Self-condensation of acetophenone to dypnone: synergism of microwave and solid acid catalysts

Ganapati D. Yadav* and Ginish George
Department of Chemical Engineering,
University Institute of Chemical Technology,
University of Mumbai,
Matunga, Mumbai - 400 019, INDIA
Email: gdyadav@yahoo.com, gdyadav@udct.org

Solid acid catalysts are widely used for the development of green technology to replace the traditional polluting catalysts in organic process industries employing alkylation, acylation, isomerization, nitration, condensation, cracking, and esterification, etc. [1,2] The activity and selectivities of different solid acid catalysts such as zeolites,[3,4] modified clays and heteropoly acids,[5-12] sulphated zirconia,[13-16] ion exchange resins[17-19] and UDCaT series of catalysts[20-26] have been successfully evaluated in our laboratory for developing green acylation, alkylation, condensation, cyclisation, esterification, etherification, isomerization, oligomerization, and nitration. The acronym UDCaT stands for the series of catalysts developed in our laboratory (named after University Institute of Chemical Technology).

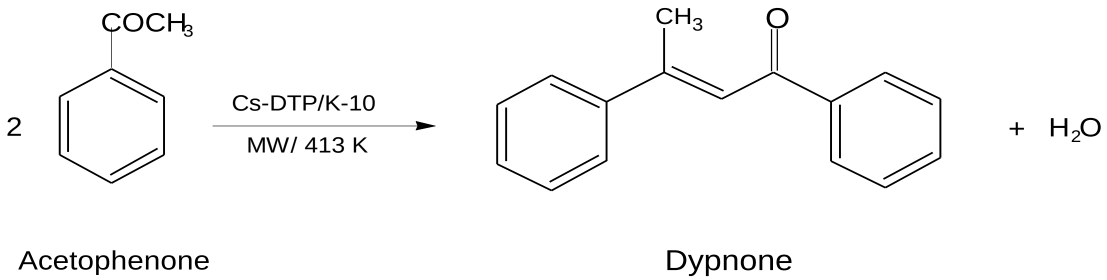
Dypnone is a useful intermediate for the production of a large range of compounds. It has been used as a sunscreen lotion, softening agent, plasticizer and perfumery base. Dypnone has been prepared conventionally by the action of sodium ethoxide, aluminum bromide, phosphorous pentachloride, aluminum triphenyl, zinc diethyl, calcium hydroxide, anhydrous hydrogen chloride, anhydrous hydrogen bromide, aluminum chloride, aluminum *tert*-butoxide or hydrogen fluoride on acetophenone as described in the earlier literature. It has also been obtained by the action of aniline hydrochloride on acetophenone, followed by treatment with hydrochloric acid. In addition, $AlCl_3$ being a strong Lewis acid also catalyzes other undesirable side reactions such as polycondensation of acetophenone to a mixture of other products.[27-30] Yatluk *et al.*[31] studied the condensation of acetophenone by using titanium ethoxide. Heterogeneous catalysts like zeolites and sulphated metal oxides were also employed in this system, but, however were more energy intensive and took longer times for equivalent conversions.[32-34]

High-speed synthesis with microwaves has attracted a considerable amount of attention in recent years.[35,36] Not only is direct microwave heating able to reduce chemical reaction times from hours to minutes, but it is also known to reduce side reactions, increase yields, and improve reproducibility.

The current work gives an insight into the self-condensation of acetophenone under microwave irradiation by using novel nanocatalyst Cs-DTP/K-10 to get dypnone (1,3-diphenyl-2-buten-1-one) as the major product including choice of catalyst and kinetic modeling.

The reaction was carried out in a 120 mL capacity glass reactor of 4 cm i.d. equipped with four equally spaced baffles and six bladed turbine impeller. The reaction conditions were controlled by using a microwave reactor setup (Discover, CEM-SP 1245 model, CEM Corp. USA), which was maintained at a desired temperature with an accuracy of ±0.5 K, in which the reaction assembly was immersed. Standard experiments were carried out by taking 0.16 mol of acetophenone, at a temperature of 413 K, and 0.10 g/cm^3 catalyst loading. 1.07 g of n-decane was used as an internal standard. All catalysts were dried at 393 K for 3 h before use. The reaction mixture was allowed to reach the desired temperature and the initial sample collected. Agitation was then commenced at a known speed. Samples were withdrawn periodically and analyzed by gas chromatography (GC). The conversion is defined as the percentage of acetophenone transformed. The products were confirmed by GC-MS.

The reaction scheme is as shown below:



Analysis of the reaction mixture was performed by GC (Chemito, model 8510) by using flame ionization detector and a stainless steel column (3.25 mm diameter and 4 m length) packed with a stationary phase of 10% SE-30 supported on chromosorb-WHP. The conversion was based on the disappearance of acetophenone peak with respect to the internal standard. Selectivity towards the products was analyzed by using GC (Chemito Model 1000, FID detector) with a BP1 capillary column (0.22 mm x 25 m).

Results and Discussion

Various solid acid catalysts were used to assess their efficacy in this reaction. A 0.10 g/cm^3 loading of catalyst based on the volume of the reaction mixture was employed at 413 K and a speed of agitation of 1000 rpm. The catalysts were UDCaT-5, Cs-DTP/K-10, 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/HMS, and UDCaT-6. The order of activity was as follows:

Cs-DTP/K-10 (most active)> UDCaT-5> Cs-DTP/HMS > UDCaT-6 (least)

Novel nanocatalyst cesium substituted dodecatungstophosphoric acid supported on K-10 clay (Cs-DTP/K-10) showed highest activity comparing to other catalysts (Fig.1). Nadir *et al.*[36] reported the synergistic combination of microwave irradiation and K-10 clay for organic synthesis. The narrow pore sizes of K-10 clay based catalysts show good selectivity towards desired product. Further experiments were conducted with Cs-DTP/K-10 due to its excellent stability and reusability under microwave condition. A brief characterization of this catalyst is presented.

Self-condensation of acetophenone was performed in the presence of microwave irradiation as well as conventional heating under otherwise similar conditions (Fig. 2). It was found that the overall conversion as well as rate of reaction was much higher under microwave vis-à-vis the conventional heating. This shows that the effect may not be purely thermal. Further, only microwave irradiation was carried out without any catalyst loading, there was no reaction. Thus, there is a definite synergism between solid acid catalyst and microwave irradiation.

The effect of speed of agitation was studied in the range of 800-1200 rpm at a catalyst loading 0.10 g/cm^3 at 413 K . There was no significant change in the rate and conversion patterns, which was indicative of the absence of any resistance to external mass transfer of acetophenone to the external surface of the catalysts. However, all further reactions were carried out at a speed of 1000 rpm. Theoretical calculations were also done to establish that there was absence of external mass transfer resistance.

The effect of catalyst loading was studied over range of 0.03-0.10 g/cm^3. In the absence of mass transfer resistance, the rate of reaction was directly proportional to catalyst loading based on the entire liquid phase volume. This indicates that, as the catalyst loading increased the conversion of acetophenone increases, which is due to proportional increase in the number of active sites. Further reactions were carried out with 0.10 g/cm^3 catalyst loading used in the standard reaction.

The effect of temperature on conversion was studied under otherwise similar conditions at 383, 393, 403 and 413 K, respectively. It was observed that the conversion increased with temperature. This would suggest a kinetically controlled mechanism. The initial rates of reaction were calculated at different temperatures and the Arrhenius plots had made to determine the energy of activation. It was found to be 16.35 kcal/mol, which is an indication of the overall rate being controlled by intrinsic kinetics.

The catalyst reusability was studied four times, including the use of fresh catalyst. After each run, the catalyst was filtered, washed with methanol, dried at 393 K for 3h, and weighed before using in the next batch of reaction. There was some attrition of catalyst particles during agitation. In a typical batch reaction, there was an inevitable loss of particles during filtration due to attrition. Although the catalyst was washed with methanol after filtration to remove all adsorbed reactant and products, there was still a possibility of retention of some amount of adsorbed reactant and products which might cause the blockage of active sites of the catalyst. The actual amount of catalyst used in the next batch, was almost 5% less than the previous batch. The volume of the reaction mixture was adjusted to make the catalyst loading 0.10 g/cm^3, the standard value. The catalyst was stable under microwave irradiation and there was only a marginal decrease in conversion.

The above results were used to build a kinetic model. A model based on two catalytic sites was proposed When the adsorption constants of all species are very weak, it is a typical second order reaction (Fig 3).

Conclusion

The current work has addressed the self-condensation of acetophenone to dypnone at 413 K over variety of solid acid catalysts such as Cs-DTP/K-10, UDCaT-5, UDCaT-6 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/HMS. Cs-DTP/K-10 was found to be the most active, stable and reusable catalyst under microwave conditions, gives very high selectivity towards *trans*-dypnone (92%). The effects of various parameters on the rates over Cs-DTP/K-10 were discussed. A positive effect of microwave irradiation on the rate of reaction was observed in comparison with conventional heating. A second order rate equation fits the data well. The apparent activation energy was estimated as 16.35 kcal/mol.

References

[1] R.A. Sheldon, *Chemistry & Industry*, 1997, **1**, 12.

[2] K. Wilson and J.H. Clark, *Pure Appl. Chem*., 2000, **72**(7), 1313-1319

[3] G.D. Yadav and A.A. Pujari, *Can. J. Chem. Eng*., 1999, **77**(3), 489-496

[4] G.D. Yadav and D.V. Satoskar, *J. Chem. Tech. Biotech*., 1997,**69**(4), 438-450

[5] G.D. Yadav, *Cat. Surveys Asia*, 2005, **9**(2), 117-137

[6] G.D. Yadav and N. Kirthivasan, *J. Chem. Soc. Chem. Commun*., 1995, 203-204

[7] G.D. Yadav and V. V. Bokade, *Appl. Catal. A: Gen.*, 1996, **147**, 299-315

[8] G.D. Yadav and N.S. Asthana, *Ind. Eng. Chem. Res.*, 2002, **41**, 5565-5575

[9] G.D. Yadav, N.S. Asthana and V S. Kamble, *App. Catal. A: Gen.*, 2003, **240**, 53-69

[10] G.D. Yadav and N.S. Asthana, *App.Catal. A: Gen.*, 2003, **244**, 341-357

[11] G.D. Yadav, N.S. Asthana and V. S.Kamble, *J. Catal.*, 2003, **217**(1), 88-99

[12] G.D. Yadav and H.G. Manyar, *Micropor. Mesopor. Mater.*, 2003, **63**(1-2), 85-96

[13] P.S. Kumbhar and G.D. Yadav, *Chem. Eng. Sci.*, 1989, **44**, 2535-2544

[14] G.D. Yadav and J.J. Nair, *Micropor. Mesopor. Mater.*, 1999, **33**, 1-48

[15] G.D. Yadav and P. Ramesh, *Can. J. Chem. Engg*., 2000, **78**, 323-327

[16] G.D. Yadav and S. Sengupta, *Org. Proc. Res. Dev.*, 2002, **6**, 256-262

[17] G.D. Yadav and S.P. Nalawade, *Chem. Eng. Sci.*, 2003, **58**, 2573-2585

[18] G.D. Yadav and M.S.M.M. Rahuman, *Org. Proc. Res. Dev*., 2002, **6**, 706-713

[19] G.D. Yadav and P.K. Goel, *Green Chem.*, 2000, **2**(2), 71-77

[20] G.D. Yadav, M.S. Krishnan, A.A. Pujari, N.S. Doshi and M.S.M.M. Rahuman, *US Pat.*, 6 204 424 B1, 2001

[21] G.D. Yadav, J.J. Nair and V. Narendra, *US Pat.*, 6 177 596 B1, 2001

[22] G.D. Yadav and J.J. Nair, *Chem. Comm.*, 1998, 2369-2370

[23] G.D. Yadav and A.D. Murkute, *Adv. Synth. Catal*., 2004, **346**, 389-394

[24] G.D. Yadav and A.D. Murkute, *Langmuir,* 2004, **20**, 11607-11619

[25] G.D. Yadav and A.D. Murkute, *J. Catal.*, 2004, **224**, 218-223

[26] G.D. Yadav and A.D. Murkute, *J.Phy.Chem. A*, 2004, **108** (44), 9557-9566

[27] H. Adkins and F.W. Cox, *J. Am. Chem. Soc.*, 1938, **60**, 1151-1159

[28] W. Wayne and H. Adkins, *Org. Synth. Coll. III*, 1955, 367

[29] N.O. Calloway and L.D. Green, *J. Am. Chem. Soc.*, 1937, **59**, 809-811

[30] J.H. Simons and E.O. Ramler, J. *Am. Chem. Soc*., 1943, **65**, 1390-1392

[31] Y.G. Yatluk, V.Y. Sosnovskikh and A.L. Suvorov, *Russian J. Org. Chem*., 2004, **40**(6), 763-765

[32] P.B. Venuto, *Micropor. Mater.*, 1994, **2**, 297-411

[33] C. Venkatesan and A.P. Singh, *J. Mol. Catal. A: Chem.*, 2002, **181**, 179-187

[34] M. Selvaraj, P.K. Sinha and A. Pandurangan, *Micropr. Mesopor. Mater*., 2004, **70**, 81-91

[35] C.O. Kappe, *Angew. Chem. Int. Ed*., 2004, **43**, 6250-6284

[36] U.K. Nadir and A. Singh, *Tet. Lett*., 2005, **46**, 2083-2086

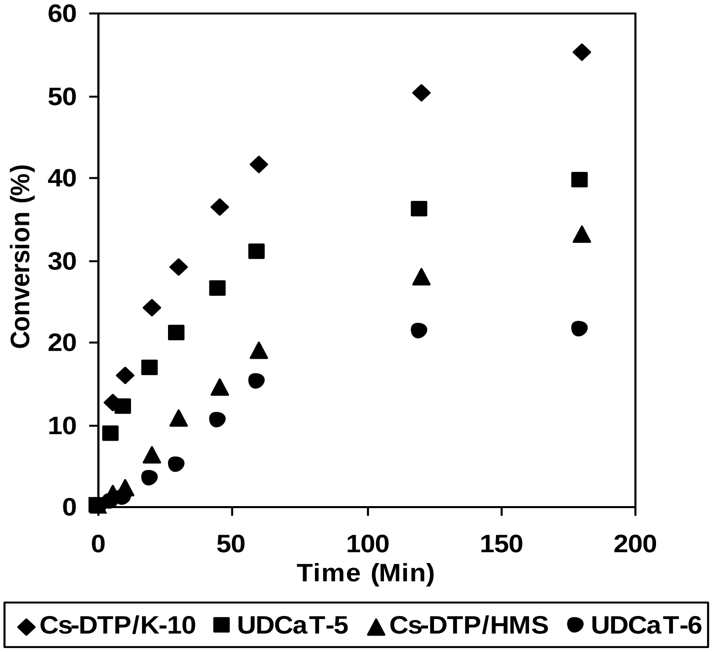


Fig. 1. Effect of various catalysts: acetophenone 0.16 mol, catalyst loading 0.10 g/cm^3, temperature 413 K, speed of agitation 1000 rpm

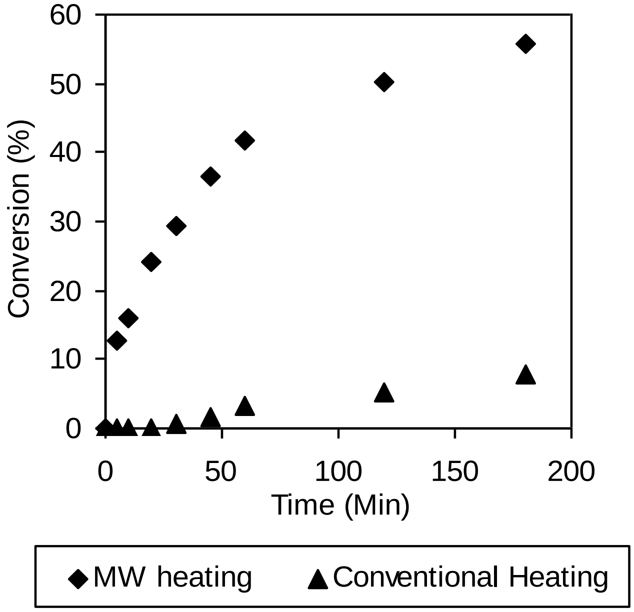


Fig. 2. Microwave vs. conventional heating: acetophenone 0.16 mol, catalyst loading 0.10 g/cm^3, temperature 413 K, speed of agitation 1000 rpm

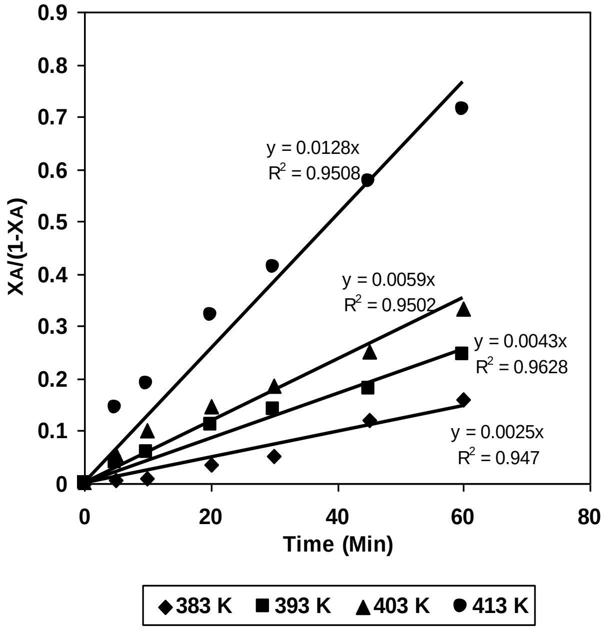


Fig. 3. Validation of the mathematical model at different temperature