Selective isomerization of isophorone oxide over zeolites

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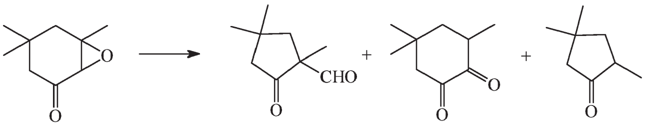
Ring-contracted main product formed by isomerization of isophorone oxide (**1**) is 2-formyl-2,4,4-trimethylcyclopentanone (**2**); a high yield of (**2**) could be achieved by use of zeolites as heterogeneous catalysts. The reaction could be carried out in a discontinuous liquid-phase batch reactor as well as in a continuous vapor-phase fixed-bed reactor. The formation of (**4**) by decarbonylation of (**2**) could be reduced by increasing the catalyst loading or by carrying out the reaction under short contact time in gas phase conditions.

Keywords: isophorone oxide, zeolites, isomerisation

1. Introduction

Terpene epoxides are very reactive compounds. Some products formed by isomerization of terpene epoxides are valuable raw materials for perfumes, synthetic flavourings and pharmaceuticals, and also provide useful intermediates in organic syntheses. The isomerization of isophorone oxide (**1**) was originally investigated by House and Wasson using boron trifluoride etherate as a homogeneous catalyst [1]. They found that at room temperature, using benzene as the solvent, only 3% consisted of the diketone (**3**) and mainly the ring-contracted products were obtained: 33% of keto aldehyde (**2**) and 28% of ketone (**4**). From an industrial point of view, the desired compound is the keto aldehyde (**2**), which is an interesting intermediate for fragrance chemicals. The acid-catalyzed reaction mechanism leading to the synthesis of keto aldehyde (**2**) had been discussed earlier [1,2]. Therefore, it is of interest to investigate whether the product distribution changes in the presence of a heterogeneous catalyst system and also whether the decarbonylation of the compound (**2**) to compound (**4**) can be suppressed.



(**1**) (**2**) (**3**) (**4**)

In the case of heterogeneous catalysis carried out with zeolites, the keto aldehyde (**2**), accompanied by the ketoenolic form of the α-diketone (**3**) [3], is mainly formed as has been reported by Sheldon et al. [4,7].

Our report on catalytic isomerization using various zeolitic catalysts in comparison to the conventional catalysts previously used gives results of reactions carried out discontinuously in a batch reactor in liquid phase, as well as for those carried out continuously in a fixed-bed reactor in the vapor phase.

2. Experimental

For the experimental standard procedure in the liquid phase, 5.0 g isophorone oxide and 10.0 g toluene were added to 0.5 g powderous catalyst in a glass flask. Under stirring conditions this slurry was heated up to the reaction temperature of 110 °C. Samples were taken from the reaction mixture by means of a syringe filter and were separated by centrifugation. The compounds were analyzed by GC and characterized by GC-MS, GC-IR, ^{1}H-NMR and ^{13}C-NMR.

In a standard vapor-phase experiment, the reaction mixture consisting of isophorone oxide and toluene (1 : 2 weight ratio) was pumped by means of a metric pump into a fixed-bed reactor, which was preheated to 250 °C. The reactor was filled with 2.0 g of granulated catalyst (1.0–1.6 mm particles), and the reaction was carried out under a nitrogen flow rate of 8 $\mathrm{l\,h^{-1}}$. The products were collected at 2 h periods and analyzed by GC. Before the reactions were carried out, the catalyts were calcined at 550 °C for 6 h.

3. Results and discussion

The results obtained in the liquid phase over heterogeneous catalysts are summarized in table 1. Small yields (<1%) of additional by-products were found, for example, 3-methoxy-5,5-dimethylcyclo-2-hexenone and 2-acetyl-4,4-dimethylcyclopentanone.

The data presented are related to a reaction time of 6 h. The numbers in parentheses correspond to the SiO_2/Al_2O_3

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Table 1
Conversion and selectivities of used zeolites in liquid-phase isomerization.[a]

Catalyst	Conversion (%)	Selectivity (%)		
		(2)	**(3)**	**(4)**
H-ZSM-5 (28)	88	68	14	1
H-ZSM-5 (60)	95	68	15	0
Na-ZSM-5 (28)	8	64	27	0
Na-ZSM-5 (100)	2	52	30	0
H-[B]-ZSM-5 (38)	52	70	12	0
H-BEA (25)	100	68	13	14
H-Y (5.2)	45	62	17	3
H-US-Y (6)	79	67	19	3
H-US-Y (70)	96	73	12	0
H-US-Y (96)	100	74	11	1
H-US-Y(96)-HCl	100	71	17	4
H-FER (18)	100	81	12	0
Silicalite	1	17	16	0
[Ti]-MFI	1	24	23	0
D11-10 (SiO_2)	9	57	7	1
D10-10 (Al_2O_3)	2	3	70	6
SAPO 11	1	51	0	0
H-Nafion	100	52	31	10

[a] $t = 6$ h; $T = 110\,^{\circ}$C; solvent: toluene; loading: 10 g(isophorone)/g(catalyst); 1 atm pressure.

or SiO_2/B_2O_3 ratios. The blank test in liquid phase yields less than 1% conversion. Unlike non-zeolitic catalysts, except for H-Nafion, most zeolites yield complete conversion. A high yield of the keto aldehyde (**2**), up to 81%, was attained by using H-FER as an heterogeneous catalyst. For the rearrangement of isophorone oxide, the presence of the acid sites is necessary for the catalytic activity. The reactivity of H-FER can be explained by the acid outer surface of the catalyst. Molecular modeling showed that in this case the isophorone epoxide is too bulky for the small pore size of ferrierite. The outer surface of H-FER and microporous structure was determined by nitrogen sorption (BET).

The ratio between the two main products (**2**) and (**3**) depends on the type and acidity of zeolite used. For example, H-BEA with a higher acid outer surface demonstrated a high activity but a low selctivity of (**2**) in comparison to H-FER or H-US-Y catalysts.

High amounts of (**2**) were also obtained by the use of H-US-Y (96) followed by H-US-Y(96)-HCl. The H-US-Y(96)-HCl used was a modified highly dealuminated ultrastable Y zeolite, which was pretreated with diluted acid according to the method described by Liebens [5,8]. This zeolitic catalyst, unlike many others, remains active at lower temperatures and also at high loadings, as was previously demonstrated in the isomerization of α-pinene oxide using this heterogeneous catalyst [5,8].

Poor results were achieved when Na-ZSM-5, silicalite, silica (D11-10), Al_2O_3 (D10-10), calcined $Al(OH)_3$ and SAPO-11 were used. It was also observed that conversion and selectivity to (**2**) tended to increase with higher SiO_2/Al_2O_3 ratios when using H-Y catalysts from H-Y (5.2) to H-US-Y (96). Higher SiO_2/Al_2O_3 ratios lead to increased acidity of the catalyst as well as to a more facile desorption of (**2**).

Table 2
Conversion and selectivities at different reaction temperatures by using H-US-Y(96)-HCl and H-BEA (25).[a]

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		
			(2)	**(3)**	**(4)**
H-US-Y(96)-HCl	60	91	71	8	1
	80	100	75	12	2
	110	100	72	16	2
	130[b]	100	72	14	2
H-BEA (25)	60	46	65	9	7
	80	100	71	12	10
	110	100	70	12	11
	130[b]	100	64	12	18

[a] $t = 2$ h; solvent: toluene; loading: 10 g(isophorone)/g(catalyst); 1 atm pressure.
[b] Solvent: *o*-xylene.

Table 3
Conversion and selectivities at increasing loadings by using H-US-Y(96)-HCl and H-BEA (25).[a]

Catalyst	Loading (g(reactant)/g(catalyst))	Conversion (%)	Selectivity (%)		
			(2)	**(3)**	**(4)**
H-US-Y(96)-HCl	10	100	71	17	4
	30	100	75	13	1
	100	97	83	11	0
	200	11	51	16	5
H-BEA (25)	10	100	68	13	14
	30	100	74	13	5
	100	84	75	11	1
	200	41	72	9	1

[a] $t = 6$ h; $T = 110\,^{\circ}$C; solvent: toluene; 1 atm pressure.

Further evidence for the excellent activity of H-US-Y(96)-HCl and H-BEA (25) was derived when investigating the influence of temperature (table 2). At 80 °C, a maximum of selectivity to (**2**) was obtained at complete conversion within a 2 h reaction time. Likewise, the formation of (**4**) by decarbonylation of (**2**) was reduced by increasing the catalyst loadings (table 3).

The influence of solvents was also investigated. A high selectivity was achieved when using less polar solvent, such as heptane or toluene. More polar solvent caused lower activity and selectivity, except for anisole, with which selectivity of (**2**) reached 85% using H-FER. An aromatic character of the solvent seems to favor the formation of keto aldehyde (**2**), as the results obtained with toluene, *o*-xylene and anisole suggest (table 4). As expected, the solvent acetonitrile totally inhibited the reaction [6].

We correlated our data to that obtained by Sheldon et al. [8] in the isophorone oxide rearrangement. There a dealuminated mordenite was used, and a selectivity of 85% to (**2**) in benzene as a solvent was found. The results are comparable to our findings over H-FER.

To our knowledge, no vapor-phase isomerization utilizing heterogeneous catalysts has been previously described in the literature. Continuous vapor-phase reactions should be preferred over discontinuous liquid-phase reactions, as this yields a higher efficiency (space time yield) as well as an easier separation of the catalyst from the reaction mixture.

A general view of the used zeolites in the vapor-phase isomerization and their conversions and selectivities are shown in table 5. The blank test yields less than 2% conversion. The presented results are related to TOS (time on stream), which in this case was 4 h, and 1 h^{-1} WHSV (weight hourly space velocity).

Table 4
Conversion and selectivities by using H-FER (18) with different solvents in the liquid phase.[a]

Solvent	Conversion (%)	Selectivity (%) (**2**)	(**3**)	(**4**)
heptane (98 °C)	100	81	13	0
toluene (110 °C)	100	81	12	0
toluene (80 °C)	92	74	11	0
toluene (60 °C)	37	62	5	1
o-xylene (130 °C)	100	81	11	3
anisole (110 °C)	100	85	12	0
1,4-dioxane (101 °C)	100	65	19	2
THF (67 °C)	20	62	5	1
ethanole (78 °C)	19	9	11	3
acetonitrile (81 °C)	0	75	0	0
without solvent (110 °C)	100	75	11	1

[a] $t = 6$ h; loading: 10 g(isophorone oxid)/1 g(catalyst); 1 atm pressure.

Table 5
Conversion and selectivities by using zeolites in gase-phase isomerization.

Catalyst	Conversion (%)	Selectivity (%) (**2**)	(**3**)	(**4**)
H-ZSM-5 (28)	99	69	18	2
H-ZSM-5 (60)	100	72	18	1
Na-ZSM-5 (28)	70	61	27	0
Na-ZSM-5 (100)	21	65	22	0
H-[B]-ZSM-5 (38)	90	82	10	1
H-BEA (25)	100	34	45	14
H-Y (5.2)	100	62	26	4
H-US-Y (6)	100	61	26	4
H-US-Y (70)	100	66	19	6
H-US-Y (96)	99	69	21	5
H-US-Y(96)-HCl	100	68	23	3
H-FER (18)	100	66	24	3
D11-10 (SiO_2)	100	71	17	3
D10-10 (Al_2O_3)	86	25	61	5
H-Nafion	100	66	24	3

[a] TOS = 4 h; $T = 250$ °C; solvent: toluene; toluene/isophorone oxide 2 : 1 wt/wt; nitrogen flow 8 l h^{-1}; WHSV = 1 h^{-1}; 1 atm pressure.

All tested zeolites yielded high conversions, except for Na-ZSM-5 and silicalite. In the vapor-phase experiments, SiO_2 (D11-10) and Al_2O_3 (D10-10) were also very active, in contrast to the results obtained in the liquid phase. Surprisingly, in the case of H-BEA and Al_2O_3 (D10-10), selectivities of 45 and 61%, respectively, for the α-diketone (**3**) were achieved. H-BEA showed a low selectivity to (**2**), but the selectivity could be influenced by changing the WHSV and the nitrogen flow rate (residence time). A shorter contact time seems to have a positive effect on the aldehyde formation, possibly due to reduced decarbonylation (table 6).

The highest selectivity obtained for the keto aldehyde (**2**) was 82% using H-[B]-ZSM-5 in the vapor-phase followed by 72% selectivity with H-ZSM-5 (60).

Unlike the other catalysts, H-[B]-ZSM-5 and H-MOR deactivated. For example, after 8 h TOS there was a poor rate of conversion, in comparison to the other catalysts used. Using H-[B]-ZSM-5 only under higher-temperature conditions (over 300 °C) good conversion rates could be obtained.

Using zeolites with the same structure but in different ratios of SiO_2/Al_2O_3, we found the tendency towards an increased selectivity to (**2**) with higher SiO_2/Al_2O_3 ratios, as was previously observed in liquid-phase isomerization.

The influence of "solvents" in the gas phase is similar to that in the liquid phase. Best yields were obtained with toluene, anisole and *o*-xylene. In acetonitrile the catalysts were found to be deactivated. The amount of solvent in the reaction mixture did not appear to influence the results, neither in liquid nor in vapor phase.

In conclusion, the use of zeolites as catalysts in the isomerization of isophorone oxide (**1**) yields up to an 86% yield of keto aldehyde. The reaction could be carried out in a discontinuous liquid-phase batch reactor as well as in a continuous vapor-phase fixed-bed reactor. The formation of (**4**) by decarbonylation of (**2**) could be reduced by increasing the catalyst loading or by carrying out the reaction under short contact time in gas-phase conditions.

The heterogeneously catalyzed isomerization of terpene epoxides over zeolites is a suitable, non-polluting method of preparing relevant and useful aldehydes for the synthesis of perfumes and synthetic flavours.

Table 6
Conversion and selectivities at increasing nitrogen flow and WHSV by using H-ZSM-5 (60) and H-BEA (25).[a]

Catalyst	WHSV (h^{-1})	Nitrogen flow (1/h)	Residence time (s)	Conversion (%)	Selectivity (%) (**2**)	(**3**)	(**4**)
H-ZSM-5 (60)	1	4	3.8	100	67	23	0
	1	8	1.9	100	72	18	1
	1	12	1.3	100	74	18	0
H-BEA (25)	1	8	1.9	100	34	44	13
	2	12	1.3	100	49	34	9

[a] TOS = 4 h; $T = 250$ °C; solvent: toluene; 1 atm pressure.

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