

# Ru Supported Catalysts Testing in the Preparation of p-Isopropylcyclohexylmethanol

Optimizing the reaction conditions for this key aromatic material.

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It is known that p-isopropylcyclohexylmethanol (CAS# 13828-37-0) is a desirable compound in the fragrance industry, featuring a green, floral, petaly, magnolialike, tuberose and muguet odor profile. It occurs in two isomers, *cis* and *trans*, whose olfactory properties differ insignificantly. For the preparation of perfumes, the ratio 70:30 (*cis:trans*), commercially named Mayol<sup>a</sup>, is usually used. The preparation of Mayol most often starts with β-pinene.<sup>1</sup> This procedure starts by epoxidation of pinene, followed by ring-opening with the intermediate perillyl alcohol, which is finally hydrogenated (Ra-Ni) to p-isopropylcyclohexylmethanol.<sup>2</sup> Another possibility for its preparation is the formation from perillyl acetate (prepared from β-pinene oxide and acetic anhydride) and perillyl alcohol. The final step of this preparation was again hydrogenation (Ni/Al<sub>2</sub>O<sub>3</sub>).<sup>3</sup> Perillyl alcohol is an intermediate for the hydrogenation, which was also prepared from β-pinene oxide using the catalytic system pyridinium nitrate—nitric acid.<sup>4</sup> p-Isopropylcyclohexylmethanol can be prepared directly from p-cymene by electrochemical methods.<sup>5</sup>

The preparation of p-isopropylcyclohexylmethanol by direct hydrogenation of cuminaldehyde is also described in the literature.<sup>6,7</sup> In these patents, the addition of solvents to cuminaldehyde was suggested, and an Ru/C catalyst was used. Another possibility offered by literature is the use of Ru supported on alumina or silica.<sup>8,9</sup> Separation of the *cis* and *trans* isomers from the reaction mixture is also possible.<sup>10</sup>

Due to the accessibility of the information about hydrogenation of cuminaldehyde only in the patent form, the study of the influence of reaction conditions (solvent type, temperature, pressure) on the selectivity to the desired p-isopropylcyclohexylmethanol was performed in this work. The authors would like to also offer insights to the range of possible Ru/C catalysts.

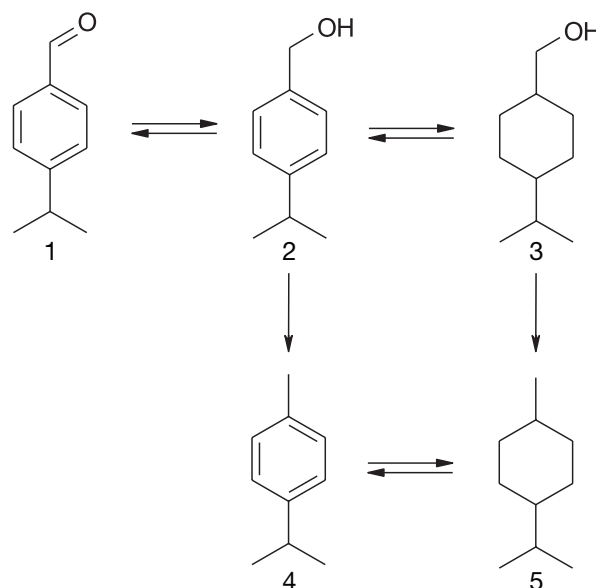
## Experimental

Commercially available catalysts (5% Ru support) used in this work are summarized in **T-1**.

**Hydrogenation experiments:** In a typical experiment, 14 g (95 mmol; or 7 g, i.e. 47.5 mmol and 7 ml of solvent) of cuminaldehyde and catalyst (0.3–5 wt.%) were inserted to the autoclave. The catalyst amount was calculated on a dry mass.

<sup>a</sup>Mayol is a trade name of Firmenich.

**F-1. Hydrogenation scheme (1: cuminaldehyde, 2: cuminal alcohol, 3: p-isopropylcyclohexylmethanol, 4: p-cymene, 5: methyl-4-isopropylcyclohexane)**



## At a Glance

p-Isopropylcyclohexylmethanol was selectively prepared from cuminaldehyde by hydrogenation using a 5% Ru supported commercial catalyst. Optimization of the reaction conditions (temperature, pressure, catalyst amount) was performed. The authors discovered that the temperature had the most significant influence on the selectivity; with increasing temperature, the selectivity decreased. The reaction conditions to obtain the selectivity to p-isopropylcyclohexylmethanol 93% at 99% conversion of cuminaldehyde were: 130°C, 15 MPa and 1 wt.% of catalyst based on substrate amount. The catalyst type selected is crucial.

### T-1. Hydrogenation catalysts (in all cases the content of Ru was 5%)

Producer	Support	Type	Declared amount of water (wt.%)
Johnson - Matthey	C	97	59.9
Johnson - Matthey	C	619	58.3
Johnson - Matthey	C	605	52.3
Johnson - Matthey	C	600	49.9
Johnson - Matthey	C - powder graphite	603	dry
Johnson - Matthey	C	620	62.6
Johnson - Matthey	Al <sub>2</sub> O <sub>3</sub>	698	1.9
Degussa AG	C	H 105 RA/W	56.4
BASF	C	reduced	53.96
Evonik Industries	C	Noblyst P3060	58.5
Evonik Industries	C	Noblyst P3055	58.5
Evonik Industries	Al <sub>2</sub> O <sub>3</sub>	Noblyst P3061	dry
C&CS	Al <sub>2</sub> O <sub>3</sub>	RD-420	dry

### T-2. Comparison of selectivity and reaction rates using different solvents

Solvent	Boiling point of the solvent [°C]	Polarity of the solvent ( $\epsilon_r$ )	Selectivity to Mayol [%]	Reaction rate [mmol*g <sub>Ru</sub> <sup>-1</sup> *min <sup>-1</sup> ]
none	-	-	76	36.1
1,4 dioxane	101	2.25	76	30.6
MTBE	55	2.60	70	28.9
diglyme	162	5.80	57	30.7
ethyl acetate	77	6.02	69	31.8
1,2 dimethoxy ethane	85	7.20	74	35.1
THF	66	7.60	66	25.7
Dowanol DME*	190	10.50	58	33.1
Dowanol PM	120	12.00	52	31.1
methanol	65	32.00	48	39.4
water	100	81.60	47	44.6

\*Dowanol is a trade name of The Dow Chemical Co.

The autoclave was washed by hydrogen and heated to the desired reaction temperature (100°–180°C). After heating, the reactor was pressurized (5–15 MPa), and the reaction was started by switching on the stirring. Samples taken during the reaction were analyzed on a GC equipped with an FID and non-polar column. The selectivity was calculated on the sum of isomers of p-isopropylcyclohexylmethanol.

## Results and Discussion

The first step of the hydrogenation of cuminaldehyde, the hydrogenation of aldehyde group, took place by forming cumin alcohol (**F-1**). Hydrogenation of the C=O double bond is less energetically demanding than the hydrogenation of the benzene ring. In the second step, the hydrogenation of the benzene ring is performed, forming the desired p-isopropylcyclohexylmethanol. Undesired reactions that can take place in this reaction mixture are the hydrogenolysis of the C-O bond, followed by the formation of the undesired products p-cymene and 1-methyl-4-isopropylcyclohexane from cuminalcohol or p-isopropylcyclohexylmethanol.

The influence of the solvent on the composition of the reaction mixture was studied, as a Firmenich patent suggested that the addition of 1,2-dimethoxy ethane (monoglyme) was advisable.<sup>6</sup> Summarized results are in **T-2**; the selectivity at total conversion of cuminaldehyde, the 99% conversion of cumin alcohol and the reaction rate are

### T-3. Influence of the temperature and pressure on the reaction using different catalyst types

Catalyst type	Catalyst amount [wt.%]	Pressure [MPa]	Temperature [°C]	Reaction rate [mmol* $g_{Ru}^{-1}$ *min $^{-1}$ ]	Composition of reaction mixture at 4 <sup>th</sup> hour [%]			
					Cumin aldehyde	Cumin alcohol	p-isopropylcyclohexyl-methanol	Undesired products
J M type 97	0.3	15	180	376.0	0.1	24.1	45.3	30.6
	0.3	15	100	112.7	59.7	34.5	1.3	4.5
	0.3	5	180	158.7	38.5	50.9	1.9	8.7
	5.0	10	130	36.1	0.5	0.9	58.9	39.8
J M type 698	0.3	15	130	158	32.4	61.8	2.3	3.5
	0.3	15	180	653	0.2	0.7	70.8	28.6
	1.0	15	130	132.9	0.0	6.8	80.1	13.1

### T-4. Testing of different catalyst types

Entry	Catalyst type	Reaction rate	Selectivity to
		[mmol*min $^{-1}$ * $g_{Ru}^{-1}$ ]	p-isopropylcyclohexyl-methanol [%]
1	5% Ru/C, Johnson Matthey, type 97	376.3	47
2	5% Ru/C, Degussa	649.6	53
3	5% Ru/C, BASF	459.2	74
4	5% Ru/C, Johnson Matthey, type 619	511.0	78
5	5% Ru/C, Johnson Matthey, type 605	444.2	73
6	5% Ru/Al <sub>2</sub> O <sub>3</sub> , Johnson Matthey, type 698	519.4	72
7	5% Ru/C, Noblyst P3060	688.0	75
8	5% Ru/C, Noblyst P3055	716.4	75
9	5% Ru/Al <sub>2</sub> O <sub>3</sub> , Noblyst P3061	597.9	65
10	5% Ru/C, Johnson Matthey, type 600	625.6	63
11	5% Ru/C, Johnson Matthey, type 603	744.8	58
12	5% Ru/C, Johnson Matthey, type 620	741.5	73
13	5% Ru/Al <sub>2</sub> O <sub>3</sub> , C & CS type RD 420	743.2	66

depicted. JM type 97 was used as a catalyst, with temperature 130°C and pressure 10 MPa.

The selectivity to the desired p-isopropylcyclohexylmethanol generally decreased with the addition of a solvent, except 1,4-dioxane and 1,2-dimethoxy ethane, where the selectivity was comparable with the experiment without any solvent. When using the most polar solvents, methanol and water, a significant difference in the reaction course was observed. In these cases, almost no cumyl alcohol was detected in the reaction mixture. The reaction rate slightly decreased using solvents, probably due to the dilution of the reaction mixture except, again, using methanol and water. In these cases the reaction rate increased. It is very difficult to explain both these facts. From a practical point of view, the use of solvent is not desirable.

The influence of the reaction conditions was also studied using two types of catalysts (Johnson-Matthey type 97 and Johnson-Matthey type 698). The results (reaction rate, composition of reaction mixture in the fourth hour) are compared in **T-3**.

From the results depicted in T-3, it is obvious that the temperature had the main influence on the reaction rate. With increasing temperature, the rate of hydrogenation of the benzene ring increased significantly, with the formation of the undesired hydrogenolytic products. Pressure also had influence

on the reaction rate. The reaction rate increased with increasing pressure. The influence on the selectivity is not obvious from the obtained results because the total conversion of the initial substance was not achieved in the chosen time range. For the increase of selectivity, it is advisable to carry out the reaction at 15 MPa and a lower temperature, i.e. 130°C. The catalyst type has the main influence on the reaction, as will be mentioned later.

The influence of the catalyst type on the reaction rate and selectivity was tested without the solvent at 180°C and 15 MPa. Summarized results are depicted in the **T-4**.

The used catalysts were prepared by different methods. The catalyst type had the main influence during the hydrogenation. The highest selectivity was obtained using Johnson-Matthey catalyst type 619. The comparable results were obtained using the catalysts Noblyst P3060 and P3055. Under these conditions, using the catalysts from Noblyst 3061 (T-3, rows nine to 13), the rate of benzene ring hydrogenation (cumyl alcohol to p-isopropylcyclohexylmethanol) was very high, and the intermediate cumyl alcohol was observed in the reaction mixture, only in low amounts.

The influence of water on the activity and selectivity of the catalyst was tested using Johnson-Matthey catalyst type 619.

The catalyst was dried before the hydrogenation reaction (50°C for 24 hours). The calculated amount of water released from the catalyst was 52 wt.%. The reaction rate and selectivity to the desired p-isopropylcyclohexylmethanol was comparable with the reactions under the same conditions using the catalyst in the form of a paste and a dried catalyst. The small amount of water had no influence (e.g., as a surface passivator) on the reaction course.

After testing of the reaction conditions, a preparative experiment in a larger scale was performed. The following reaction conditions were applied: 3 wt.% of Ru/C catalyst (Johnson-Matthey, type 619), temperature 130°C and pressure 15 MPa. The selectivity to the desired Mayol was 92% (purity after rectification 99%).

The ratio of Mayol stereoisomers was in the range of 36:64 to 29:71 *trans:cis*. This ratio was not influenced by the reaction conditions but by the stability of the isomers.

## Conclusion

The preparation of p-isopropylcyclohexylmethanol, also called Mayol, was performed. Cuminaldehyde was used as the starting material; the series of 5% Ru supported catalysts was used for the hydrogenation. It was observed that the temperature had significant influence on selectivity. The formation of hydrogenolytic products was preferred with increasing temperature. Catalyst type had the crucial effect on the selectivity. Using optimal conditions (130°C and 15 MPa), the yield of desired Mayol was 93%. After rectification, the purity of the product was 99%.

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