

Biphasic catalysis for a selective oxo–Mannich tandem synthesis of methacrolein

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Abstract

A novel biphasic approach has been proposed for the tandem synthesis of methacrolein from ethylene via hydroformylation and subsequent aldol reaction with formaldehyde. The two catalysts used, viz. one catalyzing hydroformylation of ethylene to propionaldehyde and the other for the aldol condensation of propionaldehyde with formaldehyde are incompatible with each other. The Rh-complex (hydroformylation catalyst) deactivates the aldolisation catalyst in the initial phase of the reaction, and thus prohibits the aldol condensation reaction. In this paper, a strategy of segregation of these two incompatible catalysts in two separate phases is used, which prevents the deactivation of the aldolisation catalyst, resulting in an active and stable catalyst package for the tandem synthesis of methacrolein with high selectivity (~95%). This catalyst package has been recycled for five times without any loss in activity or selectivity.

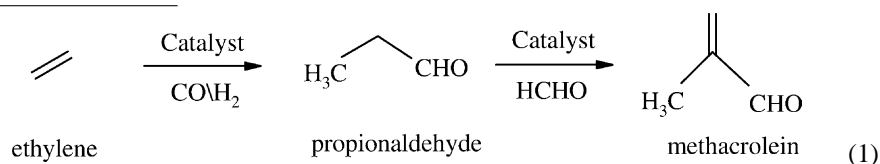
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1. Introduction

Methacrolein is an industrially important intermediate which goes into the manufacture of methacrylic acid/methyl

stage, followed by aldol condensation with formaldehyde and in second stage [2]. It would be logical to combine these two steps to obtain a tandem reaction sequence as shown below.



methacrylate, monomers for acrylate polymers [1]. Majority of methacrolein is manufactured by two processes [2]. The oxidation of iso-butene to methacrolein is an important process [3] practiced by Union Carbide, Degussa, besides others. The BASF route employs the aldol condensation of formaldehyde and propionaldehyde [4] in where the propionaldehyde is obtained from ethylene via hydroformylation [5].

The BASF process is operated in two stages involving the hydroformylation of ethylene to propionaldehyde in first

Reports on the coupling of such hydroformylation–aldol condensation reaction in a single reactor are available in literature, but they invariably deal with aldol condensation of same aldehydes that are formed during oxo reaction (homo-aldol condensation) [6]. As of now there are no reports on a tandem synthesis involving two distinct aldehydes, one already present in the reaction mixture and the other formed in the course of hydroformylation reaction, as is the case for the direct synthesis of methacrolein from ethylene/syngas and formaldehyde in a single reactor. In this paper, we report a synthesis of methacrolein by tandem oxo–aldol reactions, using a unique biphasic catalyst package. The catalyst package proposed for this synthesis has been recycled with ease to achieve high yields of

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methacrolein (~95%), which is comparable to the commercial processes [4].

2. Experimental details

2.1. Materials

The Rhodium compounds $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, $(\text{Rh}(\text{COD})\text{-Cl})_2$, and tri-phenyl phosphine tri-sulfonate sodium (TPPTS), were synthesized by known literature procedures [7–9], respectively. Ethylene, CO and hydrogen were obtained from Specialty Gas, India. All other chemicals were procured from SD Chemicals, India.

2.2. Procedure

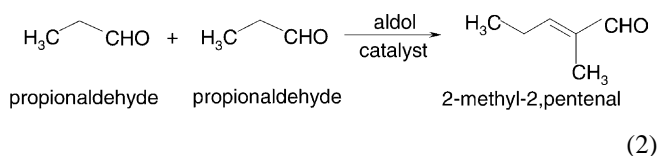
Atmospheric pressure reactions were carried out in a glass vessel equipped with magnetic stirrer bar, reflux condenser and an addition device. The condenser temperature was maintained between 283 and 293 K, to avoid losses of volatile components. An inert atmosphere was maintained in the assembly using argon blanket.

The high pressure reactions were carried out in a 316SS Parr Autoclave (300 cm³ capacity), equipped with a magnetic stirrer and automatic temperature controller. The progress of the reaction was monitored by observing the pressure drop (syngas) in the reservoir connected on-line. Liquid samples were withdrawn periodically and analyzed by GLC (HP 5890, column HP-5, 5% phenyl methyl siloxane 30 m × 320 μm × 0.25 μm, carrier gas: helium). For the reactions involving biphasic media, a suspension of the two phases was withdrawn and allowed to separate. The analysis of both the liquid phases was then carried out as mentioned above.

3. Results and discussion

Preliminary reactions were conducted for the hydroformylation of ethylene using the catalysts: (a) $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ in toluene medium, and (b) $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ in a biphasic toluene/water medium. Complete conversion of ethylene with total selectivity to propionaldehyde was observed for both the systems at a temperature of 333 K and a total pressure of 4.14 MPa (ethylene partial pressure 0.414 MPa, syngas 1:1, 3.73 MPa). The first step of the tandem reactions could therefore be carried out using any of the two catalysts.

Reactions were conducted to screen numerous bases—catalysts—for the aldol condensation of propionaldehyde and formaldehyde. Since the formation of homo-aldol as well as the hetero-aldol is possible it was necessary to identify the catalysts and conditions leading to a high selectivity to methacrolein as against 2-methyl-2-pentenal, the latter formed by the condensation of propionaldehyde with itself [10] as shown below. The results are presented in Fig. 1.



Inorganic bases like NaOH were found to be efficient aldol condensation catalysts, with predominant formation of the 2-methyl-2-pentenal. An increase in the NaOH concentration did not improve the selectivity and the best selectivity achievable for methacrolein using NaOH as a catalyst was 5%, with the rest being 2-methyl-2-pentenal, the product of the homoaldol reaction. The results indicate that NaOH being a strong base favors the homocondensation of propionaldehyde in preference to the cross aldolisation reaction of propionaldehyde and formaldehyde. Organic bases like

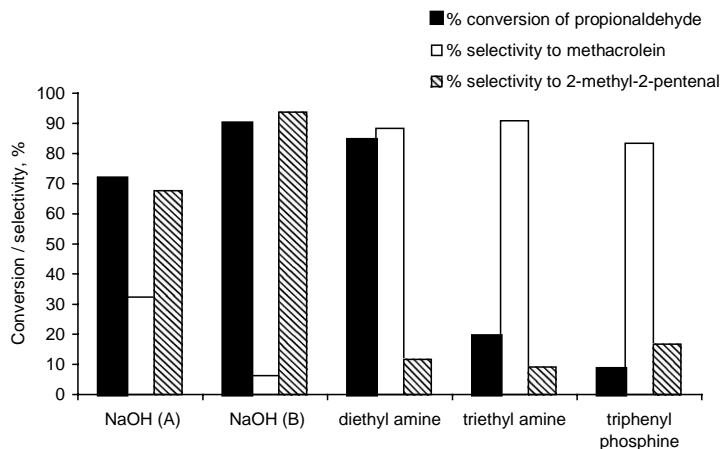


Fig. 1. Comparison of various aldol catalysts for methacrolein formation. Reaction conditions: toluene 10 cm³, (35%) formaldehyde 15 cm³, propionaldehyde 2.5 cm³, temperature 333 K, time 8 h. NaOH (A) 3×10^{-4} mol, NaOH (B) 1.5×10^{-3} mol, diethyl amine 8.4×10^{-3} mol, acetic acid 8.8×10^{-3} mol, triethyl amine 8.4×10^{-3} mol, acetic acid 8.8×10^{-3} mol, triphenyl phosphine 8.4×10^{-3} mol, acetic acid 8.8×10^{-3} mol.

triphenylphosphine/acetic acid and triethylamine/acetic acid preferentially catalyze the cross condensation reaction but have very poor activity (19% conversion in 8 h). In contrast to the tertiary amines, diethylamine/acetic acid catalyst gave reasonable activity with a good selectivity to methacrolein (84% conversion in 8 h). Thus, for the tandem reactions the diethyl amine/acetic acid catalyst was used for the second step.

As the aldol catalyst, diethylamine/acetic acid is soluble in water, the use of water-soluble oxo catalyst for tandem synthesis is more beneficial because it would permit an easy separation of the products and catalyst recycle. Also, from the analysis of reactants and products in toluene/water, it is observed that methacrolein has very low solubility in water (~5%) and preferentially stays in the organic solvent. Although, propionaldehyde is more soluble in organic solvent, the concentration of propionaldehyde in water (~43%) is sufficient for its aldol condensation with the water-soluble formaldehyde. Considering these aspects, it was decided to approach the tandem sequence using aqueous phase catalysts for both reactions.

A tandem reaction was carried out at 333 K temperature, under the following conditions: syngas 3.772 MPa, ethylene 0.419 MPa, $(\text{Rh}(\text{COD})\text{Cl})_2$ 4.09×10^{-6} mol, Rh:TPPTS 1:60, organic phase 10 cm³ toluene, aqueous phase 90 cm³ water containing 0.37 mol formaldehyde, diethyl amine 8.4×10^{-3} mol, acetic acid 8.8×10^{-3} mol. Unlike the normal oxo reactions with $(\text{Rh}(\text{COD})\text{Cl})_2/\text{TPPTS}$ catalyst [5], an induction period of 30 min was observed. Thereafter, the hydroformylation reaction proceeded as usual. Propionaldehyde formation, commensurate with ethylene consumption was observed but no methacrolein was detected. These results indicate that the condensation reaction does not take place under the reaction condition. This observation was reconfirmed several times, particularly, since such induction

periods are unusual in hydroformylation reactions with rhodium catalysts. Moreover, since the condensation reaction did not occur, the deactivation of the secondary amine catalyst was suspected.

According to literature reports, in the presence of a secondary amine like diethylamine, the Rh/TPPTS catalyst can catalyze hydroamination of ethylene [11] or the reductive amination with the aldehyde [12]. Under the existing reaction conditions, the concentration of the amine was too low to assess the fate of the amine catalyst. Hence, reactions were conducted at higher concentration of amine/acetic acid catalyst to accurately identify the cause of deactivation. Initially, reactions were performed in the absence of formaldehyde to look at the possibility of hydroamination of ethylene. Analysis of this reaction mixture did not show formation of triethyl amine. Therefore, the deactivation of amine by ethylation was ruled out. Alternatively when a similar reaction was carried out in the presence of formaldehyde an induction period was observed. Analysis of the reaction mixture indicated the formation of methyl diethyl amine, which was confirmed by GC–MS. The formation of methyl diethyl amine indicates that formaldehyde undergoes reductive amination and converts the diethyl amine to methyl diethyl amine, which is inactive towards aldol condensation. The Rhodium catalyst thus deactivates the secondary amine when they are in intimate contact, as in the present case.

To achieve a stable and active/selective catalyst for the tandem synthesis of methacrolein it is essential to ensure no interaction between the two catalysts. Since the diethylamine/acetic acid catalyst is soluble in the aqueous phase, a hydroformylation catalyst soluble in the organic phase would be ideal for ensuring a tandem reaction sequence.

The feasibility of the tandem reaction with this modification was assessed. The results are presented in Fig. 2. In

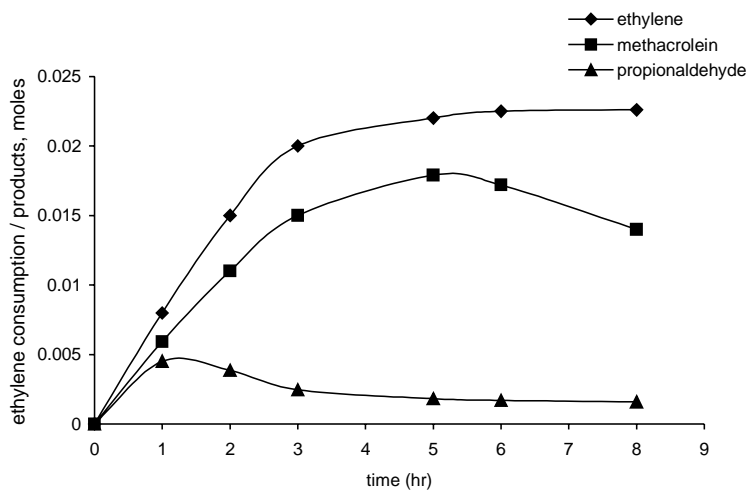


Fig. 2. Concentration–time profile for the tandem reaction of ethylene to methacrolein. Reaction conditions: toluene 20 cm³, (35%) formaldehyde 30 cm³, water 50 cm³, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ 2.72×10^{-5} mol, PPh_3 1.83×10^{-4} mol, diethyl amine 8.4×10^{-3} mol, acetic acid 8.8×10^{-3} mol, temperature 333 K, P_{total} 4.191 MPa, CO/H_2 1, ethylene 0.419 MPa.

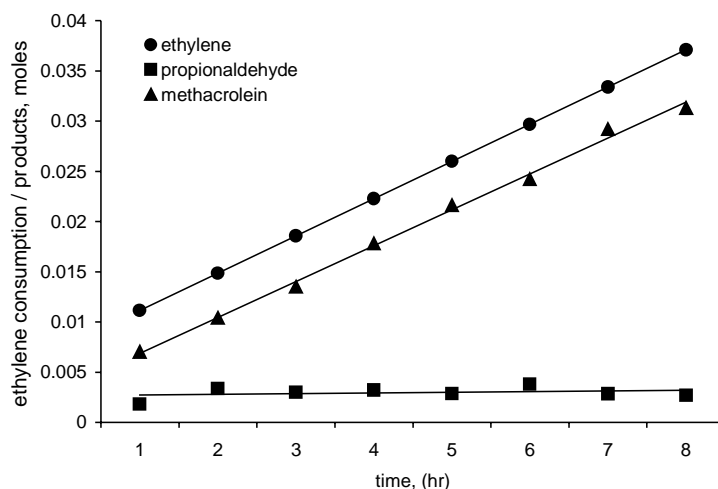


Fig. 3. Concentration–time profile for the tandem reaction of ethylene to methacrolein with continuous gas feed. Reaction conditions: toluene 20 cm³, (35%) formaldehyde 30 cm³, water 50 cm³, HRh(CO)(PPh₃)₃ 5.44 × 10⁻⁵ mol, PPh₃ 3.66 × 10⁻⁴ mol, diethyl amine 1.68 × 10⁻² mol, acetic acid 1.76 × 10⁻² mol, temperature 333 K, P_{total} 4.191 MPa, CO/H₂ 1, ethylene 0.419 MPa. In this reaction, ethylene and syngas in required stoichiometry were continuously supplied to the reactor as per the consumption.

contrast to the previous reaction, methacrolein was formed in high selectivity (85%) and no induction period was observed. A typical concentration profile for consecutive reactions is observed. The propionaldehyde concentration initially builds up and passes through a maximum. The methacrolein formation is also observed from the initial period. The maximum propionaldehyde formation was observed after 1 h. The build up of propionaldehyde during initial period indicates that the rate of condensation is relatively lower than that of the hydroformylation of ethylene. The maximum methacrolein formation is observed at the end of ~4 h. After which concentration of methacrolein drops. This is due to degradation

of methacrolein. The degradation of methacrolein is probably caused by the interaction with the aldolisation catalyst. Towards end of reaction the concentration of propionaldehyde is very low and so methacrolein undergoes reaction. Thus, to avoid further degradation of methacrolein it is necessary to maintain a reasonable concentration of propionaldehyde.

From the trend observed during the course of the reaction, the separation of the two catalysts in distinct phases provides an efficient catalyst package for methacrolein synthesis. The hydroformylation of ethylene occurs in the organic phase, and produces propionaldehyde, which migrates

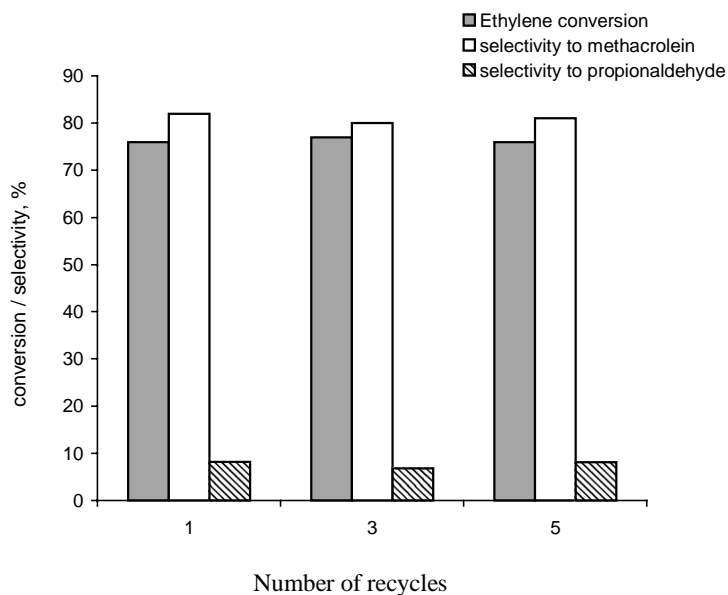


Fig. 4. Catalyst recycle studies for tandem synthesis of methacrolein from ethylene. Reaction conditions: toluene 20 cm³, (35%) formaldehyde 30 cm³, water 50 cm³, HRh(CO)(PPh₃)₃ 5.44 × 10⁻⁵ mol, PPh₃ 3.66 × 10⁻⁴ mol, diethyl amine 1.68 × 10⁻² mol, acetic acid 1.76 × 10⁻² mol, temperature 333 K, P_{total} 4.191 MPa, CO/H₂ 1, ethylene 0.419 MPa.

to the aqueous phase. In the presence of the aldolisation catalyst in the aqueous phase, the propionaldehyde reacts with formaldehyde to yield methacrolein. The methacrolein in turn migrates to the organic phase due to limited solubility in water. This movement of the molecules in between the two phases is advantageous for the overall efficiency of the catalyst system. Since the aldolisation reaction takes place in water, which is a propionaldehyde lean, formaldehyde rich medium, exclusively cross aldolisation takes place leading to a high selectivity to methacrolein. Secondly as methacrolein is preferentially soluble in the organic phase, any further interaction of the methacrolein with the aldolisation catalyst is avoided, thereby preventing degradation/condensation of the methacrolein. Under conditions wherein low propionaldehyde concentrations exist in the aqueous phase (towards the end of the reaction) the degradation of methacrolein commences, lowering the selectivity. Thus, to ensure a high yield of methacrolein, it is necessary to ensure a high concentration of propionaldehyde in the aqueous phase and this prevents a reaction of methacrolein. This is achievable by a continuous feed of ethylene and syngas to the reactor, instead of a batch operation as in the present case.

To improve the selectivity to methacrolein and to avoid methacrolein degradation a tandem reaction was conducted in the presence of a continuous feed of ethylene and syngas (CO/H₂) in a stoichiometry of 1:1:1 as per the consumption. As seen from the concentration profile in Fig. 3, a constant concentration of propionaldehyde is observed during the course of reaction leading to a high selectivity (~95%) to methacrolein. From Fig. 3, it is also observed that the continuous build-up of the methacrolein is commensurate with the ethylene consumption. This trend also confirms that the reactions are sequential in nature.

The catalyst was recycled by stripping the volatiles—methacrolein and propionaldehyde—from the organic phase. For this purpose, the autoclave was chilled to 0 °C at the end of the reaction, discharged, and the organic phase containing the HRh(CO)(PPh₃)₃ catalyst was stripped of methacrolein and propionaldehyde under vacuum at room temperature. Subsequently, the aqueous phase along with the organic phase (stripped of methacrolein/propionaldehyde and made up to 20 cm³ by additional toluene) was recycled to the reactor. The results in Fig. 4 indicate that the activity and selectivity of the catalyst is maintained as original for five recycles. Since the untoward interaction between the two catalysts is effectively bypassed, the activity of the catalysts is maintained throughout the recycle study.

Thus, this simple approach of a biphasic catalyst coupled with the concept of segregating the two incompatible catalysts into distinct phases cannot only transform the conventional two-stage methacrolein synthesis into a one-step process, but also improve the selectivity to methacrolein.

4. Conclusion

In conclusion, methacrolein, which is an important monomer intermediate, can be effectively synthesized from formaldehyde, syngas, and ethylene using a tandem oxo–Mannich sequence of reactions. It has been shown that the oxo and Mannich catalysts have to be segregated into two different liquid phases to minimize contact between them. In the absence of such segregation, the rhodium catalyst causes the methylation of the secondary amine, which is the condensation catalyst. The methylated amine catalyst is inactive for the Mannich reaction and therefore the tandem reaction cannot be achieved. Methacrolein, being a relatively volatile product, can be recovered from the two phase reaction mixture by distillation and the catalyst package along with residual formaldehyde can be recycled without any further treatment. The strategy of compartmentalization prevents the untoward interaction of the two catalysts in this tandem synthesis of methacrolein. Such a compartmentalization strategy may prove to be effective in other tandem sequences, wherein the contact between the two catalysts is undesirable.

References

- [1] K. Weissmerl, H.-J. Arpe, *Industrial Organic Chemistry*, third ed., VCH Publishers, 1997, pp. 281–285.
- [2] T. Ohara, T. Sato, N. Shimizu, G. Prescher, H. Schwind, O. Weiburg, *Acrolein and Methacrolein*, Ullmann's Encyclopedia of Industrial Chemistry, vol. A1, fifth ed., 1985, pp. 149–160.
- [3] (a) A. Aoshima, Y. Kohoku, R. Mitsui, T. Yamaguchi, DE 2941341 (1979) [Chem. Abstr. 93:71019];
(b) H. Engelbach, H. Krabetz, G. Duembgen, C.-H. Willersin, W. Breitelschmidt, DE 2909597 (1979) [Chem. Abstr. 94:102833];
(c) T.H. Vanderspurt, DE 2943707 (1979) [Chem. Abstr. 93:94806];
(d) W. Schlaefer, US Patent 4151117 (1979) [Chem. Abstr. 78:124031].
- [4] (a) F. Merger, H.J. Foerster, BASF, EP 58927 (1982);
(b) G. Duembgen, G. Fouguet, R. Krabetz, E. Lucas, F. Merger, F. Nees, EP92097 (1982) [Chem. Abstr. 100:7382].
- [5] R.M. Deshpande, B.M. Bhanage, S.S. Divekar, S. Kanagasabapathy, R.V. Chaudhari, *Ind. Eng. Chem. Res.* 37 (1998) 2391–2396 [Chem. Abstr. 128:294486].
- [6] (a) R. Paciello, F. Merger, M. Roper, H.-J. Kneuper, US Patent 5689010 (1997);
(b) C.R. Green, Berkeley, Shell Oil Company, US Patent 3278612 (1966).
- [7] D. Evans, Yagupaski, G. Wilkinson, *J. Chem. Soc. A* 3133 (1968).
- [8] S. Komiya, *Synthesis of Organometallic Compounds: A Practical Guide*, Wiley, New York, 1997.
- [9] B.M. Bhanage, S.S. Divekar, R.M. Deshpande, R.V. Chaudhari, *Org. Proc. Res. Dev.* 4 (2000) 342–345.
- [10] F. Merger, H.J. Foerster, BASF, US Patent 4408079 (1983) [Chem. Abstr. 98:71487].
- [11] D.R. Coulson, *Tetrahedron Lett.* 12 (1971) 429–430.
- [12] H.T. Clarke, et al., *J. Am. Chem. Soc.* 55 (1933) 4571.