.G. Ruhrchemie, *Oil Gas J.* 68 (1970) 59.