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Effect of Reaction Conditions on the Conversion and Selectivity of MCM-41 and Al-20-MCM-41 Catalyzed Amine Coupling Reactions

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The study has been performed to examine the effect of different reaction conditions (presence of a solvent, absence of solvent, presence of air and closed vessel with an absence of air) on the conversion and selectivity of oxidative coupling reactions of amines to imines using MCM-41 and Al-20-MCM-41 catalysts. Two types of coupling reactions were discussed *viz.* self-coupling and cross coupling. Self-coupling reaction was observed to be faster with Al-20-MCM-41 than MCM-41, while the cross-coupling reactions with Al-20-MCM-41 was slightly slower than MCM-41. The conversion and selectivity of self and cross coupling reactions in different reaction conditions were also investigated. The reaction was found to be of shifting order, initially first order when amine concentration was high and tending towards zero at lower amine concentration. It was evident that both catalysts Al-20-MCM-41 and MCM-41 showed a good catalytic activity on the oxidative coupling reactions of amine but somewhat higher conversion was obtained with Al-20-MCM-41 because of presence of acidic site.

Keywords: Oxidative coupling reaction, Primary amines, Imines, MCM-41, Al-20-MCM-41.

INTRODUCTION

Imines are often known as Schiff bases or azomethines [1], which are used as intermediates in the synthesis of nitrogen heterocycles, fine chemicals and pharmaceuticals in chemistry and biology [2,3]. The direct synthesis of imines through oxidative self-condensation of primary and secondary amines has shown significant interest among different groups in recent past years [4,5]. In literature, number of procedures are proposed for the imines preparations like the use of ionic liquids [6], infrared [7], microwave [8] and ultrasound [9] irradiation. The main problem, which affects the yield of the products, is due to equilibrium conditions exists between the reactants and the corresponding imines, along with water as byproduct of the reaction. This problem is minimized by using various dehydrating agents like P_2O_5/SiO_2 [10], $MgSO_4$-$Mg(ClO_4)_2$ [11], fuming $TiCl_4$ [12] or aromatic solvents forming azeotropic mixtures with water at high temperatures.

Since last few years, oxidative coupling (self and cross) of amines to imines using a suitable catalyst and atmospheric oxygen as an oxidant has shown significant interest as a greener route for synthesis of imines. Amine coupling reactions using solid catalysts like bulk copper [13] and gold powder [14] as well as with supported precious metals like gold nanoparticles [15,16] and ruthenium [17] are proposed due to the benefits of heterogeneous catalysts. Such methods often create complications due to clumsy procedures, moisture sensitive catalysts or reagents, large quantities of toxic aromatic solvents, high reaction temperatures and long reaction times. Therefore, the need of developing new environment friendly procedures for the synthesis of imines is a very crucial subject in modern organic synthesis.

Heterogeneous solid catalysts made from ordered mesoporous materials are widely used in chemical synthesis [18]. Al grafted MCM-41 is such catalyst, which is widely used in the coupling reactions [19]. MCM-41 materials possess an ordered structure with uniform mesopores arranged into a hexagonal lattice and use as a support material for development of heterogeneous catalysts. The Al grafted MCM-41 (Al-MCM-41) has been used extensively as catalyst for numerous acid catalyzed reactions like esterification [20,21], acetalization [22] and alkylation [23,24]. MCM-41 and Al-MCM-41 mesoporous catalysts have been suggested for the oxidative coupling of amines with the use of polar solvent nitro benzene [19].

Catalytic properties of MCM-41 and Al grafted MCM-41 acidic materials for oxidative coupling of amines play a vital role during synthesis process. The catalyst activity and conversion of reaction are affected in the oxidative coupling reactions of amines to imines with MCM-41 and Al-20-MCM-41 [25]. Herein, the effect of different reaction conditions for the coupling reactions (self- and cross-) to check conversion and selectivity of the reaction are investigated.

EXPERIMENTAL

Oxidative coupling of amine to imine with MCM-41 and Al-20-MCM-41: In this study, oxidative coupling of amine to imine was carried out using two different catalysts MCM-41 and Al-20-MCM-41 with different reaction conditions. Two different types of reactions were performed (i) self-coupling reaction and (ii) cross coupling reaction.

Coupling reaction was carried out in a reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, U.K.) by taking calculated amount of reaction mixture in a reaction tube along with the activated catalyst in two different situations. In first case, the reaction was carried out in presence of solvent with desired temperature with proper stirring for required reaction time. In second case, no solvent was used during course of reaction means solvent free reaction. Both reactions were performed in a closed condition as well as with continuous air purging to provide excess oxygen for the reaction. After the completion of the reaction, the mixture was cooled and diluted with dichloromethane, which was analyzed by gas chromatography (Agilent 7890A) having a HP-5 (60 m) capillary column with a programmed oven temperature from 50 to 280 ºC, 0.5 mL/min flow rate of N_2 as a carrier gas and FID detector. The products formed during the reactions were characterized by GC-MS analysis and the data were verified with those reported in the literature. The GC-MS analysis was carried out using gas chromatograph mass spectrometer (Agilent 5975C GC/MSD with 7890A GC system) having HP-5 capillary column of 60 m length and 250 mm diameter with a programmed oven temperature from 50 to 280 ºC, at 1 mL/min^{-1} flow rate of helium as a carrier gas and ion source at 230 ºC.

Self-coupling reactions of amines: Self-coupling reactions were carried out in a reaction station by taking weighed amounts of reaction mixture comprises of benzyl amine and nitrobenzene as a solvent into a reaction tubes and 0.05 g of freshly activated catalyst was added. Activation of the catalyst was performed at 180 ºC for 1 h. The reaction was carried out at 160 ºC for different time intervals. After the reaction, the reaction tubes were cooled to room temperature and the mixture was collected from the tubes and diluted with dichloromethane. The conversion of reaction with respect to different time of benzylamine and selectivity of product were studied for MCM-41 and Al-20-MCM-41 catalysts with and without using solvent in presence of air and closed vessel (**Scheme-I**). The self-coupling reactions were performed under four different conditions *viz.*, (i) without solvent and closed vessel (ii) with solvent and closed vessel; (iii) without solvent and excess of air; and (iv) with solvent and in excess of air, in order to check the conversion effectively and selectively.

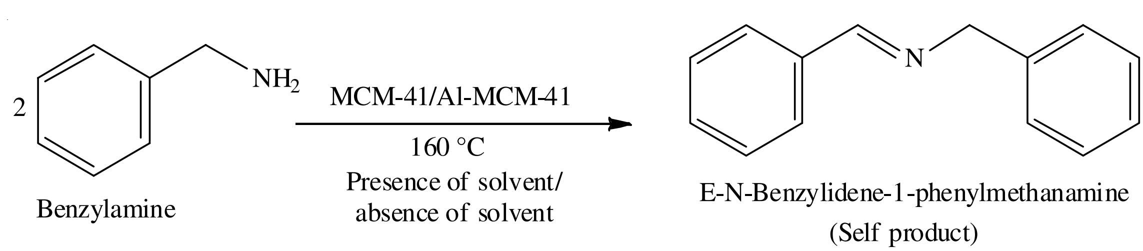
Mechanism of formation of imine from amine for self-coupling: Reaction mechanism refers to a step or a series of steps by which the initial reactants interact in the process of forming products. Formation of imine from amine is two steps process:

Formation of imine intermediate (step-1): In oxidative coupling of benzylic amines in water under reflux condition the amines are activated by water molecules by hydrogen bonding through amino group, thus it reacts with oxygen to form an imine intermediate.

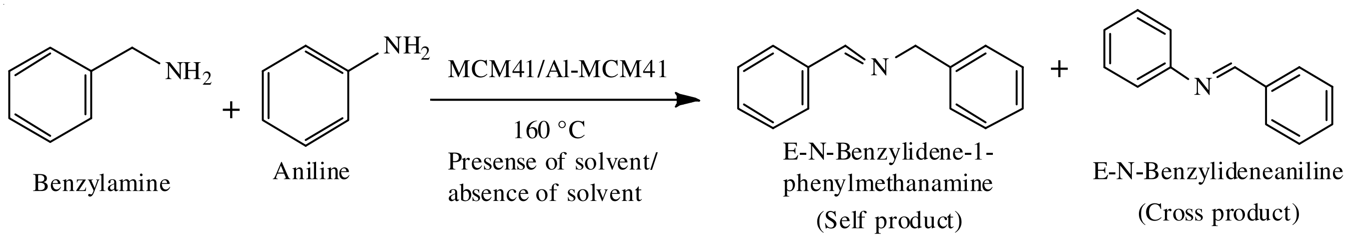
Formation of imine product from imine intermediate (step-2): Imine intermediate reacts with free amines to give imine product. From two steps, it has been identified that step 2 is the rate determining step.

Cross coupling reactions of amines: In cross coupling benzylamine, aniline used as reactants and nitrobenzene as a solvent (in case of reaction carried with solvent). Calculated amount of reactants and solvent were taken into 50 mL reaction tube. MCM-41 and Al-20-MCM-41 were used as catalysts, which were activated at 180 ºC for 1 h and then added into reaction tube. Reactions were carried out at 160 ºC and 1 atm. pressure for different time intervals. After the reaction, the reaction mixture was cooled to room temperature, the reaction mixture was collected from the tubes and diluted with dichloromethane (**Scheme-II**). Cross coupling reactions were also carried out under two different conditions *viz.*, (iii) with solvent and in excess of air (iv) without solvent and in excess of air in order to check the conversion effectively and selectively.

Mechanism: Using cross coupling reaction, the formation of imine from amine is a three steps process *viz.* formation of imine intermediate (step-1); formation of imine product from imine intermediate (step-2), where the imine intermediate gets reacted with free amines to give imine product. Finally, the self product react with another reactant aniline and form cross



Scheme-I. Self-coupling reaction of benzylamine



Scheme-II. Cross coupling reaction of benzylamine with aniline

imine product (step-3). From all three steps, it has been identified that step 3 is the rate determining step for coupling reaction.

RESULTS AND DISCUSSION

Temperature study: Both oxidative coupling reactions were carried out at different temperatures to achieve the higher conversion. Fig. 1 shows that higher conversion obtained when reaction was conducted at 160 ºC and 1 atm. pressure respectively for self-coupling and cross coupling.

Study of self coupling reactions with respect to different reaction conditions: Self-coupling reaction were conducted at four different conditions *viz*. (i) without solvent and closed vessel; (ii) with solvent and closed vessel; (iii) without solvent and excess of air; and (iv) with solvent and in excess of air.

Effect on the conversion of oxidative self-coupling reaction without solvent and closed vessel: Fig. 2a-b show that without solvent and closed vessel, the reaction occurs slowly and 11.4% conversion was obtained for Al-20-MCM-41 at

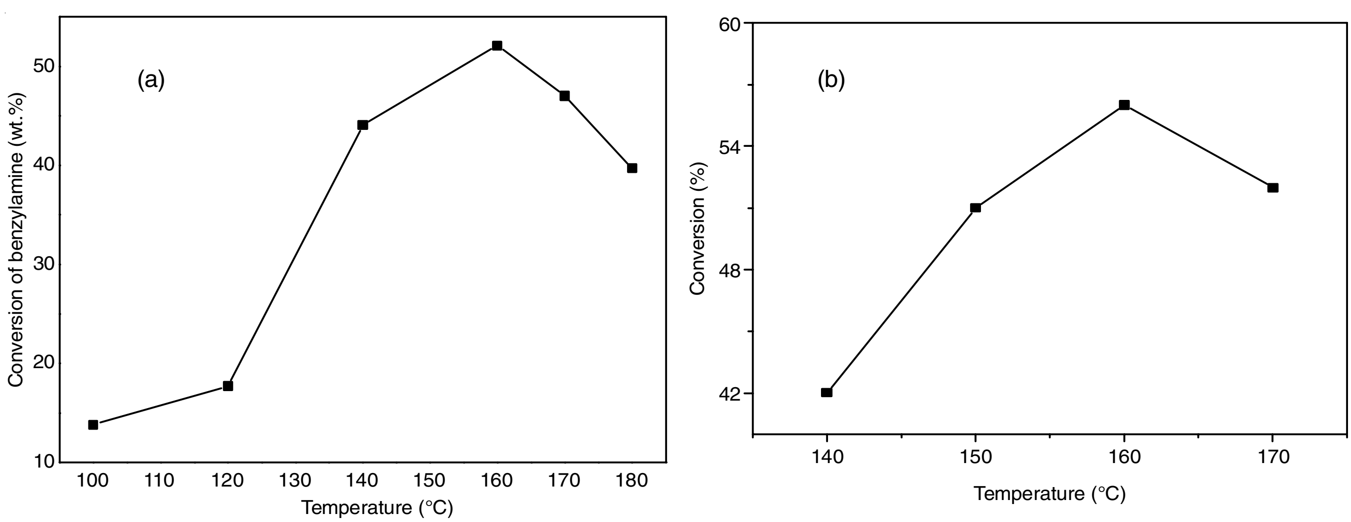


Fig. 1. Effect of temperature on conversion of benzylamine for self-coupling reaction (a) cross coupling reaction (b)

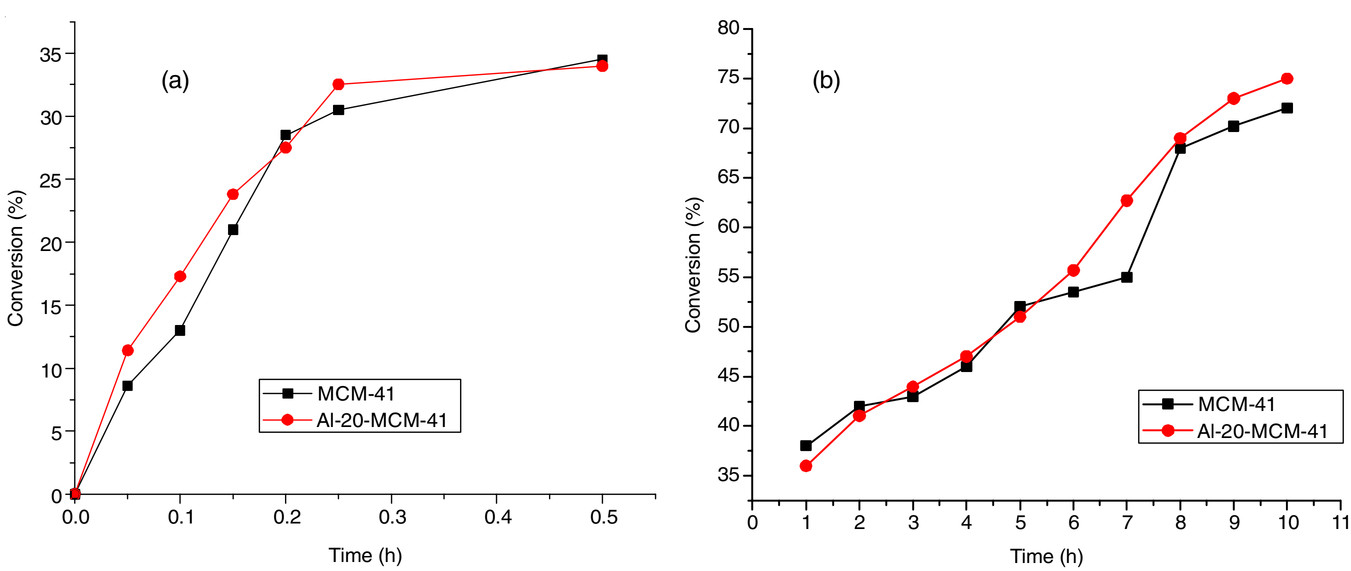


Fig. 2. Effect on conversion with respect to time without solvent and closed vessel (a) Lower time, (b) Higher time [Reactant: Benzylamine (1 g), Catalyst: MCM-41, Al-20-MCM-41 (0.05 g), Temperature: 160 °C, Pressure: 1 atm]

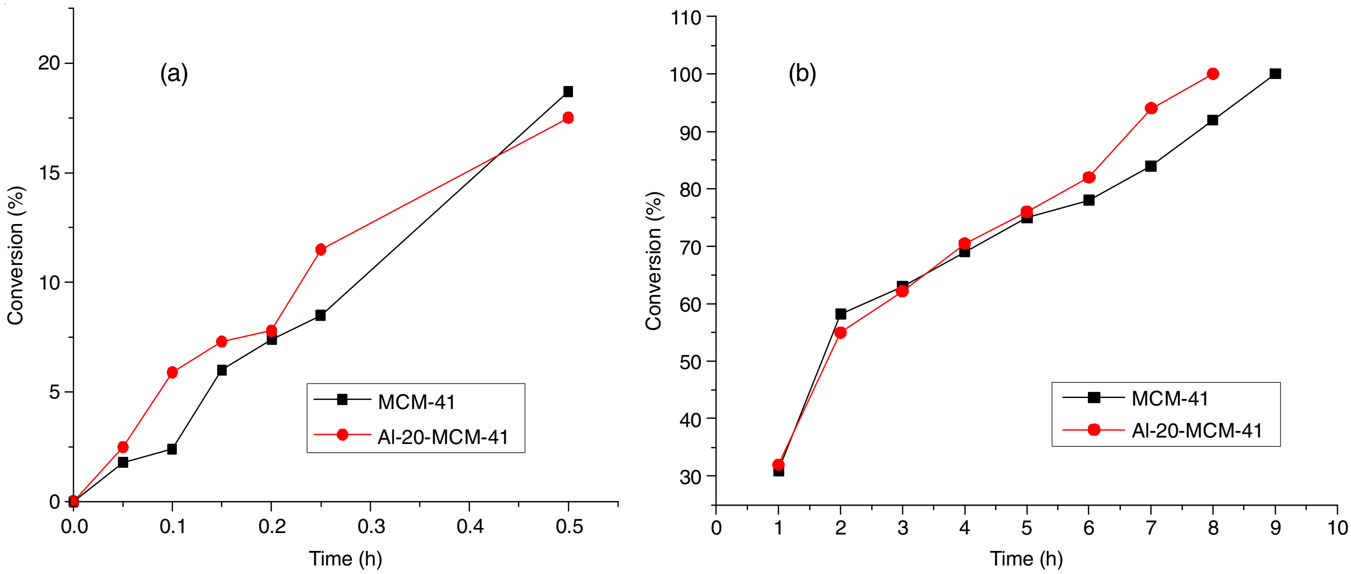


Fig. 3. Effect on conversion with respect to time with solvent and excess air (a) Lower time (b) Higher time [Reactant: Benzylamine (1 g), Catalyst: MCM-41, Al-20-MCM-41 (0.05 g), Nitrobenzene (solvent), Temperature: 160 °C, Pressure: 1 atm

0.05 h and 8.6% conversion for MCM-41 at 0.05 h (3 min), which increased to 75% at 10 h for Al-20-MCM-41 and 72% at 10 h for MCM-41 catalyst. No difference in the conversion using MCM-41 and Al-20-MCM-41 were observed. But somewhat higher conversion was observed when Al-20-MCM-41 used. A 100% selectivity was obtained using both MCM-41 and Al-20-MCM-41 catalysts.

Effect on conversion of oxidative self-coupling reaction with solvent and excess air: Self-coupling reaction were also conducted at four different conditions. Among these four conditions, it can be observed that 100% conversion was obtained at 8 h for Al-20-MCM-41 and at 9 h for MCM-41, while reaction was carried out using solvent with excess air (Fig. 3). It has also been observed that around 75% conversion was obtained within 10 h in case of reaction carried out without solvent and in closed vessel, while within 8 to 9 h 100% conversion was obtained.

In this work, nitrobenzene was used as a polar solvent due to its high dielectric constant (34.8), high boiling point (205 ºC) 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 high boiling point polar solvent can be explored to promote the efficiency of MCM-41 catalysts for amine coupling reactions.

From these studies, it was also evident that the presence of polar solvent (nitrobenzene) and excess air in the reaction could promote the catalysts activity. Along with the nitrobenzene, the presence of excess air significantly enhanced the conversion of amine with all the samples showing that the presence of polar solvent and excess air facilitates the reaction. The Al-20-MCM-41 catalyst showed the higher activity than MCM-41 (Fig. 4) due to grafting of aluminium.

Cross coupling reactions with respect to different reaction conditions: Cross coupling reaction were also conducted at two different conditions to check the conversion and selectivity of catalyst (i) without solvent and excess air, and (ii) with solvent and excess air.

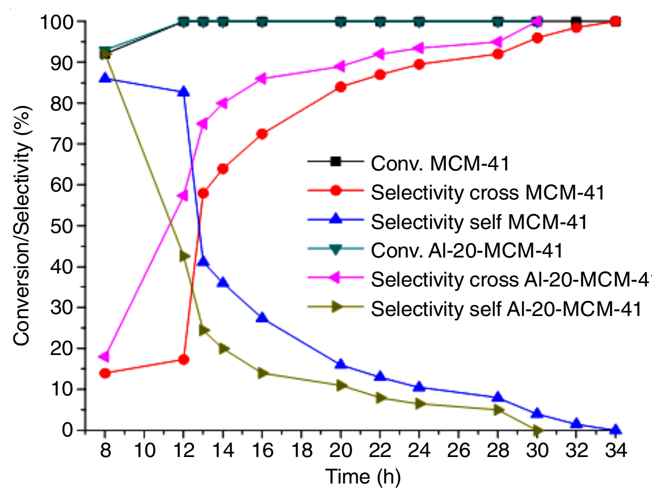


Fig. 4. Effect on conversion and selectivity with respect to time without solvent with excess air

Effect on conversion and selectivity of oxidative cross coupling reaction without solvent and excess air: Cross coupling reaction carried out without solvent and with excess air, which reveals that the selectivity of formation of cross product is higher at lower time for MCM-41 compare to Al-20-MCM-41 (Fig. 5). Selectivity of cross product was obtained at 30 h and 34 h using Al-20-MCM-41 and MCM-41, respectively. Thereafter, there is no formation of self-product. In both cases, 100% conversion was achieved within 12 h using Al-20-MCM-41 and MCM-41 catalysts.

Effect on conversion and selectivity of oxidative cross coupling reaction with solvent and excess air: Fig. 5 shows the effect on conversion and selectivity for the case of cross coupling reaction using with solvent and excess of air. It can be observed that higher conversion was obtained in MCM-41 then Al-20-MCM-41 but in both cases 100% conversion was achieved at 8 h. The formation of cross product using MCM-41 was higher as compared to Al-20-MCM-41. Selectivity of

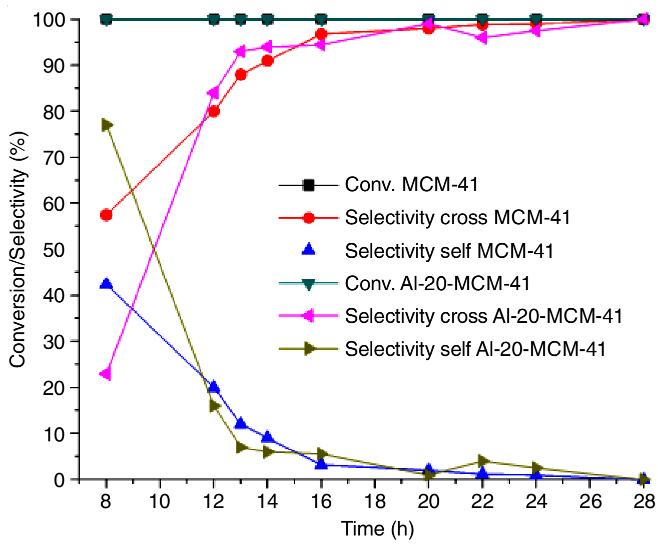


Fig. 5. Effect on conversion and selectivity with respect to time with solvent and excess air

cross product using MCM-41 was found to be higher compare to Al-20-MCM-41. Ultimately, 100% cross product was obtained at 28 h in both catalyst and after 28 h, no formation of self-product was obtained.

Conclusions

For both self and cross coupling reactions at 160 ºC was optimized as optimum temperature. Both self and cross-amine coupling reactions were influenced by presence of Al, acidity of catalyst, presence of polar solvent and excess air. Both catalysts Al-20-MCM-41 and MCM-41 shows the good activity on oxidative self and cross coupling of amine but somewhat higher conversion was achieved with Al-20-MCM-41 due to the presence of acidic site. Self-coupling reactions were carried out for four different conditions out of which Al-20-MCM-41 gave higher conversion when reactions carried out using solvent and excess air then MCM-41 catalyst, closed vessel and without solvent. Using Al-20-MCM-41 catalyst, higher conversion was obtained in all cases of self-coupling reaction compared to MCM-41 due to higher surface acidic sites for interaction with amino group of benzylamine. Presence of solvent and excess air in the reaction using both catalysts Al-20-MCM-41 and MCM-41 could promote the catalyst activity as these reactions give higher conversion in all mentioned cases of self-coupling reactions. This shows that solvent and excess air facilitates the reaction. The use of the solvent with both catalysts MCM-41 and Al-20-MCM-41 during reactions promotes higher conversion compare to non-use of solvent. With excess air higher conversion was obtained with both catalysts then closed vessel.

For cross coupling reaction of benzylamine, in the presence of solvent and excess air with MCM-41 catalyst, the higher conversion was obtained in lower time then Al-20-MCM-41 catalyst, due to the fast interaction of aniline molecule with acidic sites. While in case of without solvent and excess air the higher conversion was observed with Al-20-MCM-41 as compared to MCM-41 catalyst. The higher selectivity in the presence of solvent was obtained in lesser time for both catalysts compared to no solvent reaction medium. Moreover, presence of solvent (nitrobenzene) in both catalysts gives higher conversion compared to reactions without solvent which might be due to the reduction of possible surface sites blockage by removing the adsorbed species. Finally, it would be concluded that both Al-20-MCM-41 and MCM-41 as catalysts are good for self and cross coupling of amines but somewhat higher conversion was achieved with the use of Al-20-MCM-41 catalyst.

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CONFLICT OF INTEREST

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

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