Estd. 1989
Asian Journal of Chemistry; Vol. 33, No. 6 (2021), 1245-1248
ASIAN JOURNAL OF CHEMISTRY
https://doi.org/10.14233/ajchem.2021.23154

Influence of Reaction Conditions in the Selective Hydrogenation of Isophorone to 3,3,5-Trimethylcyclohexanone over NiC Composite Catalyst

KAMALA MANDY HANSDA, ANUPAMA MAHATO, PURNIMA SINGH, AJIT DAS and NAGENDRANATH MAHATA*

Center for Adsorption and Reaction Engineering on Surface (CARES), Department of Chemistry, Sidho-Kanho-Birsha University, Purulia-723104, India

*Corresponding author: E-mail: nagendranath_mahata.chem@skbu.ac.in

Received: 4 February 2021; *Accepted*: 22 March 2021; *Published online*: 5 June 2021; AJC-20350

NiC composite catalyst was synthesized by carbon deposition over skeletal Raney nickel by exploiting methane decomposition reaction and applied in the hydrogenation of isophorone. Nickel content in the composite catalyst was ascertained by atomic emission spectroscopy. Influence of operating variables (agitation, solvent, temperature, H_2 pressure and isophorone concentration) on the hydrogenation of isophorone over the NiC composite catalyst was investigated. Ethyl acetate was observed to be an excellent solvent for the reaction in terms of both isophorone conversion as well as 3,3,5-trimethylcyclohexanone selectivity. The catalytic reaction was observed to be 0.06 order with respect to isophorone and 0.82 order with respect to H_2.

Keywords: Isophorone, 3,3,5-Trimethylcyclohexanone, Hydrogenation, Reaction order.

INTRODUCTION

Selective reaction at a functional group in the presence of another reactive centre is of immense interest [1-8]. Thus, the selective reduction of carbon-carbon multiple bonds in presence of other unsaturated function carries great importance in laboratory practice as well as in fine chemicals production. In multistep organic synthesis, intermediate products containing carbon-carbon double bond functionality together with another reducible group are very common; selective hydrogenation at the C=C double bond functionality leaving the other reducible groups untouched is often required. Heterogeneous catalytic hydrogenation is the most useful method to add molecular hydrogen into carbon-carbon multiple bonds. Nickel based catalysts are widely used for such process in the laboratory as well as in industry. Low cost makes nickel based catalysts attractive provided acceptable catalytic performance is achieved [2,7-9].

Isophorone (ISP) contains two functionalities that can be hydrogenated an olefinic C=C bond, whose hydrogenation leads to the saturated ketone, 3,3,5-trimethylcyclohexanone (TMCHN) and a keto group, reduction of which results in the unsaturated alcohol, 3,5,5-trimethylcyclohexenol (TMCEL). Hydrogenation of both the groups leads to 3,3,5-trimethylcyclohexanol (TMCHL). Hydrogenation of isophorone can be accompanied by the formation of several by-products [8,10]. The selective hydrogenation of C=C double bond in isophorone to achieve selectively 3,3,5-trimethylcyclohexanone is highly desirable; the product is used extensively as solvent for laquers, vinyl resins, varnishes, paints and other coatings [11,12]. 3,3,5-Trimethylcyclohexanone is also used in the synthesis of high density fuel [10]. The selectivity of TMCHN varies considerably depending on the method of catalyst preparation, the amount of catalyst, the additives, the solvents, the process conditions employed, because both the keto and olefin functional groups can be reduced. Even though reduction of the C=C double bond is thermodynamically more favourable, there is always a probability of the hydrogenation of the C=O group. Hence, selective reduction of the C=C double bond to achieve the corresponding saturated ketone, TMCHN, is challenging and is of great importance. Studies on the influence of operating conditions in the hydrogenation of isophorone are rare. The present work deals with the selective reduction of C=C double bond in isophorone over NiC composite catalyst. Influence of operating conditions such as solvent, agitation of reaction mixture, temperature, H_2 pressure and isophorone concentration are explored.

EXPERIMENTAL

Commercial Ni-Al alloy powder (Ni/Al = 50/50 w/w) was procured from SRL Pvt. Ltd. and used to prepare skeletal Raney nickel catalyst. The NiC composite catalyst was synthesized by means of controlled decomposition of methane and thereby deposition of carbon over the Raney nickel catalyst [2,7,9]. Explicitly, Ni-Al alloy was reacted with concentrated NaOH solution for 5 h at ambient temperature; thereby Al was leached out. Thereafter, the obtained Raney nickel catalyst was washed extensively with double distilled water followed by ethanol. The Raney nickel catalyst was then carefully taken into a quartz tubular reactor avoiding exposure to air and dried for 2 h at 363 K under argon flow (50 mL min^{-1}). Decomposition of methane over the Raney nickel catalyst was carried out under controlled way at 668 K (methane space velocity: 12 mL min^{-1} g^{-1} Ni) for 7 h. In this way, carbon was deposited over the skeletal Raney nickel and NiC composite catalyst was synthesized. The reactor was eventually cooled to room temperature slowly under argon flow and the catalyst was collected. Nickel content in the NiC composite catalyst was ascertained by elemental analysis (atomic emission spectroscopy).

Hydrogenation of isophorone (ISP) was carried out in a stainless steel semi-batch reactor. The influence of reaction solvent was examined by applying five solvents, namely cyclohexane, ethyl acetate, *m*-xylene, toluene and isopropanol. The influence of reaction temperature was verified in the temperature range of 353 to 393 K. Influence of H_2 pressure was examined in the pressure range of 0.6 to 1.8 MPa, whereas effect of concentration of isophorone was explored in the concentration range of 0.302 to 0.804 mol L^{-1}. In a typical reaction run, required amounts of isophorone, solvent and catalyst were taken into the reactor and purged six times with H_2. The reactor was then heated to the reaction temperature at a heating ramp of 20 K min^{-1} under low H_2 pressure (0.01 MPa). Once the reaction temperature was reached, the H_2 pressure was adjusted to the reaction pressure and immediately the reaction was started by initiating stirring of the reaction mixture. Periodically, aliquots of reaction mixture were withdrawn and analyzed chromatographically to estimate isophorone conversion and product selectivities. Conversion of isophorone and selectivity of the products were calculated as follows:

$$\text{Conversion of ISP }(\%) = 1 - \frac{\text{Conc. of ISP}}{\text{Conc. of all products} + \text{Conc. of ISP}} \times 100$$

$$\text{Selectivity of product, P }(\%) = \frac{\text{Concentration of P}}{\text{Concentration of all products}} \times 100$$

Initial catalytic reaction rate was calculated as:

$$\text{Initial rate} = \frac{\text{Initial amount ISP} \times \text{Fractional conversion of ISP}}{\text{Amount of NiC catalyst} \times \text{time}}$$

RESULTS AND DISCUSSION

Nickel content in the catalyst was examined by atomic emmision spectroscopy. The content of Ni (wt%) was found to be 77.9%. Erstwhile XRD and XPS studies performed on this type NiC composite catalysts unveiled that Ni remains mainly in metallic form with only a superficial oxide layer; the deposited carbon behaves as stabiliser to preserve Ni in zerovalent metallic form [2,7,9]. Also, quondam SEM studies on this type NiC catalyst revealed that the surface is characterized by roughness and non-uniformity with microporosity [7].

Hydrogenation of isophorone was carried out in solution phase. It is well known that heterogeneously catalyzed reactions are slower compared to homogeneously catalyzed reactions. One of the obvious reasons is the fact that diffusion of reactants may be somewhat restricted and hence certainly more important in surface catalyzed reactions than in homogeneously catalyzed reactions [13]. Reaction runs of isophorone hydrogenation were conducted to assess the impact of the agitation of reaction mixture on the reaction rate.

Stirring speed: Fig. 1 shows the influence of stirring speed on the reaction rate. The results clearly revealed that reaction rate increases with increase in intensity of agitation, up to 1000 rpm. However, no noticeable change in reaction rate has been observed beyond 1000 rpm. It is obvious that the reaction is limited by mass transfer at mild agitation and stirring the system at the speed of lower than 1000 rpm is not sufficient to overcome the diffusion control. However, the mass transfer limitation/diffusion control is overcome at higher agitation speed (> 1000 rpm) and the reaction is in kinetic control regime.

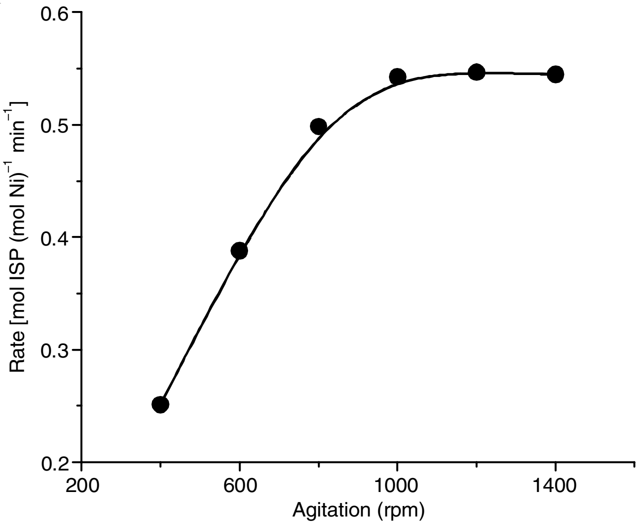

Fig. 1. Influence of agitation of reaction mixture on the initial rate of isophorone hydrogenation on NiC catalyst. Reaction conditions: 0.0753 g catalyst (1 mmol Ni), 9 mL isophorone (60.3 mmol), 91 mL solvent (ethyl acetate), 1.5 MPa H_2, 383 K, 1200 rpm

Choice of solvent: The influence of solvent on selective hydrogenation of isophorone was assessed by carrying out the reaction runs by applying five solvents, *viz.* cyclohexane, ethyl acetate, *m*-xylene, toluene and isopropanol. The results (Table-1) clearly disclose that reaction solvent significantly outlines the catalytic performance, particularly activity. A critical observation to Table-1 indicated that probably solvent polarity favours isophorone conversion. Prakash *et al.* [14] has observed the role of solvent polarity in the catalytic hydrogenation of cinnamaldehyde. Dipole moment of the solvents

TABLE-1
INFLUENCE OF SOLVENT IN THE HYDROGENATION OF ISOPHORONE (ISP) OVER NiC CATALYST

Solvent	ISP conversion (%)	Product selectivity (%)		
		TMCHN	TMCEL	TMCHL
Cyclohexane	10	93	–	7
Ethyl acetate	27	97	–	3
m-Xylene	23	95	–	5
Toluene	19	94	–	6
Isopropanol	25	96	–	4

Reaction conditions: 0.0753 g catalyst (1 mmol Ni), 9 mL ISP (60.3 mmol), 91 mL solvent, 1.5 MPa H_2, 383 K, 1200 rpm, time 30 min

changes in the order: ethyl acetate > isopropanol > *m*-xylene > toluene > cyclohexane; isophorone conversion followed the same order. Selectivity of TMCHN was above 93% in all the five sovents. Ethyl acetate induce highest (97%) TMCHN selectivity. The profiles of variation of TMCHN selectivity with isophorone conversion are shown in Fig. 2. The profiles appear to follow more or less similar trend when the solvent is ethyl acetate, *m*-xylene, toluene or isopropanol. Selectivity of TMCHN increases slowly, attains maximum value at around 60-75% isophorone conversion and then declines slowly. On the other hand, cyclohexane, as solvent, seems to act in a little different way. TMCHN selectivity increases slowly to maximal value at around 50% isophorone conversion and then drops rapidly at the higher isophorone conversion. This outcome may be due to the non-polar nature of cyclohexane.

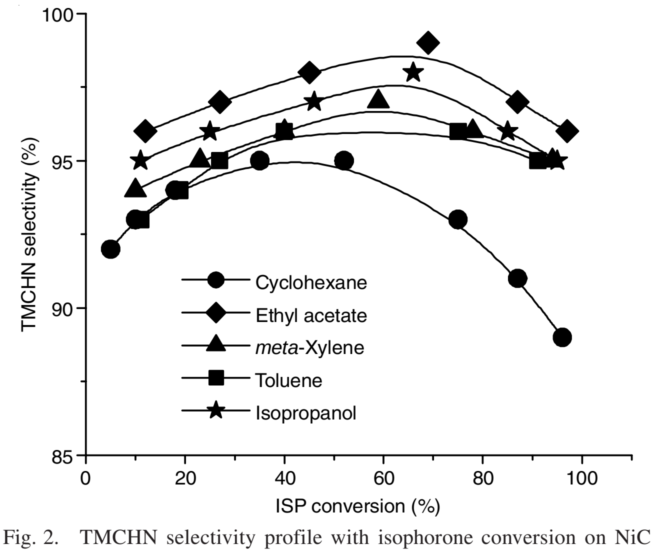

Fig. 2. TMCHN selectivity profile with isophorone conversion on NiC catalyst in different solvents. Reaction conditions: 0.0753 g catalyst (1 mmol Ni), 9 mL isophorone (60.3 mmol), 91 mL solvent, 1.5 MPa H_2, 383 K, 1200 rpm

The influence of temperature, hydrogenation of on isophorone reaction rate was assessed by running the reaction in five temperatures in the range of 353 to 393 K. Initial concentration of isophorone (0.603 mol L^{-1}) and H_2 pressure (1.5 MPa) were kept fixed in all the five reaction runs. The variation of initial rate with temperature is presented in Fig. 3. As anticipated, initial reaction rate increases hand by hand with increase in reaction temperature. More and more reactant molecules get energized and becomes successful in crossing the activation barrier, consequently rate increases with increase in reaction temperature. An interesting observation is that reaction rate increases slowly at the lower domain of temperature, however increment becomes rapid at the higher domain of temperature, beyond 373 K. Probably, activation energy of isophorone hydrogenation over the composite NiC catalyst is moderately high.

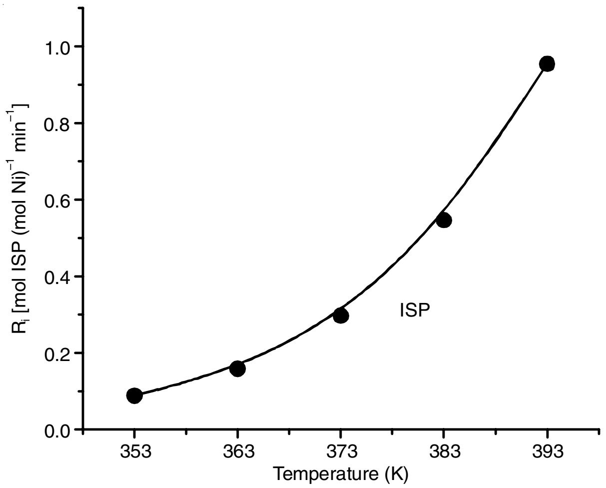

Fig. 3. Influence of temperature on the initial rate of hydrogenation of isophorone on NiC catalyst. Reaction conditions: 0.0753 g catalyst (1 mmol Ni), 9 mL isophorone (60.3 mmol), 91 mL solvent (ethyl acetate), 1.5 MPa H_2, 1200 rpm

Effect of concentration: The influence of isophorone concentration on the reaction rate was assessed in the concentration range of 0.302 to 0.804 mol L^{-1}; H_2 pressure was kept fixed at 1.5 MPa. The reaction runs were carried out at 373 K. The results are listed in Table-2. Initial reaction rate increases very very leisurely with increase in isophorone concentration. This indicates that concentration of isophorone in the solution has only a little effect on the active concentration of isophorone *i.e.*, adsorbed isophorone on the catalyst surface.

TABLE-2
INFLUENCE OF ISOPHORONE CONCENTRATION ON THE INITIAL RATE OF REACTION

H_2 pressure [MPa]	ISP concentration [mol L^{-1}]	Initial rate, Ri [mol ISP (mol Ni)$^{-1}$ min^{-1}]
1.5	0.302	0.2859
	0.402	0.2908
	0.603	0.2975
	0.804	0.3028

Reaction conditions: 0.0753 g catalyst (1 mmol Ni), 1.5 MPa H_2, 88-95.5 mL solvent (ethyl acetate), 373 K, 1200 rpm.

A slope of the fitted straight line was determined which is the order of the reaction with respect to isophorone (Fig. 4). The observed order was found to be 0.06, which is very close to 0. This indicates that the catalyst surface remains almost completely saturated with respect to isophorone in the range of examined concentration in the present study. Hence, adsorbed isophorone was involved in the rate determining step.

Effect of pressure: The effect of H_2 pressure on the reaction rate was assessed in the H_2 pressure range of 0.6 to 1.8 MPa; while the initial concentration of isophorone was taken constant at 0.603 mol L^{-1}. The experiments were performed at 373 K.

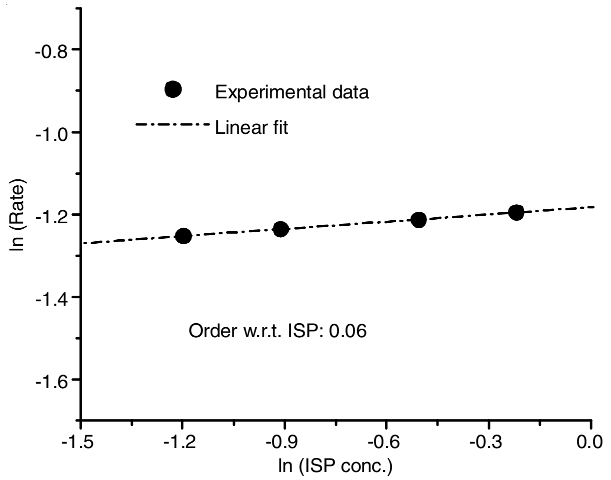

Fig. 4. Kinetic plot of hydrogenation of ISP at 373 K under variable ISP concentration and fixed H_2 pressure

The results (Table-3) evidently revealed that the hydrogenation of isophorone reaction rate vividly depends on H_2 pressure. Increase in H_2 pressure strongly increases the reaction rate; the degree of increament of initial reaction rate is close to that of H_2 pressure. This indicates a change in H_2 gas pressure strongly changes the concentration of H_2 in the solution and probably on the catalyst surface too. The slope of the fitted straight line was determined which is the order of the reaction with respect to H_2 (Fig. 5). The order was observed to be 0.82 (close to 1), thus, it is evident that high pressure of H_2 induces high isophorone the hydrogenation rate. Han *et al.* [15] reported similar observations in the hydrogenation of cinnamaldehyde.

TABLE-3
INFLUENCE OF H_2 PRESSURE ON
THE INITIAL RATE OF REACTION

ISP concentration [mol L^{-1}]	H_2 pressure [MPa]	Initial rate, Ri [mol ISP (mol Ni)$^{-1}$ min^{-1}]
0.603	0.6	0.1427
	0.9	0.1950
	1.2	0.2472
	1.5	0.2975
	1.8	0.3518

Reaction conditions: 0.0753 g catalyst (1 mmol Ni), 9 mL ISP (60.3 mmol), 91 mL solvent (ethyl acetate), 373 K, 1200 rpm.

Conclusion

Reaction conditions/operating variables asserted the effective influence on the hydrogenation of isophorone over NiC composite catalyst. Thorough agitation of reaction mixture was necessary to put the reaction into kinetic control regime by overcoming mass transfer limitation. Ethyl acetate was appeared to be very good reaction medium for high conversion of isophorone as well as for high 3,3,5-trimethylcyclohexanone selectivity. Moderately high temperature was favorable for the high rate of reaction. It was observed that the hydrogenation of isophorone is of 0.06 order with respect to isophorone whereas 0.82 order with respect to H_2. The catalyst surface practically remains saturated with respect to isophorone and it is plausible that the rate determining step involves adsorbed isophorone.

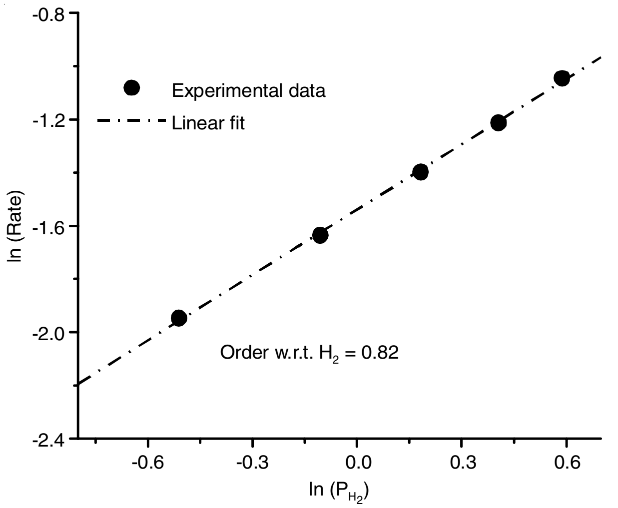

Fig. 5. Kinetic plot of hydrogenation of ISP at 373 K under variable H_2 pressure and fixed ISP concentration

ACKNOWLEDGEMENTS

The authors are grateful to Government of West Bengal, India for Swami Vivekananda Merit-cum-Means Scholarship to Anupama Mahato and Purnima Singh.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P. Gallezot and D. Richard, *Catal. Rev., Sci. Eng.*, **40**, 81 (1998); https://doi.org/10.1080/01614949808007106
2. N. Mahata, A.F. Cunha, J.J.M. Orfao and J.L. Figueiredo, *Chem. Eng. J.*, **188**, 155 (2012); https://doi.org/10.1016/j.cej.2012.01.127
3. A.S. Nagpure, L. Gurrala, P. Gogoi and S.V. Chilukuri, *RSC Adv.*, **6**, 44333 (2016); https://doi.org/10.1039/C6RA04154J
4. Y. Hou, S. Ren, M. Niu and W. Wu, *R. Soc. Open Sci.*, **5**, 171523 (2018); https://doi.org/10.1098/rsos.171523
5. N. Mahata, F. Goncalves, M.F.R. Pereira and J.L. Figueiredo, *J. Appl. Catal. A*, **339**, 159 (2008); https://doi.org/10.1016/j.apcata.2008.01.023
6. L. Xu, S. Sun, X. Zhang, H. Gao and W. Wang, *RSC Adv.*, **11**, 4465 (2021); https://doi.org/10.1039/D0RA08107H
7. N. Mahata, A.F. Cunha, J.J.M. Orfao and J.L. Figueiredo, *ChemCatChem*, **2**, 330 (2010); https://doi.org/10.1002/cctc.200900299
8. M. Pisarek, M. Lukaszewski, P. Winiarek, P. Kedzierzawski and M. Janik-Czachor, *Mater. Chem. Phys.*, **114**, 774 (2009); https://doi.org/10.1016/j.matchemphys.2008.10.027
9. A. Das, K.M. Hansda and N. Mahata, *J. Indian Chem. Soc.*, **95**, 1531 (2018).
10. W. Wang, Y. Liu, N. Li, G. Li, W. Wang, A. Wang, X. Wang and T. Zhang, *Sci. Rep.*, **7**, 6111 (2017); https://doi.org/10.1038/s41598-017-06556-7
11. T. Sato, C.V. Rode, O. Sato and M. Shirai, *Appl. Catal. B*, **49**, 181 (2004); https://doi.org/10.1016/j.apcatb.2003.12.010
12. M. Pisarek, M. Lukaszewski, P. Winiarek, P. Kedzierzawski and M. Janik-Czachor, *J. Appl. Catal. A*, **358**, 240 (2009); https://doi.org/10.1016/j.apcata.2009.02.012
13. R.L. Augustine, P. Goel, N. Mahata, C. Reyes and S.K. Tanielyan, *J. Mol. Catal. Chem.*, **216**, 189 (2004); https://doi.org/10.1016/j.molcata.2004.03.009
14. M.G. Prakash, R. Mahalakshmy, K.R. Krishnamurthy and B. Viswanathan, *Catal. Sci. Technol.*, **5**, 3313 (2015); https://doi.org/10.1039/C4CY01379D
15. S. Han, Y. Liu, J. Li, R. Li, F. Yuan and Y. Zhu, *Catalysts*, **8**, 200 (2018); https://doi.org/10.3390/catal8050200