MCM-41 AND AL-20-MCM-41 CATALYZED AMINE COUPLING REACTIONS: A KINETIC STUDY

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ABSTRACT

The study examines the influence of varying reaction conditions like solvent presence, solvent absence, air exposure, and air exclusion in a closed vessel on the kinetics of oxidative coupling reactions of amines to form imines, utilizing MCM-41 and Al-20-MCM-41 catalysts. The investigation encompasses both self-coupling and cross-coupling reactions. Results indicate that the self-coupling reaction proceeds at a faster rate with the Al-20-MCM-41 catalyst compared to MCM-41, whereas cross-coupling reactions exhibit a slightly reduced rate with Al-20-MCM-41 relative to MCM-41. Detailed kinetic analysis was conducted for oxidative coupling reaction of amines to imines using Al-20-MCM-41 catalyst under these various conditions to determine the reaction order and rate constants. The reactions demonstrated a shifting order, displaying first-order kinetics at high amine concentrations and approaching zero-order kinetics as the amine concentration decreased.

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INTRODUCTION

In 1864, Hugo Schiff first identified the condensation reaction of carbonyl compounds with primary amines to produce imines, subsequently known as Schiff bases or azomethines [1]. Imines are critical intermediates in the synthesis of nitrogen heterocycles, fine chemicals, and pharmaceuticals, playing a significant role in both chemistry and biology [2, 3]. Recently, the direct synthesis of imines via oxidative self-condensation of primary and secondary amines has garnered considerable attention [4,5]. The literature describes numerous methodologies for imine preparation, including the utilization of ionic liquids [6], infrared [7], microwave [8], and ultrasound [9] irradiation. A primary challenge affecting product yield is the equilibrium between reactants and imines, with water as a byproduct. This issue is mitigated by employing dehydrating agents such as P_2O_5/SiO_2 [10], $MgSO_4$-Mg $(ClO_4)_2$ [11], fuming $TiCl_4$ [12], or by using aromatic solvents that form azeotropic mixtures with water at elevated temperatures.

In recent years, the oxidative coupling (both self- and cross-coupling) of amines to imines using appropriate catalysts and atmospheric oxygen as an oxidant has gained considerable interest as a greener synthetic route. Solid catalysts such as bulk copper [13] and gold powder [14], as well as supported precious metals like gold nanoparticles [15, 16] and ruthenium [17], have been proposed for amine coupling reactions due to the advantages of heterogeneous catalysis. However, these methods often encounter challenges, including cumbersome procedures, moisture-sensitive catalysts or reagents, the use of large quantities of toxic aromatic solvents, high reaction temperatures, and extended reaction times. Consequently, the development of new, environmentally friendly procedures for imine synthesis is a critical focus in contemporary organic synthesis. Ordered mesoporous materials as heterogeneous solid catalysts are extensively utilized in chemical synthesis, offering a promising solution to these challenges.

Al-grafted MCM-41 is a widely utilized catalyst in coupling reactions. MCM-41 materials are characterized by their ordered structure, featuring uniform mesopores arranged in a hexagonal lattice, making them an effective support material for the development of heterogeneous catalysts. Al-grafted MCM-41 (Al-MCM-41) has been extensively employed as a catalyst in various acid-catalyzed reactions, including esterification [18, 19], acetalization [20], and alkylation [21, 22]. Additionally, MCM-41 and Al-MCM-41 mesoporous catalysts have been proposed for the

oxidative coupling of amines using the polar solvent nitrobenzene [23].

The catalytic properties of MCM-41 and Al-grafted MCM-41 acidic materials are crucial in the oxidative coupling of amines during the synthesis process. The activity of these catalysts and the reaction conversion are significantly influenced in the oxidative coupling of amines to imines using MCM-41 and Al-20-MCM-41 [24]. In this study, we have examined the impact of various reaction conditions on these coupling reactions to determine the reaction order and rate constant.

Raman spectroscopy is an effective method for monitoring imine synthesis reactions and studying the kinetics of imine formation in chloroform solvent [25]. Experiments involved reacting a primary amine with a carbonyl ketone at various temperatures, utilizing molecular sieves to remove water during the reaction. It was concluded that the reaction exhibited second-order kinetics across different temperatures. Additionally, various Ru-based catalysts containing methoxy or methyl groups, as well as monomeric and quinone structures, were used in kinetic studies of amine reactions in toluene at 110°C [26].

The investigation into the substrate effects on the catalytic rate reveals that the rate of hydrogen transfer between amines and imines is influenced by the electronic properties of the substrates. Specifically, substrates with a methoxy or methyl group on one of the aromatic rings exhibit a higher reaction rate compared to monomeric groups. However, the introduction of multiple methoxy groups results in a slower reaction rate. Replacing the methyl group with an ethyl group does not yield a significant improvement in reaction rate. Additionally, a classical study on the organolanthanide-catalyzed cyclization of 4-pentyn-1-amine demonstrates that the reaction follows zero-order kinetics with respect to the substrate and first-order kinetics with respect to the catalyst concentration [27].

The rate constant for the overall reaction has been determined, although the rate constants for the individual steps of the catalytic cycle have not been derived. The activation parameters, ΔH and ΔS, were calculated at various temperatures. A palladium (II) catalyst was employed in the kinetic study of amine reactions. The palladium (II)-catalyzed oxidation of methylamine and ethylamine by Ce (IV) in perchloric acid was found to be dependent on the acid concentration [28].

The kinetic study was conducted to determine the reaction order, revealing a shifting order from first to zero. The reaction exhibited first-order kinetics at low amine concentrations, transitioning to zero-order kinetics at higher concentrations. Similarly,

the kinetic analysis and mechanism of the ruthenium (III)-catalyzed oxidation of tris(2-aminoethyl) amine by hexacyanoferrate (III) in an aqueous alkaline medium showed first-order behaviour at low alkali concentrations, which approached zero-order at higher concentrations [29].

EXPERIMENTAL

Oxidative Coupling of Amine to Imine with MCM-41 and Al-20-MCM-41

The oxidative coupling of amines offers an alternative approach for synthesizing imines, which serve as versatile intermediates in various organic transformations and hold significance in biological systems. Imines act as chemical intermediates that can readily convert into other functional groups, such as nitroxides, oxoaziranes, nitrones, and carbonyl compounds. Typically, imines are synthesized through the condensation of primary amines with aldehydes, and less frequently with ketones.

In this study, the oxidative coupling of amines to imines was conducted using two catalysts, MCM-41 and Al-20-MCM-41, under different reaction conditions. Two distinct types of reactions were investigated: (i) self-coupling reactions and (ii) cross-coupling reactions. The primary objective of this work was to analyse the reaction kinetics under varying conditions.

The coupling reaction was conducted within a controlled environment utilizing a 12-place heated carousel reaction station (RR99030, Radleys Discovery Technologies, UK). Precise quantities of the reaction mixture and activated catalyst were introduced into reaction tubes under two distinct conditions. In the first scenario, the reaction proceeded in the presence of a solvent at the desired temperature with adequate stirring for the specified reaction duration. Conversely, the second condition involved a solvent-free reaction. Both reactions were performed in sealed vessels, with the option of continuous air purging to ensure an excess supply of oxygen for the reaction.

Upon completion of the reaction, the mixture was cooled and diluted with dichloromethane for subsequent analysis via gas chromatography (Agilent 7890A) equipped with an HP-5 (60 m) capillary column. The chromatographic conditions involved a programmed oven temperature ranging from 50 to 280°C, with a flow rate of 0.5 cm³/min of N_2 as the carrier gas and detection performed via a flame ionization detector (FID). The products generated during the reactions were further characterized using gas chromatography-mass spectrometry (GC-MS) analysis. This analysis was conducted using a gas chromatograph-mass spectrometer (Agilent 5975C GC/MSD with 7890A GC system) equipped with an HP-5 capillary column of 60 m length and 250 µm diameter. The programmed oven temperature ranged from 50 to 280°C, with a flow rate of 1 mL/min of helium as the carrier gas, and the ion source maintained at 230°C.
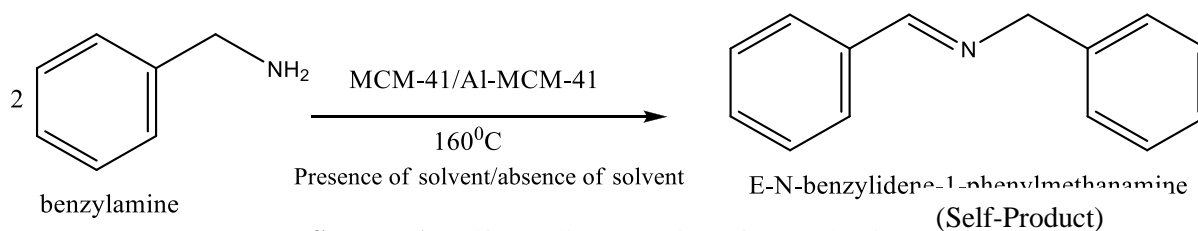
Self-coupling Reactions of Amines

Self-coupling reactions were conducted within a reaction station, wherein predetermined quantities of a reaction mixture containing benzylamine and nitrobenzene (in cases where the reaction was performed with a solvent) were introduced into reaction tubes. Subsequently, 0.05 g of freshly activated catalyst was added to each tube after activation at 180°C for 1 hour. The reactions were conducted at 160°C for varying time intervals.

Following the reaction, the reaction tubes were cooled to room temperature, and the reaction mixture was collected and diluted with dichloromethane. The conversion of benzylamine over different time intervals and the selectivity of the product were evaluated for both MCM-41 and Al-20-MCM-41 catalysts, under conditions with and without solvent, and in the presence of air in closed vessels.

Analysis of the reaction mixture was performed via gas chromatography, and product identification was accomplished through gas chromatography-mass spectrometry (GC-MS).

Self-coupling reactions were investigated under two distinct conditions to assess conversion rates: (i) without solvent in closed vessels, (ii) with solvent with excess air.


Scheme 1. Self-coupling Reaction of Benzylamine

benzylamine — MCM-41/Al-MCM-41, 160°C, Presence of solvent/absence of solvent → E-N-benzylidene-1-phenylmethanamine (Self-Product)

**Mechanism of Formation of Imine from Amine for Self-coupling**
The reaction mechanism pertains to a sequence of steps through which the initial reactants engage in interactions leading to the formation of products. The conversion of an amine to an imine typically involves a two-step process

Step 1: Formation of Imine intermediate

In the oxidative coupling of benzylic amines under reflux conditions in water, the activation of amines occurs through hydrogen bonding facilitated by water molecules, primarily interacting with the amino group. Subsequently, the activated amine species reacts with oxygen to generate an imine intermediate.

Benzylamine   Imine Intermediate   water
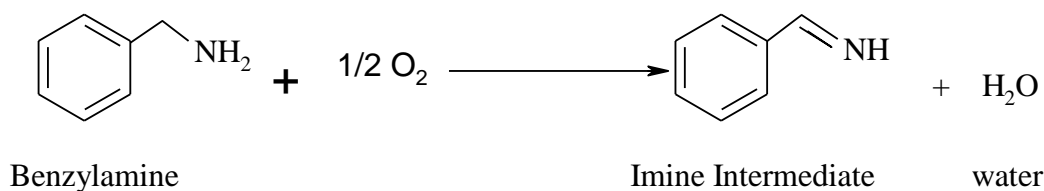
Scheme 1 (a). Imine Intermediate Formation

Step 2: Formation of imine product from imine intermediate
The imine intermediate undergoes a reaction with unbound or free amines to yield the final imine product.

Benzylamine   Imine Intermediate   E-N-benzylidene-1-phenylmethanamine
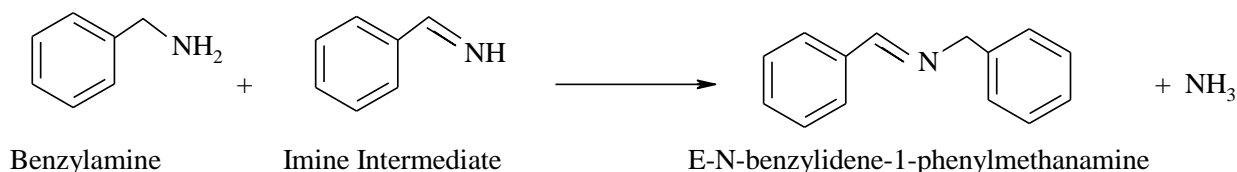
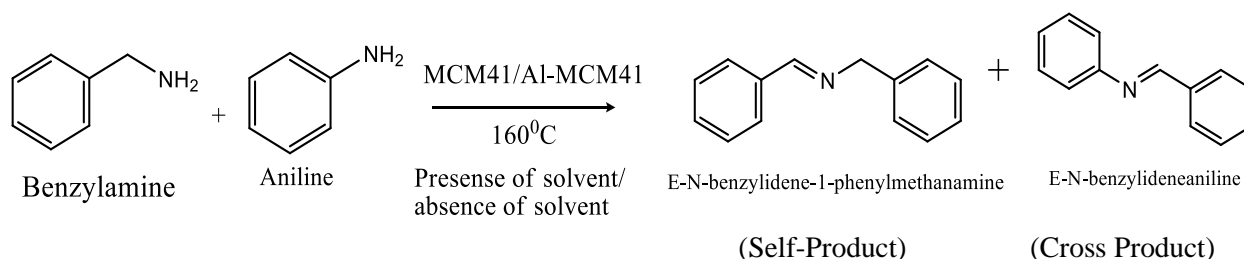**Scheme 1 (b)**. Imine Formation from Imine Intermediate

It has been identified that in the two-step process, step 2 serves as the rate-determining step.

Cross coupling Reactions of Amines
In the cross-coupling of benzylamine and aniline, nitrobenzene was employed as the solvent where applicable. Precise quantities of the reactants and solvent were introduced into 50 mL reaction tubes. Catalysts, MCM-41 and Al-20-MCM-41, were pre-activated at 180°C for 1 hour prior to their addition to the reaction vessels. The reactions were carried out at 160°C under 1 atmosphere of pressure for various time intervals.

Post-reaction, the mixtures were cooled to ambient temperature, extracted from the reaction tubes, and subsequently diluted with dichloromethane. The reaction mixtures were analysed via gas chromatography (GC), and product identities were confirmed using gas chromatography-mass spectrometry (GC-MS).
Cross-coupling reactions were performed under two distinct sets of conditions to evaluate conversion rates: (iii) in the presence of the solvent with excess air, and (iv) in the absence of solvent with excess ai

Benzylamine   Aniline   MCM41/Al-MCM41   E-N-benzylidene-1-phenylmethanamine   E-N-benzylideneaniline
160^0C
Presense of solvent/   (Self-Product)   (Cross Product)
absence of solvent

Scheme 2. Cross coupling Reaction of Benzylamine with Aniline

Mechanism of Formation of Imine from Amine for Cross coupling
Step 1: Formation of imine intermediate
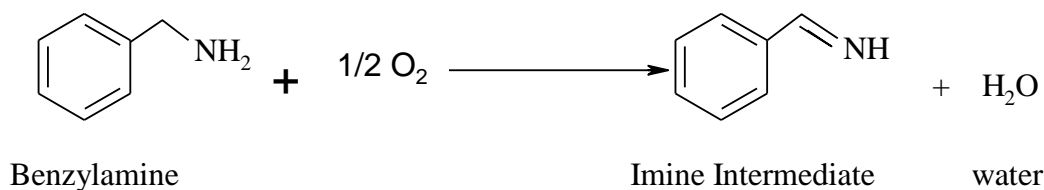
Scheme 2 (a). Imine Intermediate Formation

Step 2: Formation of imine product from imine intermediate

Imine intermediate gets reacted with free amines to give imine product.
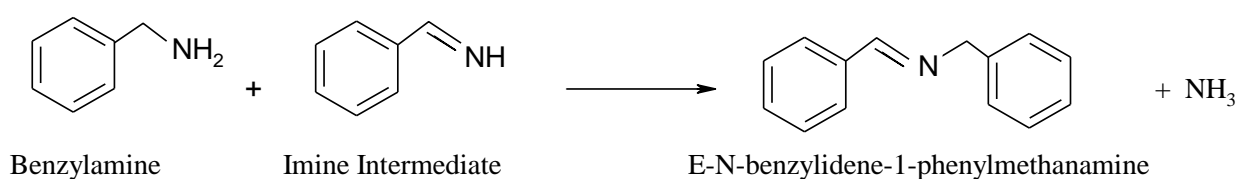
Scheme 2 (b). Reaction between Amine and Imine Intermediate

Step 3: Self product reacts with another reactant aniline and form cross imine product.
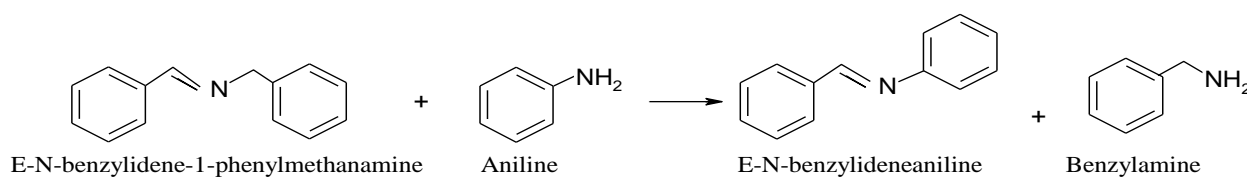
Scheme 2 (c). Cross Imine Product Formation

Among the three steps, step 3 has been identified as the rate-determining step in the coupling reaction.

RESULTS AND DISCUSSION
Study of Self coupling reactions with respect to different reaction conditions.
Self-coupling reaction were conducted for two different conditions as mentioned earlier (i) without solvent and closed vessel (ii) with solvent and in excess of air. The aim of conducting these reactions is to check the effect of solvent and excess air over the kinetics of the reaction.
In this work, nitrobenzene was used as a polar solvent due to its high dielectric constant (34.8),

high boiling point (205 ^{0}C) and non-reactive nature. It has already been used as a polar solvent in high temperature heterogeneous catalytic reactions [12]. This study reveals that a suitable (greener) high boiling point polar solvent can be explored to promote the efficiency of MCM-41 catalysts for amine coupling reactions.

Effect on conversion of oxidative self-coupling reaction with respect to time using MCM-41 and Al-20-MCM-41 catalysts for different conditions.
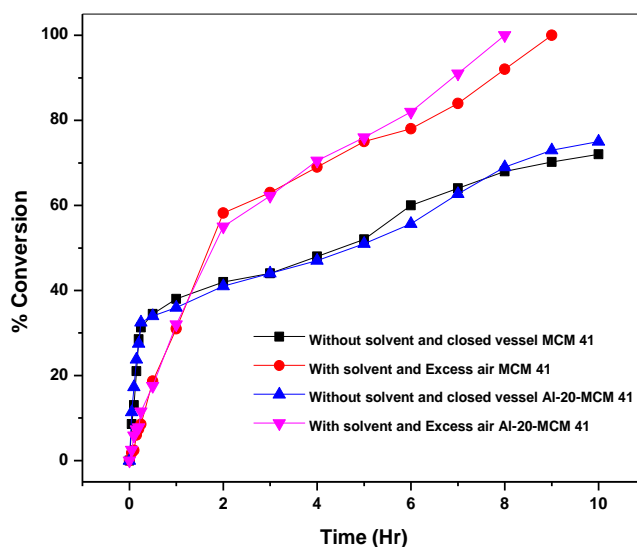
Figure 1. Conversion of self-coupling reaction using MCM-41 and Al-20-MCM-41

Figure 1 illustrates that, in the absence of solvent and within a closed vessel, the reaction proceeds slowly, achieving 72 percent conversion with MCM-41 and 75 percent conversion with Al-20-MCM-41 after 10 hours. In contrast, when conducted with solvent and in the presence of excess air, 100 percent conversion is attained within 9 hours for MCM-41 and within 8 hours for Al-20-MCM-41. The presence of solvent and excess air not only accelerates the reaction but also significantly enhances conversion rates while maintaining 100 percent selectivity. These findings clearly indicate that a polar solvent (nitrobenzene) combined with excess air substantially promotes catalyst activity. The synergistic effect of nitrobenzene and excess air greatly increases amine conversion across all samples. Furthermore, comparing the catalytic performance, Al-20-MCM-41 exhibits higher activity than MCM-41, as

evidenced by achieving 100 percent conversion within 8 hours.

Study of Cross coupling reactions with respect to different reaction conditions.

Cross-coupling reactions were conducted under two distinct conditions to evaluate catalyst conversion and selectivity: (i) without solvent and in the presence of excess air, and (ii) with solvent and in the presence of excess air. The primary objective of these experiments was to investigate the impact of varying reaction conditions on the kinetic behaviour of the reactions. Nitrobenzene was employed as the solvent in these reactions.

Effect on conversion of oxidative cross coupling reaction with respect to time using MCM-41 and Al-20-MCM-41 catalysts for different reaction conditions
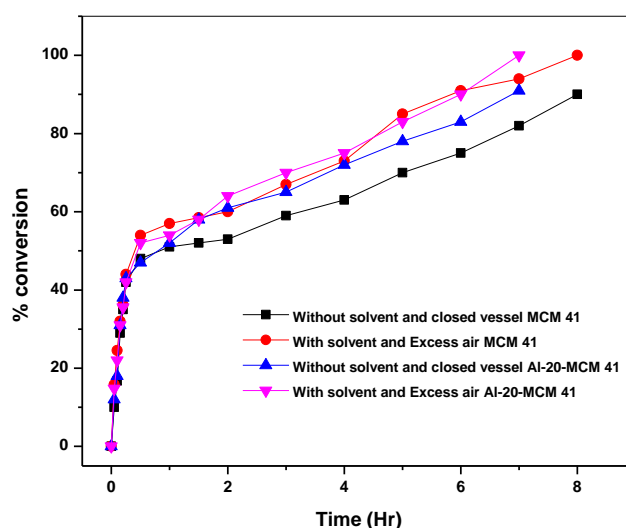

Figure 2. Conversion of cross-coupling reaction using MCM-41 and Al-20-MCM-41

Figure 2 shows that in the absence of solvent and within a closed vessel, the reaction progresses slowly, achieving 90 percent conversion with MCM-41 after 8 hours and 91 percent conversion with Al-20-MCM-41 after 7 hours. Conversely, in the presence of solvent and excess air, 100 percent conversion is reached within 8 hours for MCM-41 and within 7 hours for Al-20-MCM-41. The inclusion of solvent and excess air not only accelerates the reaction but also significantly improves conversion rates while maintaining 100 percent selectivity.These results clearly demonstrate that using a polar solvent, such as nitrobenzene, in combination with excess air markedly enhances catalyst activity. The synergistic effect of nitrobenzene and excess air substantially increases amine conversion across all samples. Additionally, when comparing catalytic performance, Al-20-MCM-41 shows higher activity than MCM-41, as it achieves 100 percent conversion within 7 hours.

Kinetics Study
Kinetics involves studying the rates at which chemical reactions occur and examining the influence of variables such as temperature, pressure, and reactant concentration on these rates. It provides quantitative information about the speed of chemical reactions. To elucidate the kinetic parameters, reactions were conducted under various conditions at the optimal temperature. This section covers the kinetic study of self-coupling and cross-coupling of amines using the Al-20-MCM-41 catalyst, which demonstrates higher selectivity compared to MCM-41.

Kinetics Study of Self-Coupling of Amines
Stoichiometry self-coupling of reaction of Benzylamine is
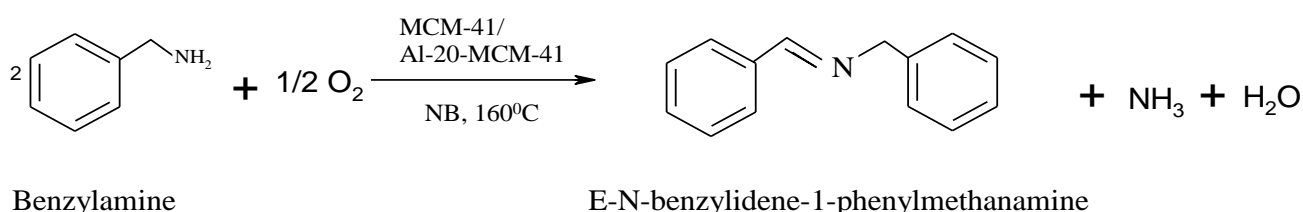
Benzylamine   E-N-benzylidene-1-phenylmethanamine
Scheme 3. Stoichiometry of Self-Coupling Reaction Using Solvent Nitro-Benzene

Kinetics study of reaction without solvent and closed vessel (absence of air) using Al-20-MCM-41 Catalyst
The C_A vs Time curve reveals a distinct shift in reaction order occurring between 0.25 and 0.5 hours. Using the integral method of analysis, a first-order reaction was initially assumed, and a plot of $-\ln(1-X_A)$ vs Time was constructed, as shown in Figure 4(a).

For various time intervals, the concentration of reactant A, C_A vs Time was plotted, as shown in Figure 3. The curve clearly indicates a shifting order reaction beginning from 0.25 hours onward.
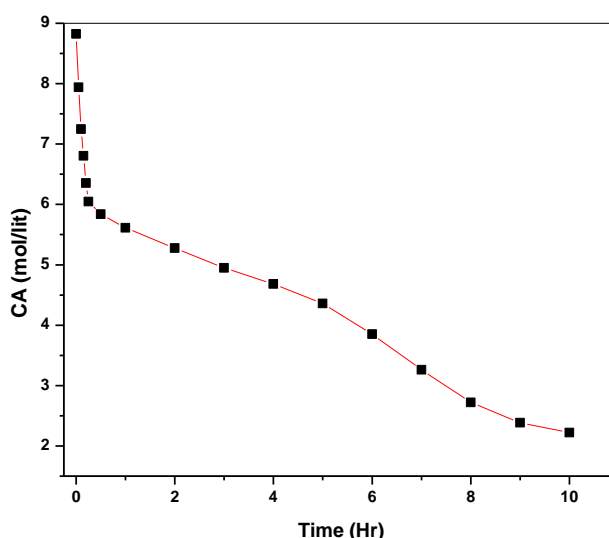
Figure 3. C_A vs Time

This plot demonstrates that the data fit a first-order reaction model up to 0.25 hours. Subsequently, from 0.5 hours onward, a plot of C_A vs Time was created, as illustrated in Figure 4(b), which clearly depicts a zero-order reaction as it produces a

straight line. Consequently, it can be concluded that the reaction followed first-order kinetics during the initial period up to 0.25 hours, after which it shifted to zero-order kinetics.
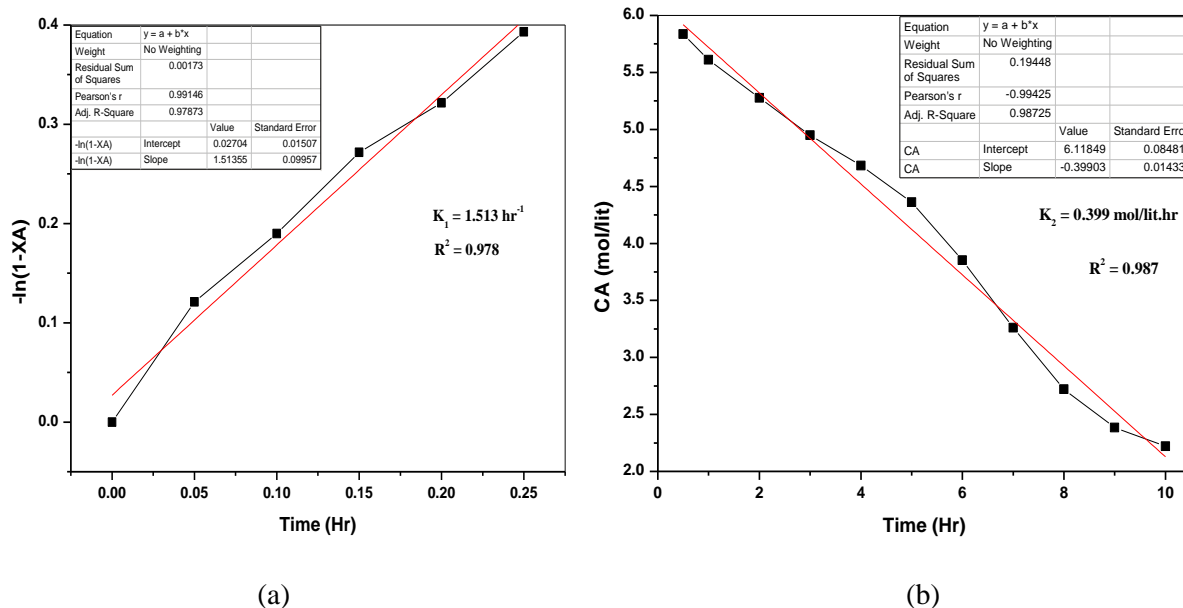

(a)

(b)

Figure 4. (a) $-\ln(1-X_A)$ vs Time **(b)** C_A vs Time

Kinetics study of reaction with solvent and excess air using Al-20-MCM-41 Catalyst

A graph of C_A vs Time was constructed from the experimental concentration and time values, as

shown in Figure 5. This graph indicates that the reaction order shifts from first-order to zero-order after 2 hours.
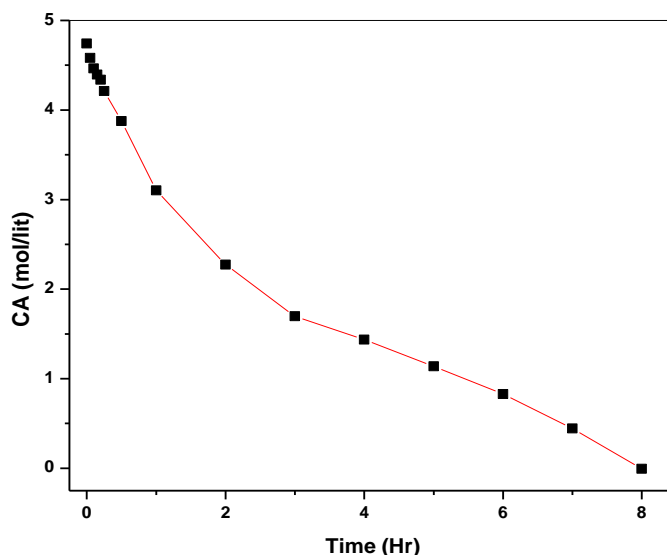

Figure 5. C_A vs Time

Figure 6(a) illustrates that the reaction follows first-order kinetics for the initial 2 hours, as indicated by the straight line observed in the $-\ln(1-X_A)$ vs Time plot. From 2 hours onwards, the reaction transitions to zero-order kinetics, as depicted in Figure 6(b), which also shows a straight line. For zero-order

reactions, the reaction rate becomes independent of the concentration, whereas for first-order reactions, the rate is directly proportional to the concentration.
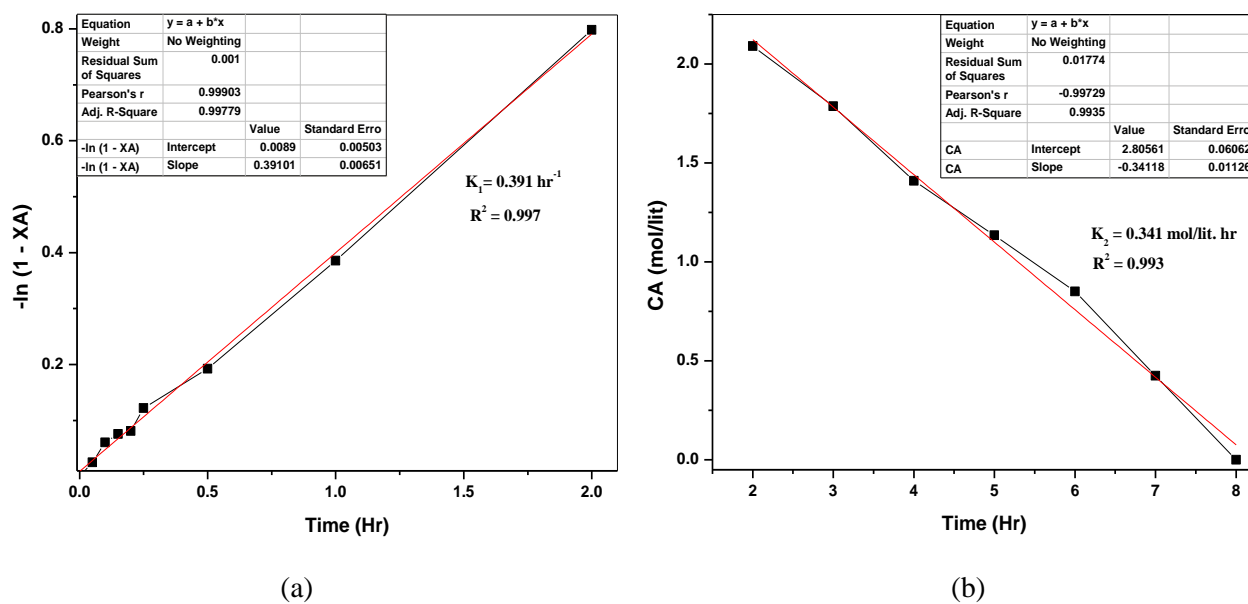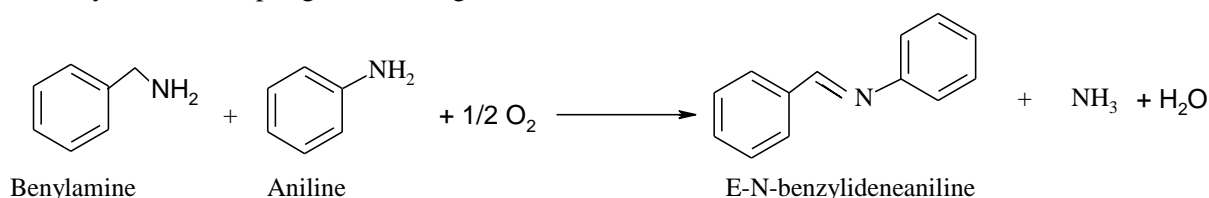
(a)   (b)

Figure 6.(a) –ln(1-X_A) vs Time (b) C_A vs Time

Kinetic Study of Cross Coupling of Amines

Stoichiometry of cross coupling reaction is given as

Benylamine   Aniline   E-N-benzylideneaniline

Scheme 4. Cross coupling reaction of Benzylamine with Aniline

Kinetics study of reaction without solvent and excess air using Al-20-MCM-41 Catalyst

The initial experimental data of concentrations at different time intervals were plotted as concentration versus time, as shown in Figure 7.

From the graph, it can be observed that the reaction exhibits shifting order kinetics, with the reaction order transitioning from first-order to zero-order after 0.25 hours.
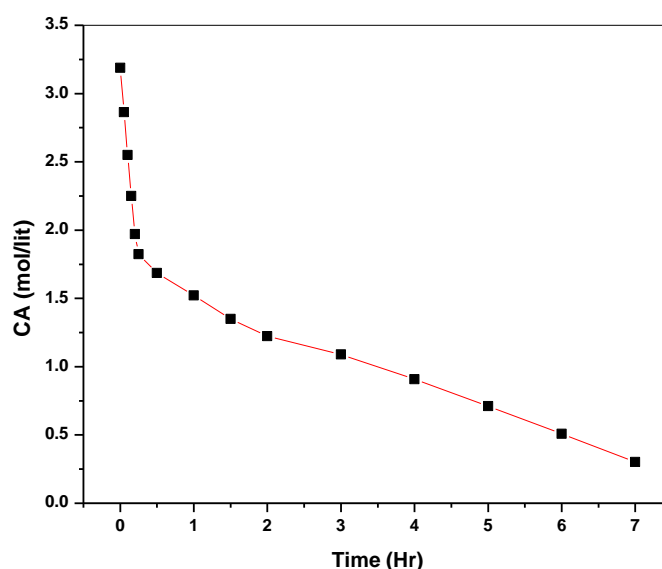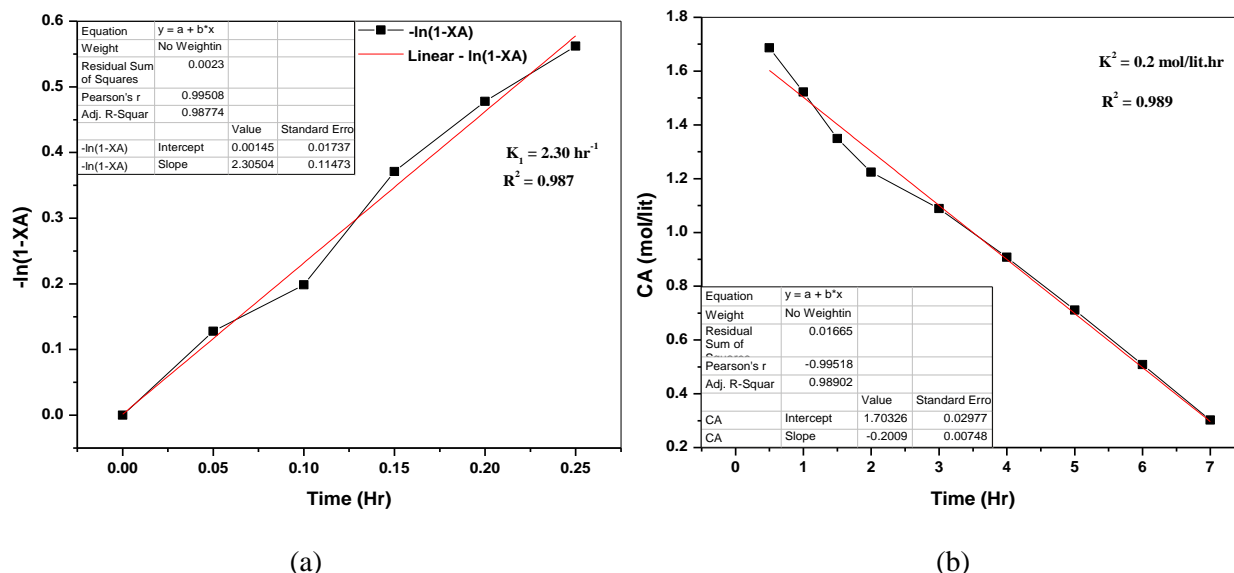

Figure 7. C_A Vs Time

(a)

(b)

Figure 8. (a) $-\ln(1-X_A)$ vs Time (b) C_A vs Time

Figure 8(a) shows the plot of $-\ln(1-X_A)$ vs Time, indicating first-order kinetics with a straight line up to 0.25 hours. From 0.5 hours (30 minutes) onward, the reaction follows zero-order kinetics, as illustrated by the straight line in Figure 8(b). In zero-order reactions, the rate is independent of the concentration, whereas in first-order reactions, the rate is directly proportional to the concentration.

Kinetic study of reaction with solvent and excess air using Al-20-MCM-41 Catalyst

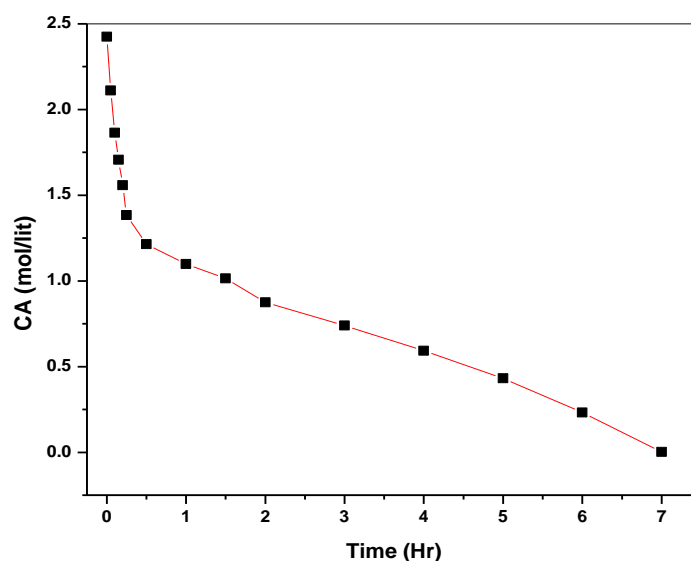The concentration versus time curve for all reactions is shown in Figure 9.

Figure 9. C_A vs Time

It again demonstrates the trend of a shifting order reaction after 0.25 hours. Figure 10(a) shows the plot of $-\ln(1-X_A)$ vs Time for the initial 0.25 hours, indicating that the reactions follow first-order kinetics, as evidenced by the straight line. From 0.5 hours (30 minutes) onward, the reactions follow zero-order kinetics, as shown by the C_A vs Time graph in Figure 10(b). For zero-order reactions, the rate does not depend on concentration, whereas for first-order reactions, the rate is directly proportional to concentration.
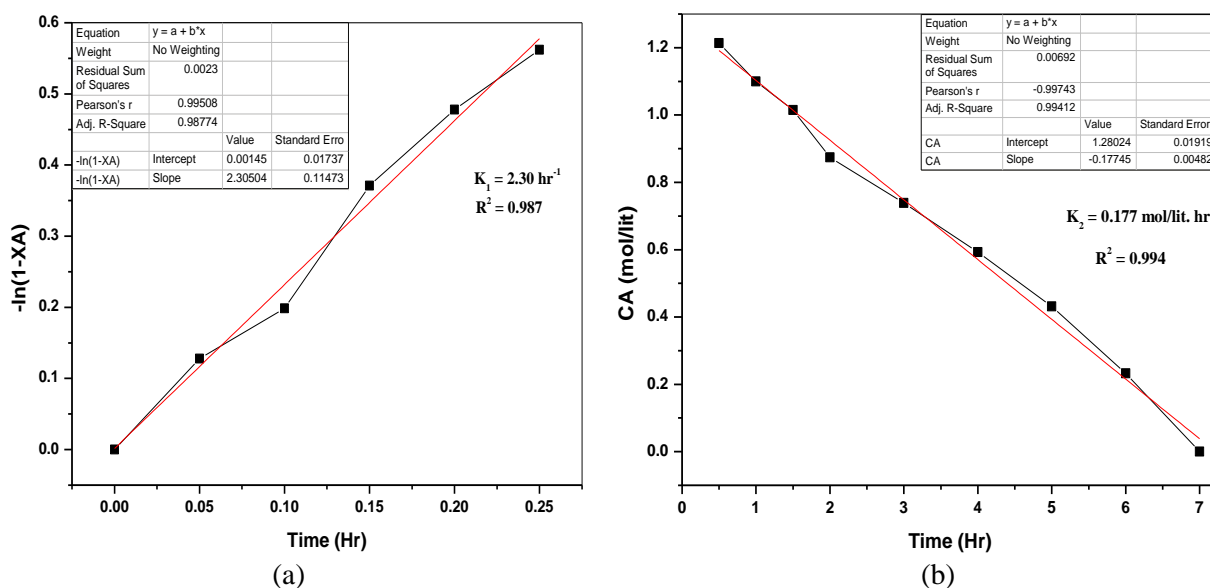
Figure 10.(a) –ln(1-X_A) vs Time (b) C_A vs Time

Rate constant

The rate constants for both self-coupling and cross-coupling reactions were determined under various reaction conditions using the Al-20-MCM-41 catalyst. As shown in Table 1, the rate constant for self-coupling reactions was higher when conducted without solvent in a closed vessel and lower when conducted with solvent and in the presence of excess air. For cross-coupling reactions, the rate constants were found to be higher and nearly identical under both conditions: without solvent and excess air, and with solvent and excess air.

Table 1. Rate Constant For Oxidative Coupling Reaction using Al-20-MCM-41

CASES	Self Coupling Reaction		Cross Coupling Reaction	
	1st Order (hr⁻¹)	Zero order (mol/ lit hr)	1st Order (hr⁻¹)	Zero order (mol/ lit hr)
Without solvent + closed vessel	1.513	0.399	--	--
Without solvent + Excess Air	--	--	2.30	0.20
With solvent + Excess Air	0.391	0.341	2.305	0.177

CONCLUSION

Both self-coupling and cross-coupling reactions were conducted at an optimized temperature of 160°C. These reactions are influenced by the presence of aluminum (Al), the acidity of the catalyst, the presence of a polar solvent, and excess air. Both Al-20-MCM-41 and MCM-41 catalysts exhibit good activity for the oxidative self-coupling and cross-coupling of amines. However, higher conversion rates were achieved with Al-20-MCM-41 due to the presence of acidic sites.

Self-coupling reactions were performed under four different conditions, leading to the conclusion that Al-20-MCM-41 yields higher conversion when reactions are conducted with solvent and excess air compared to using MCM-41, a closed vessel, or without solvent. This higher conversion with Al-20-MCM-41 is attributed to its higher surface acidity, which enhances interaction with the amino groups of benzylamine. In the presence of solvent and excess air, both Al-20-MCM-41 and MCM-41 catalysts showed increased activity, facilitating higher conversion rates. This indicates that solvent and excess air promote the reaction.

For cross-coupling reactions of benzylamine, using solvent and excess air with the MCM-41 catalyst resulted in higher conversion in a shorter time than with the Al-20-MCM-41 catalyst, due to the interaction of aniline molecules with acidic sites. Conversely, without solvent and excess air, higher conversion was observed with Al-20-MCM-41 compared to MCM-41. Solvent use also enhanced selectivity in a shorter time for both catalysts compared to reactions without solvent. Using nitrobenzene as a solvent with both Al-20-MCM-41 and MCM-41 resulted in higher conversion rates, likely due to nitrobenzene reducing surface site blockage by removing adsorbed species.

In conclusion, both Al-20-MCM-41 and MCM-41 are effective for self-coupling and cross-coupling of amines, with Al-20-MCM-41 achieving somewhat higher conversion rates. The reaction order was found to shift from first-order to zero-order for both self-coupling and cross-coupling reactions, typically between 0.25 hours and 0.5 hours. In self-coupling reactions with excess air and solvent, the shift occurred after 2 hours. The overall reaction order was determined to be first-order, and the kinetic rate of reactions increased with the concentration of amine in the feed stream.

REFERENCES:

1. Layer, R.W.: The Chemistry of Imines. Chemical Reviews. 63(5), 489–510 (1963).

2. Murahashi, S.I. and Imada, Y.: Transition Metals for Organic Synthesis. 2nd ed., Wiley–VCH, Weinheim, Germany, 2, 497 (2004).

3. Adams, J.P.: Imines, Enamines and Oximes. Journal of Chemical Society. Perkin Trans.1,125–139 (2000). https://doi.org/10.1039/a808142e

4. Wendlandlt, A.E. and S. S. Stahl, S.S.: Chemo selective Organocatalytic Aerobic Oxidation of Primary amines to Imines. Organic Letter.14 (11), 2850–2853(2012). https://doi.org/10.1021/ol301095j

5. Huang, H., Huang, J., Liu, Y.M., He, H.Y., Kao, Y. and Fan, K. N.: Graphite oxide as an efficient and durable metal-free catalyst for aerobic oxidative coupling of amines to imines Green Chemistry. 14, 930–934. https://doi.org/10.1039/c2gc16681j

6. Law, M.C., Cheung, T.W., Wong, K.Y. and T.H. Chan, T.H.:Synthetic and mechanistic studies of indium-mediated allylation of imines in ionic liquids. Journal of Organic Chemistry.72(3), 923–929 (2007). https://doi.org/10.1021/jo062198x

7. Vazquez, M.A., Landa, M., Reyes, L., Miranda, R., Tamariz, J. and Delgado, F.: Infrared irradiation: effective promoter in the formation of N-benzylideneanilines in the absence of solvent. Synthetic Communication. 34(15), 2705–2718 (2009). https://doi.org/10.1081/SCC-200026190

8. Gopalakrishnan, M., Sureshkumar, P., Kanagarajan, V. and Thanusu, J.: New environmentally-friendly solvent-free synthesis of imines using calcium oxide under microwave irradiation. Research on Chemical Intermediates. 33(6), 541–548 (2007). https://doi.org/10.1163/156856707782565822

9. Guzen, K.P., Guarezemini, A.S., Orfao, A.T.G., Cella, R., Pereira, C.N.P. and Stefani, H.A.: Eco-friendly synthesis of imines by ultrasound irradiation. Tetrahedron Letter. 48(10), 1845–1848 (2007). https://doi.org/10.1016/j.tetlet.2007.01.014

10. Naeimi, H., Sharghi, H., Salimi, F. and Rabiei, K.: Facile and efficient method for preparation of schiff bases catalyzed by P_2O_5/SiO_2 under free solvent conditions. Heteroatom Chemistry. 19(1), 43–47 (2008). https://doi.org/10.1002/hc.20383

11. Chakraborti, A.K., Bhagat, S. and Rudrawar, S.: Magnesium perchlorate as an efficient catalyst for the synthesis of imines and phenylhydrazones. Tetrahedron Letter. 45(41), 7641–7644 (2004). https://doi.org/10.1016/j.tetlet.2004.08.097

12. Weingarten, H., Chu, J.P. and White, W.A.: Ketimine syntheses. Use of titanium tetrachloride in a new procedure for their preparation. The Journal of Organic Chemistry. 32(10), 3246–3249 (1967). https://doi.org/10.1021/jo01285a088

13. Patil, R.D. and Adimurthy, S.: Copper(0)-catalyzed aerobic oxidative synthesis of imines from amines under solvent-free conditions. RSC Advances.5119–5122 (2012). https://doi.org/10.1039/c2ra20339a

14. Zhu, B. and Angelici, R.J.:Non-nanogold catalyzed aerobic oxidation of secondary amines to imines. Chemical Communication. 2157–2159(2007). https://doi.org/10.1039/b700555e

15. Zhu, B., M. Lazar, M., Trewyn, B.J. and R.J. Angelici, R.J.: Aerobic oxidation of amines to imines catalyzed by bulk gold powder and by alumina-suorted gold. Journal of Catalysis. 260(1), 1–6 (2008). https://doi.org/10.1016/j.jcat.2008.08.012

16. Grirrane, A. Corma, H. Garcia (2009), "Highly active and selective gold catalysts for the aerobic oxidative condensation of benzylamines to imines and one-pot, two-step synthesis of secondary benzylamines, Journal of Catalysis, 264(2), 138–144(2009). https://doi.org/10.1016/j.jcat.2009.03.015

17. Yamaguchi, K. and Mizuno, N.: Efficient Heterogeneous Aerobic Oxidation of Amines by a Supported Ruthenium Catalyst. Angewandte Chem. Int. Ed., 42., 1480–1483 (2003). https://doi.org/10.1002/anie.200250779

18. Carmo, A.C. Jr., L.K.C. De Souza, L.k.C., Da Costa, C.E.F.,Longo, E., Zamian, J.R. and Da Rocha Filho, G.N.: Production of biodiesel by esterification of palmitic acid over mesoporous aluminosilicate Al-MCM-41. Fuel. 88 (2), 461–468(2009). https://doi.org/10.1016/j.fuel.2008.10.007

19. Jermy, B.R., and Pandurangan, A.: Catalytic application of Al-MCM-41 in the esterification of acetic acid with various alcohols Applied Catalysis A: General. 288 (1),25–33 (2005). https://doi.org/10.1016/j.apcata.2005.03.047

20. Jermy, B.R. and Pandurangan, A.: Al-MCM-41 as an efficient heterogeneous catalyst in the acetalization of cyclohexanone with methanol, ethylene glycol and pentaerythritol. Journal of Molecular Catalysis A: Chemical. 256(1), 184–192 (2006). https://doi.org/10.1016/j.molcata.2006.04.045

21. Selvara, M., Pandurangan, A., Seshadri, K.S., Sinha, P.K.,Krishnasamy, V., and Lal, K.B.: Comparison of mesoporous Al-MCM-41 molecular sieves in the production of *p*-cymene for isopropylation of toluene Journal of Molecular Catalysis A: Chemical. 186 (1), 173–186 (2002). https://doi.org/10.1016/S1381-1169(02)00134-6

22. Bhattacharyya, K.G., Talukdar, A.K., Das, P., Sivasanker, S. Al-MCM-41 catalysed alkylation of phenol with methanol. Journal of Molecular Catalysis A: Chemical. 197(1), 255–262(2003). https://doi.org/10.1016/S1381- 1169(02)00624-6

23. Tayade, K.N. and M. Mishra, M.: Catalytic activity of MCM-41 and Al grafted MCM-41 for oxidative self and cross coupling of amines Journal of molecular catalysis A :Chemical. 382, 114– 125 (2014). https://doi.org/10.1016/j.molcata.2013.11.001

24. Patel, V., Bhavsar, N., Mishra, M.: Study of Self and Cross Coupling Reaction of Amines to Imines Using MCM-41 and Al-20-MCM catalyst. JETIR. 5(6), 777-782 (2018).

25. Lee, M.K., Kim, H.S., Rhee, H.J.,Choo, J.B.: Reaction Monitoring of Imine Synthesis Using Raman Spectroscopy. Bulletin of Korean Chemical Society. 24(2), 205-208(2012). http://dx.doi.org/10.5012/bkcs.2003.24.2.205

26. Samec, J. S. M.: Ruthenium-catalyzed hydrogen. transfer involving amine and imines: Mechanistic studies and synthetic applications. DiVA, 44 (2005).

27. Li, Y and Marks, T.J.: Organolanthanide-Catalyzed Intramolecular Hydroamination/Cyclization of Aminoalkynes. Journal of American. Chemical Society. 118(39), 9295-9306 (1996). https://doi.org/10.1021/ja9612413

28. Singh, A.K., Jaiswal, J., Singh, R.A., Singh, K.: Mechanism of Pd (II) Catalysis in Ce (IV) Oxidation of Amines in Acidic Medium. Asian Journal of Chemistry. 21(2), 858-862(2009)

29. Naik, R.M., Srivastava, A., Verma, A.: The Kinetics and Mechanism of Ruthenium (III)-Catalyzed Oxidation of Tris(2-aminoethyl) amine by Hexacyanoferrate (III) in Aqueous Alkaline Medium. Tubitak Journal of Chemistry 32, 495 – 503 (2008).