

# SELECTIVE DIBENZOYLATION OF BIPHENYL TO 4,4'-DIBENZOYLBIPHENYL OVER H-AL-MCM-41

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## ABSTRACT

Dibenzoylation of benzoyl chloride in the presence of mesoporous H-Al-MCM-41 forms the biphenyl 4,4'-dibenzoylbiphenyl (DB) with 100% selectivity.  $^{27}\text{Al}$  MAS NMR, pyridine adsorption and XRD data reveal that both Brønsted and Lewis acidities play a role in the production of DB and the catalytic activity is dependent on the structure of the mesoporous H-Al-MCM-41.

**Keywords:** H-Al-MCM-41, dibenzoylation, acidity, 4,4'-dibenzoylbiphenyl

## INTRODUCTION

Benzoylation is a significant Friedel-Crafts acylation used in the commercial production of important chemicals such as benzophenone and its substituted analogues as additives in the synthesis of fine chemicals and dyes [1-5]. Recent interest is on the benzoylation of biphenyl with benzoyl chloride, from which the monosubstituted product, 4-phenyl-benzophenone or 4-benzoylbiphenyl; a useful precursor in perfumes [6], and the disubstituted product, 4,4'-dibenzoylbiphenyl (DB); an important monomer in the polymerisation of poly(4,4'-diphenylene diphenylvinylene) or namely PDPV [7,8] are formed.

Current production of disubstituted 4,4'-dibenzoylbiphenyl is still via the difficult homogeneously catalysed process. Despite the increase of research activities in the field of heterogeneous catalysis, synthesis of disubstituted compound using zeolite has not so far been successful. For example, microporous zeolite beta only gives monosubstituted product as mentioned above. Although heterogeneously catalysed reactions using microporous molecular sieve did not show much potential, mesoporous molecular sieve MCM-41 is a promising alternative for reactions involving large molecules. The large internal surface area and channel apertures of the MCM-41 would allow, in principle, large molecules to access the active sites. Besides, the presence of Brønsted and Lewis acid sites in H-Al-MCM-41 play significant roles in enhancing the catalytic activity and adsorptive capacity. From this point of view, mesoporous MCM-41 molecular sieve was chosen to catalyse the dibenzoylation of biphenyl with benzoyl chloride. This paper reports the first attempt on heterogeneous synthesis of 4,4'-dibenzoylbiphenyl over H-Al-MCM-41.

## EXPERIMENTAL

### Synthesis of H-Al-MCM-41

Direct synthesis of Al-MCM-41 with Si/Al ratios of 11, 45, 58, 82 were based on the following basic mole compositions: 6  $\text{SiO}_2$  : CTABr : 1.5  $\text{Na}_2\text{O}$  : 0.15  $(\text{NH}_4)_2\text{O}$  : 250  $\text{H}_2\text{O}$ . Sodium silicate solution was prepared by stirring 42.80 g of 1.00 M aqueous NaOH solution with 17.14 g colloidal silica (30 wt%  $\text{SiO}_2$ ) at 353 K. The sodium silicate solution was then added dropwise to a polypropylene bottle containing mixtures of 0.29 g of 25 wt% aqueous  $\text{NH}_3$  solution, 5.20 g of cetyltrimethyltetrammonium bromide (CTABr) and  $\text{NaAlO}_2$ , followed by vigorous stirring and heating at 370 K. Subsequently, the pH of the reaction mixture was adjusted to 10.2 by adding 30 wt% acetic acid ( $\text{CH}_3\text{COOH}$ ). The heating and pH adjustment procedures were repeated three times. The precipitated product, Al-MCM-41 with CTA template was filtered, washed, dried and calcined at 823 K overnight. H-Al-MCM-41 was prepared by ion exchange of 1 g of the calcined Al-MCM-41 sample in excess 0.5 M aqueous ammonium nitrate solution ( $\text{NH}_4\text{NO}_3$ ) overnight at 353 K, followed by washing, air-drying and calcination of the  $\text{NH}_4^+$  samples at 773 K for 4 hours. H-Al-MCM-41 samples with Si/Al ratios of 11, 45, 58 and 82 are labelled as HAM-1, HAM-2, HAM-3 and HAM-4 respectively.

## Characterisations

X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5000 powder diffractometer with Cu K $\alpha$  radiation. The BET surface areas and the pore size distributions were measured on a Micromeritics volumetric adsorption analyzer (ASAP 2010). Ammonia-TPD spectra were measured using Thermoquest TPDRO 1100, in which the desorbed NH $_3$  was recorded using a thermal conductivity detector. The samples were purged at 393 K in a nitrogen stream for 1 h. NH $_3$  was adsorbed at 393 K. Desorption of NH $_3$  was initiated by heating the sample continuously in a 0.5 mLs $^{-1}$  flow of nitrogen up to 873 K at a heating rate of 10 Kmin $^{-1}$  in a helium flow as the carrier gas. Infrared spectra of pyridine adsorbed on mesoporous H-Al-MCM-41 were recorded on Shimadzu FTIR 8300 spectrometer using self-supporting wafer. Pyridine was adsorbed onto the sample for 5 minutes and desorbed at 298 K and 423 K under 10 $^{-2}$  mbar for 1 hour.  $^{29}\text{Si}$  MAS NMR spectra were recorded on a Bruker 400 MHz Avance at a frequency of 79.5 MHz, spinning at 10 kHz using 45 $^\circ$  pulses with a relaxation delay of 600 seconds.  $^{27}\text{Al}$  MAS NMR spectra were recorded at a frequency of 104.2 MHz, spinning at 7 kHz using 1.9  $\mu\text{sec}$  pulses with 2 seconds relaxation time delays and 6000 scans.

## Catalysis

H-Al-MCM-41 sample was activated in a sintered glass tube under a nitrogen gas flow and heated at 523 K for 4 hours. The liquid phase acylation of biphenyl with benzoyl chloride was carried out in a 50 mL two necked flask attached to a condenser and supplied with nitrogen gas. The temperature of the reaction vessel was maintained at 353 K using an oil bath. Biphenyl (0.001 mol), benzoyl chloride (0.01 mol), nitrobenzene (6 mL) and H-Al-MCM-41 (0.5 g) were slowly added, followed by stirring and heating for 3 hours. The resulting products were analysed by gas chromatography (GC-HP 6890/Ultra-1 column/FID) and verified by gas chromatograph-mass selective detector (GC-MSD/Agilent Technologies). Each sample was analysed by the splitless method using helium as the carrier gas.

## RESULTS AND DISCUSSION

### Characterisation of H-Al-MCM-41

X-ray diffractograms of H-Al-MCM-41 samples in Figure 1 consist of up to four reflections typical of hexagonal lattice structure of mesoporous MCM-41; indexed as (100), (110), (200), (210) respectively. The strong intense (100) peak observed indicates that the long-range order of the sample is retained. A less intense (100) reflection was observed in sample HAM-1 which suggests that there is an increase in disorder of the sample, which must have resulted during the ion exchange modification. Although the NH $_4^+$  ions prefer to be ionically bonded to the negatively charged Al atoms in the framework, it is evident that sample HAM-1 with a high amount of framework Al atoms could not withstand the massive amount of NH $_4^+$  ions; causing the framework to collapse.

Table 1. Physical properties of H-Al-MCM-41 and yield of 4,4'-dibenzoylbiphenyl (DB).

Sample	Si/Al ratio*	Surface Area (m $^2$ /g)	Total amount of adsorbed ammonia (mmol/g)	Yield of DB ( $\mu\text{mol}$ ) **
HAM-1	11	1093	1.19	0.21
HAM-2	45	943	1.21	0.32
HAM-3	58	1171	0.96	0.36
HAM-4	82	1186	1.48	0.45

\* Si/Al ratios are calculated from the SiO $_2$ :Al $_2$ O $_3$  mole ratios of as-synthesised Al-MCM-41 starting materials in the formation of the gel composite.

\*\* Reactions were carried out in 3 hours.

Surface areas calculated from nitrogen adsorption analysis and tabulated in Table 1 confirm the mesoporosity of MCM-41. Data from TPD profiles of NH $_3$  adsorption in Table 1 indicate the presence of physisorbed ammonia in all samples.

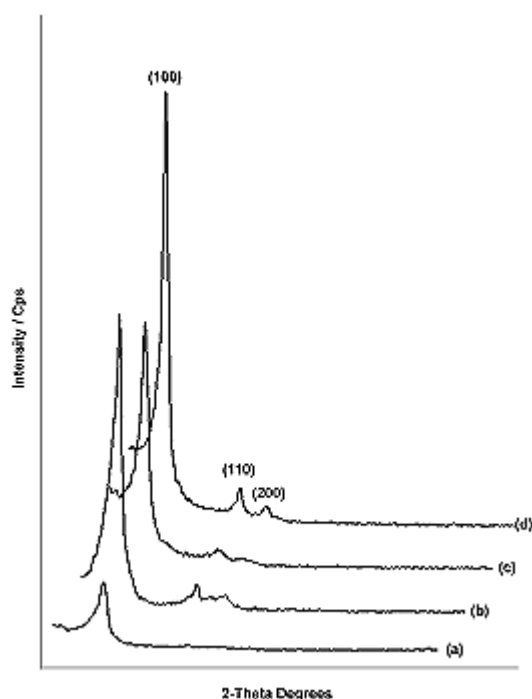


Figure 1. X-ray diffractograms of (a) HAM-1, (b) HAM-2, (c) HAM-3 and (d) HAM-4.

In order to determine the acid strength of Lewis and Brønsted acid sites, pyridine adsorption analysis as monitored in situ with infrared spectroscopy was carried out for all samples. Figure 2 shows the pyridine desorption FTIR spectra of samples HAM-3 and HAM-4 at 298 K and 423 K. FTIR spectra of samples HAM-1 and HAM-2 show similar characteristics and are not shown here. As observed, Lewis and Brønsted acid sites appear at  $1450\text{ cm}^{-1}$  and  $1550\text{ cm}^{-1}$ , respectively. Generally, in all samples, pyridine was more adsorbed on the Lewis acid sites rather than the Brønsted acid sites. In fact, sample HAM-3 shows a balance in the strength of Lewis and Brønsted acid sites and, compared to other samples, the strengths are indeed weaker at the beginning of pyridine desorption. The presence of Lewis acid sites in most samples suggests that extraframework Al (EFAL) are likely to exist on the structure of H-Al-MCM-41; which was confirmed by  $^{27}\text{Al}$  MAS NMR analysis.

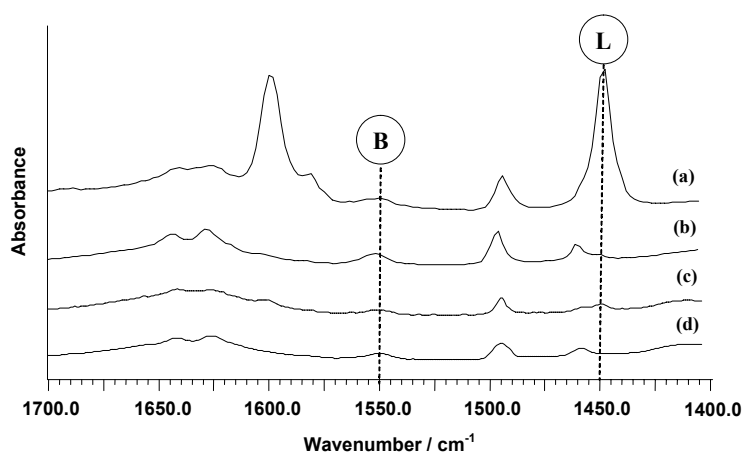


Figure 2. FTIR spectra of pyridine desorption of sample HAM-4 at (a) 298 K, (b) 423 K and HAM-3 at (c) 298 K (d) 423 K.

The  $^{27}\text{Al}$  MAS NMR spectra of H-Al-MCM-41 with various Si/Al ratios in Figure 3 show a broad peak at ca. 53 ppm; confirming the incorporation of aluminium into the framework of MCM-41 as tetrahedral aluminium ( $\text{Al}_{\text{tet}}$ ) whereas the intense peak at 0 ppm indicates that octahedral aluminiums ( $\text{Al}_{\text{oct}}$ ) are present as EFAL. EFAL may be present in many forms, such as  $\text{Al}^{3+}$ ,  $\text{AlO}^+$ ,  $\text{Al}(\text{OH})^{2+}$  and charged  $\text{Al}_x\text{O}_y^{n+}$  clusters within the catalyst [9]. The relative areas of the peaks as measured from their intensities indicate that

samples HAM-1 and HAM-4 contain higher amount of tetrahedral Al compared to samples HAM-2 and HAM-3. In addition, the sharp and intense peak assigned to octahedral aluminium observed in samples HAM-2, HAM-3 and HAM-4 reflects the chemical equivalence of the highly mobile EFAL on H-Al-MCM-41 structure.

The presence of EFAL on H-Al-MCM-41 was further verified by treatment with methanolic HCl solution [10].  $^{27}\text{Al}$  MAS NMR of EFAL containing sample HAM-4 after treatment with methanolic HCl solution as shown in Figure 5, exhibits only a single broad peak of tetrahedral aluminium, confirming that octahedral aluminium or EFAL has been removed.

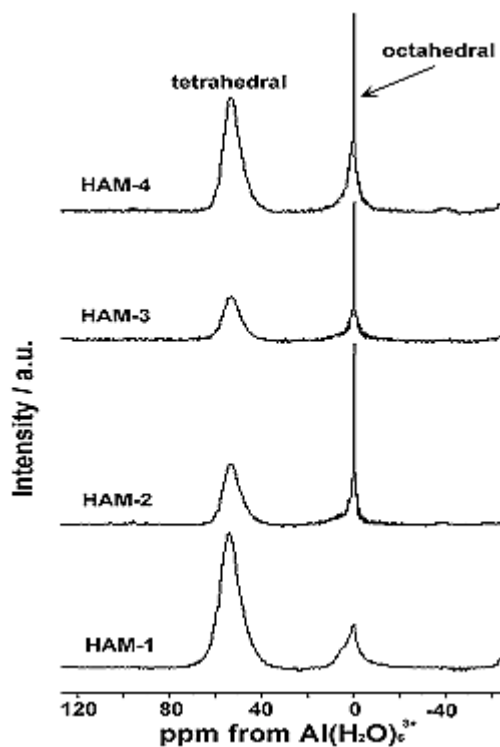


Figure 3.  $^{27}\text{Al}$  MAS NMR spectra of calcined H-Al-MCM-41 samples of various Si/Al ratios.

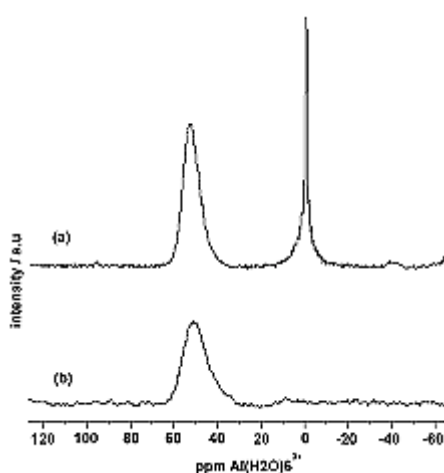


Figure 4.  $^{27}\text{Al}$  MAS NMR spectra of sample HAM-4: (a) before treatment and (b) after treatment with 1.0 M of methanolic HCl solution

## Catalysis

Analysis by gas chromatography indicates that 4,4'-dibenzoylbiphenyl was the only product formed; implying the presence of Lewis acid sites in all the catalytic systems used. Catalytic results in Table 1 indicate that samples with higher Si/Al ratios produced higher yields of 4,4'-dibenzoylbiphenyl. Sample HAM-4 with the highest Si/Al ratio produced 0.45  $\mu\text{mol}$  4,4'-dibenzoyl biphenyl; the highest yield, after 3 hours of reaction. Sample HAM-1 produced a low quantity of 4,4'-dibenzoylbiphenyl although it contains a high amount of Al since its structure has collapsed as explained in Section 4.1. It is noted that the steep increase in the yield of 4,4'-dibenzoylbiphenyl occurs during the first hour of reaction (Figure 5). The catalytic test results indicate that the product yield is influenced and determined by the presence of both Lewis and Brønsted acid sites. The results in Figure 5 also show that the yield of the product was reaching saturation for all samples after 1 hour of reaction time; due to deactivation as a consequent of deterioration in crystallinity of the catalyst. Indeed, sample HAM-1 being the least crystalline to XRD (Figure 1) gave the lowest yield of product.

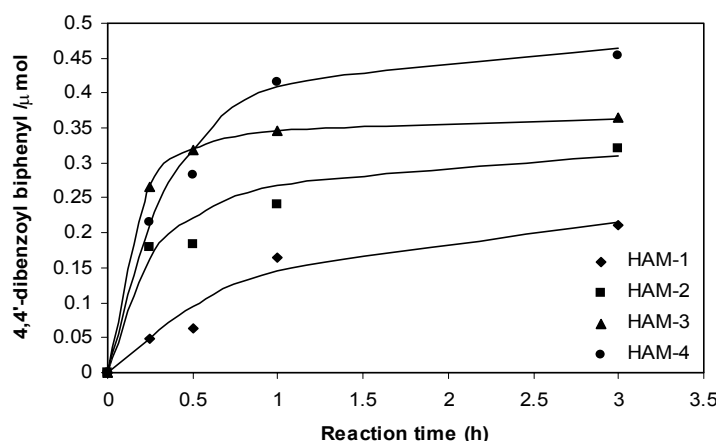


Figure 5. Effect of reaction time on the yield of 4,4'-dibenzoylbiphenyl over H-Al-MCM-41.

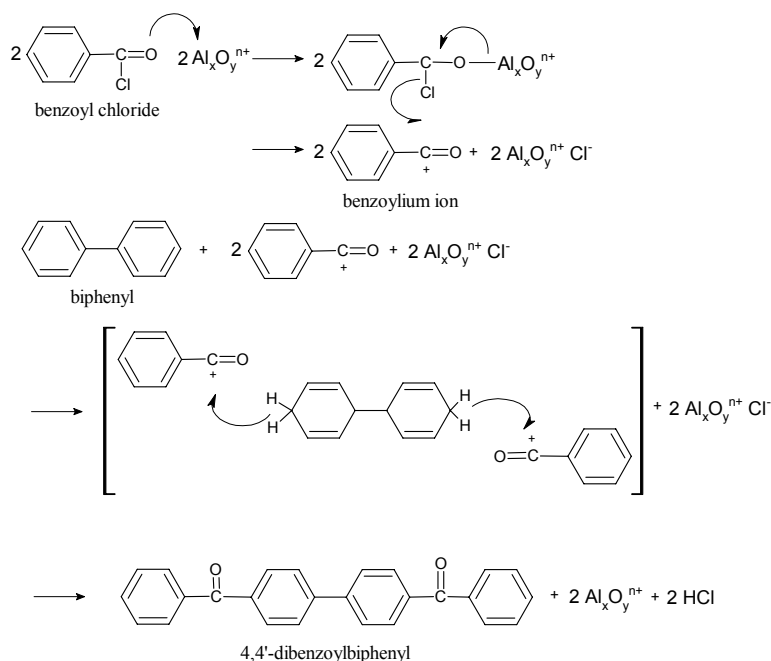


Figure 6. Proposed mechanism of the benzoylation of biphenyl with benzoyl chloride over H-Al-MCM-41.

Although the conversion calculated is very low ( $<0.05\%$ ), this is the first example of successful formation of disubstituted 4,4'-dibenzoylbiphenyl. Our study has demonstrated that Al-MCM-41 plays a role in the catalytic system and induces the production of DB, which was not achieved using homogeneous  $\text{AlCl}_3$ .

system by itself. However there is a possibility that the homogeneous  $\text{AlCl}_3$  present also contribute towards the reaction and is currently being studied. The mechanism of the formation of 4,4'-dibenzoylbiphenyl using EFAL is proposed in Figure 6; however the influence of framework Al or Brønsted acid sites in the mechanism is not yet understood.

## CONCLUSION

The production of 4,4'-dibenzoylbiphenyl catalysed by mesoporous H-Al-MCM-41 is achieved with 100% selectivity. The presence of EFAL and framework Al affect the reactivity of H-Al-MCM-41 catalyst and the yield of DB.

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