

Liquid-phase synthesis of mesityl oxide from pure acetone over ion-exchange resins: catalysts screening study.

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Highlights

- Mesityl oxide synthesis from acetone was performed over acidic and basic ion-exchange resins.
- Low acetone conversions ($\approx 15\%$) were obtained, owing to unfavored DAA or MO formation thermodynamics.
- Methyl oxide selectivity was high for acid resins (80-90%), while rather low (0.90-11.0%) for basic ones.
- Ion-exchange resins show a great ability to tune the reactions involved in the two-step mechanism.

1. Introduction

The need for green carbon materials substitutive of current platform chemicals derived from oil is an irrefutable reality. In such scenario, acetone (AC) plays a pivotal role as building block for many chemicals, since it can be produced by the Acetone-Butanol-Ethanol (ABE) fermentation method [1], being the simplest and most important aliphatic ketone. Mesityl oxide (MO) is an oily, colorless to light yellow volatile liquid, flammable organic compound, which presents several important applications in fine chemistry, cellulose and plastic industries (e.g. PVC and urea derivatives), pharmaceutical chemistry, and food industry (e.g. as flavoring agent) [2]. Among its most important applications, it is as solvent for synthetic fibers and rubbers, oils, gums, resins, lacquers, varnishes, inks, stains, or insect repellent [3]. MO can be synthesized from acetone by two reactions in series (see Fig.1): i) acid or base catalyzed aldol condensation of acetone (R1) to form diacetone alcohol (DAA), and ii) dehydration of DAA (R2) yielding MO and water. To the best of our knowledge, the relations between the morphological properties of typically used ion-exchange resins (IERs) catalysts with their activity have not been tackled hitherto.

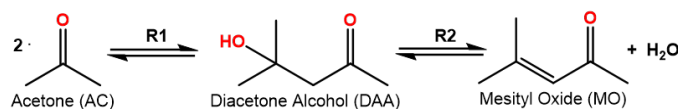


Figure 1. Chemical reactions involved in the synthesis of mesityl oxide from acetone.

2. Methods

All the experiments used pure acetone (200 mL) as reactant. The runs were carried out in an autoclave stainless steel jacketed batch reactor equipped with an overhead stirrer and 6-bladed impeller shaft and two baffles, and coupled to GC/MS analysis system. The experiments, lasting about 7 h, were performed at 90 °C, 25 bar, 750 rpm, and using 1 g of previously dried acid/basic ion-exchange resins (IERs) of different morphological and chemical properties, all in their as received particle size. The basic resins used were AmberlystTM A26OH and Purolite[®] CT196. Acid resins were of gel-type (Purolite[®] CT124 (CT124), Dowex 50Wx2 (Dow2), Dowex 50Wx4 (Dow4), Dowex 50Wx8 (Dow4)), macroreticular-type of high DVB % (AmberlystTM A15 (A15), AmberlystTM A35 (A35), AmberlystTM 45 (A45), AmberlystTM 46 (A46), Purolite[®] CT275 (CT275)), and Purolite[®] MN500, a hypercrosslinked one. As regards acid sites, A46 and MN500 are mainly sulfonated in the polymer surface, A15 and A45 are conventionally sulfonated, A35 and CT275 are oversulfonated.

3. Results and discussion

Figure 2 illustrates an example of the product distribution evolution obtained during a run for the resin Dowex®8, being representative of the trends observed for the most active resins. The mass balance was always fulfilled within $\pm 5\%$ wt. ACE concentration followed an exponential-like decrease, while both MO and H₂O followed an opposite nonlinear trend. Isomesityl oxide (i-MO), a double bond isomer of MO, was the only detected byproduct.

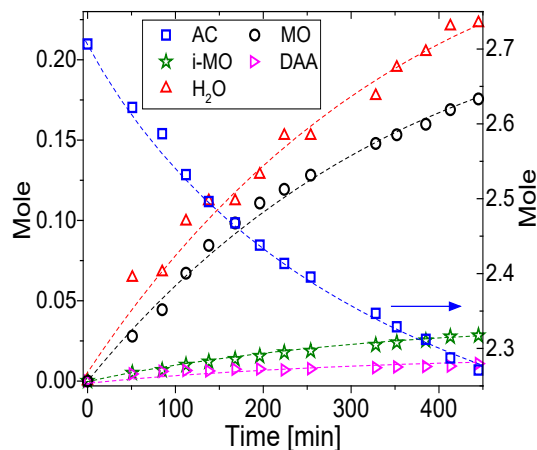


Figure 2. Example of the mole evolution obtained for the run with Dowex 8 (1.001 g), at 90 °C, 30 bar, 750 rpm and $n_{AC}^0 = 2.71$. Dashed lines are guide to the eye.

Globally, low acetone conversions, up to 15%, were obtained, which can be explained by unfavored thermodynamics towards DAA or MO formation. acid resins showed better catalytic performance in the mesityl oxide synthesis than basic ones Acetone selectivity towards MO was relatively high for acid resins (80-90%) while rather low (0.90-11.0%) for basic resins, the latter more selective towards DAA formation (89.0-99.1%). Results highlight the capability of acid IERs to catalyze the complete two-step mechanism, while the activity of basic resins is mainly restricted to the aldol condensation reaction (R1).

The rank of catalytic activity observed in terms of the estimated initial MO formation rates r_{MO}^0 [mol/(h·kg cat)] was: Dow4 (81.0) > A35 (46.8) > Dow8(38.4) > Dow2 (34.1) > A15 (33) > CT275 (32.6) > MN500 (25.2) > CT124 (18.0) > A46 (6.0) > A26OH (1.0) > CT196 (0.81). It is seen that acid resins exhibited a remarkably high activity toward MO synthesis in comparison to basic ones, being the acid gel-type resin Dowex®4 the most active. A separate analysis of estimated reaction rates of the two-step mechanism indicates that under the explored concentrations, DAA formation rate is much faster than MO formation. Acid catalysts accelerate DAA transformation to MO, on the contrary of basic ones, which explain the quite higher differences observed in selectivity. Finally, it is concluded that resins with high acid capacity favor MO formation.

4. Conclusions

This work unveils the role of acid/basic active sites and gel-type/macroporous resins structure for the MO synthesis. Despite the low acetone conversions ($\approx 15\%$) achieved, resins seem promising catalysts capable of tuning reactions involved in the two-step MO synthesis from acetone.

References

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Keywords

Mesityl oxide, aldol condensation/dehydration, ion-exchange resins, catalyst screening.