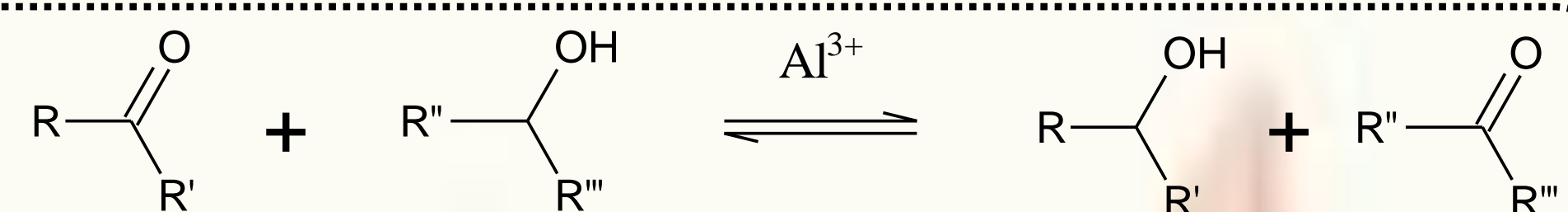


## INTRODUCTION



**Fig.1:** Course of the Meerwein-Ponndorf-Verley (MPV) reduction and Oppenauer oxidation

The aim of this work was to find suitable heterogeneous catalyst for the Meerwein-Ponndorf-Verley (MPV) reduction of cinnamaldehyde to cinnamyl alcohol. The heterogeneous catalysts should serve as an alternative to homogeneous catalysts due to its possible recovery and reuse and simple separation from the reaction mixture.

MPV reduction has been investigated using different heterogeneous catalysts, including hydrous zirconia, hydrotalcites, magnesium-aluminium mixed oxide previously obtained from a layered double hydroxide or magnesium-gallium and magnesium-indium hydrotalcite – like compounds, zeolites,  $\text{TiO}_x/\gamma\text{-Al}_2\text{O}_3$ , metal alkoxides immobilized on mesoporous materials based on silica, aluminosilicates or titanosilicates and metal oxides such as  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{ZrO}_2$  modified by boron or alkaline-earth metal (Mg, Ca, Sr, Ba) to enhance their acid and basic properties in the MPV reduction.

## EXPERIMENTAL

### Reaction conditions:

- cinnamaldehyde: 3 g
- propan-2-ol: 30 ml
- catalyst: 3 g
- reaction temperature: 95 °C

### Used catalysts:

- alumina CG-20
- acid activated aluminas
  - commercial type I 504 C
  - laboratory-prepared
- aluminosilicate 80/20
- MCM-41
- mixed oxides with different molar ratio of Mg / Al (MOx)
- rehydrated hydrotalcites with different molar ratios of Mg / Al (rHTx)

### Catalyst pretreatment:

- drying at 300 °C at least for 6 hours

### Acid activation of alumina (CG-20):

- stirring with 10%  $\text{HNO}_3$ , 24 h, room temperature
- filtration, washing and drying at 300 °C for 6 hours

### Catalyst regeneration (acid-activated alumina I 504 C):

- washing with propan-2-ol
- oxygen atmosphere (25-85% nitrogen)
- 550 °C for at least 8 hours

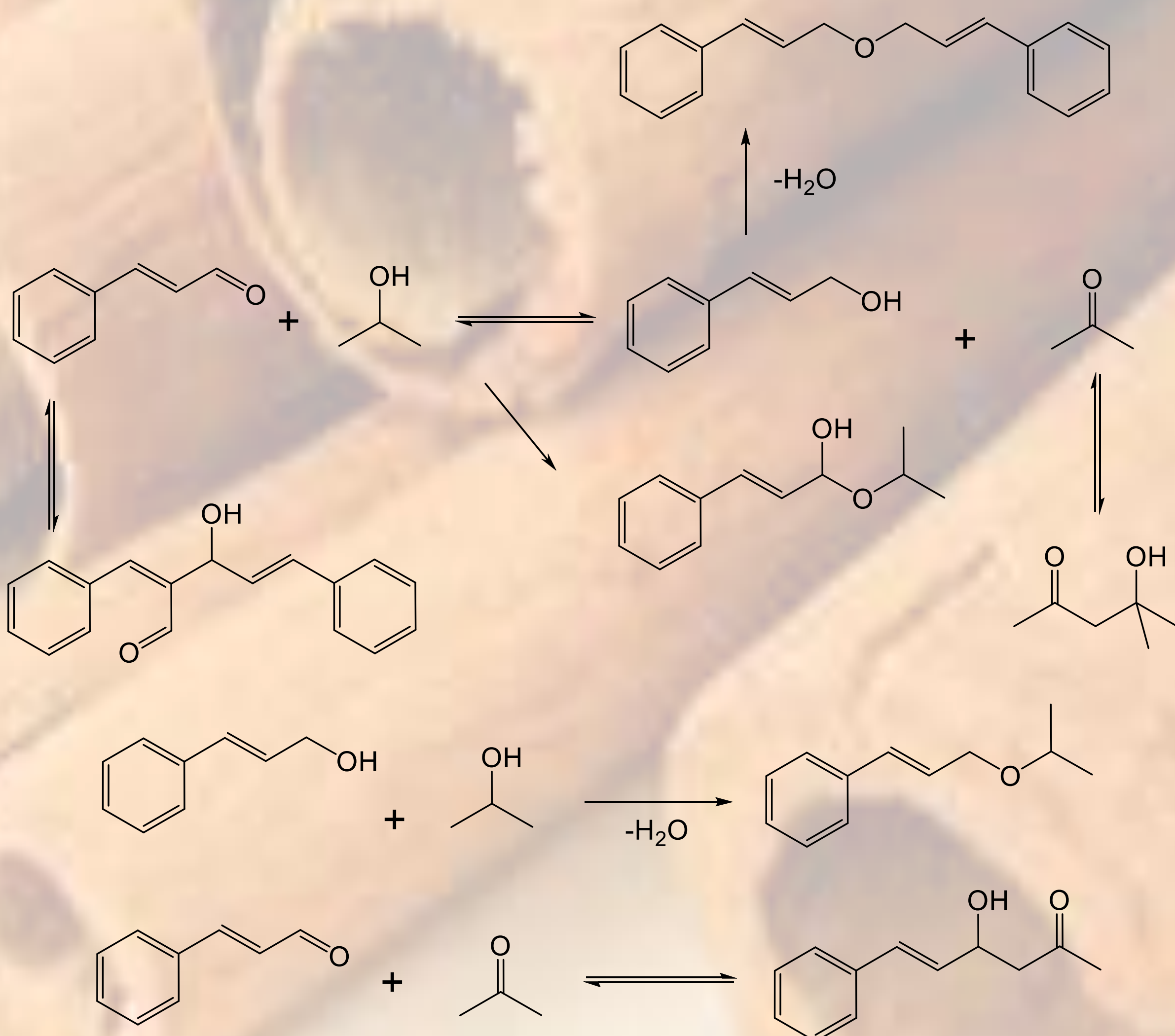
### Preparation of MOx:

- calcination of the corresponding hydrotalcites at 500 °C for 6 h

### Process of preparation of rHTx:

1. preboiled demineralized water
2. sparging by nitrogen for 15 minutes
3. addition of calcined hydrotalcite
4. stirring for 90 minutes and sparging by nitrogen
5. evaporation of water under an argon atmosphere

## RESULTS



**Fig.2:** Reaction scheme for MPV reduction of cinnamaldehyde by propan-2-ol and formation of by-products

**Table 1:** Comparison of materials used for MPV reduction of cinnamaldehyde to cinnamyl alcohol

Parameter	Alumina CG-20	Acid activated alumina I 504 C	Acid activated alumina (prepared)	Aluminosilicate	MCM-41	MO <sub>2,5</sub>
Time for the 30 % conversion [h]	12	6	6	7	-	-
Conversion after 12 h [%]	30	64	68	38	4	20
Selectivity after 12 h [%]	71	77	71	68	-	62
Conversion after 24 h [%]	42	70	72	50	-	24
Time for 100 % conversion [h]	-	55	-	-	-	-

**Table 2:** Comparison of catalysts based on hydrotalcite – like compounds used for MPV reduction of cinnamaldehyde to corresponding alcohol

Catalyst	MO <sub>2,5</sub>	MO <sub>3</sub>	MO <sub>3,5</sub>	rHT <sub>2,5</sub>	rHT <sub>3</sub>	rHT <sub>3,5</sub>
Conversion after 3 h [%]	12	8	7	4	3	6
Selectivity after 3 h [%]	57	69	65	56	42	44

**Table 3:** Recycling of acid activated alumina I 504 C

Reuse number	0	1	2	3
Conversion after 3 h [%]	56	45	47	46
Selectivity after 3 h [%]	75	70	68	69

## CONCLUSION

- Heterogeneous alumina-based materials were used as catalysts for MPV reduction of cinnamaldehyde to cinnamyl alcohol.
- Commercial acid activated alumina (I 504 C) showed optimistic results: 64% conversion with 77% selectivity to the desired product after 12 hours.
- Acid activated alumina can be separated and at least two times reused in the reaction without significant loss of activity and selectivity.