Chapter 2

Experimental and instrumental methods
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2.1. Modification of zeolite HBeta

Impregnation method [1]: Zeolite Beta in ammonia form (NH$_4$Beta) with SiO$_2$/Al$_2$O$_3$ = 38 supplied by Sud-Chem. The zeolite NH$_4$Beta was calcined at 500°C for 10 h to obtain zeolite HBeta. Metal modified Zeolite HBeta was prepared by wet impregnation using the metal precursors (Table 2.1) with various percentages. Metal precursor was dissolved in distilled water and then added to zeolite HBeta. The mixture was mixed homogenously using a magnetic stirrer. The ratio of the weight of zeolite to the volume of distilled water used to dissolve the metal salt was 1:3. After impregnation the catalyst was dried overnight at 100°C and calcined at 450°C for 6 h in the presence of static airflow before using it for the reaction. The catalysts are denoted as 5 wt% Mβ, Where M is Ni, Cu, Pb, La, Ce, Cr, Fe, W, Zn, Co, Mo, Zr and Sn. The catalysts were characterized by XRD, EDX and FTIR.

Table 2.1. Metal precursors used for impregnation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni</td>
<td>Ni(NO$_3$)$_2$.6H$_2$O [Nickel(II) nitrate hexahydrate]</td>
</tr>
<tr>
<td>2</td>
<td>Cu</td>
<td>Cu(NO$_3$)$_2$.3H$_2$O [Copper(II) nitrate trihydrate]</td>
</tr>
<tr>
<td>3</td>
<td>Pb</td>
<td>Pb(NO$_3$)$_2$ [Lead(II) nitrate]</td>
</tr>
<tr>
<td>4</td>
<td>La</td>
<td>La(NO$_3$)$_3$.6H$_2$O [Lanthanum(III) nitrate hexahydrate]</td>
</tr>
<tr>
<td>5</td>
<td>Ce</td>
<td>Ce(NO$_3$)$_3$.6H$_2$O [Cerium(III) nitrate hexahydrate]</td>
</tr>
<tr>
<td>6</td>
<td>Cr</td>
<td>Cr(NO$_3$)$_3$.9H$_2$O [Chromium(III) nitrate nonahydrate]</td>
</tr>
<tr>
<td>7</td>
<td>Fe</td>
<td>Fe(NO$_3$)$_3$.9H$_2$O [Iron(III) nitrate nonahydrate]</td>
</tr>
</tbody>
</table>
2.2. Synthesis of NaMCM-41

NaAlMCM-41 material is prepared by the procedure reported by Ortalm et al. [2]. Tetraethyloxysilicic acid (TEOS) and aluminiumisopropoxide (Al(OiPr)₃) are used as the sources of silica and alumina respectively. Cetyl trimethyl ammonium bromide (CTAB) has been employed as template. In addition, tetraethylammonium hydroxide (TEAOH, 40 wt% solution in water) and sodium hydroxide are used to maintain the basicity of the gel. The molar composition of the synthesis gel is 1.0 Al₂O₃: 31.01 SiO₂: 2.2 (surfactant)₂O: 3.16 (TEA)₂O : 1.89 Na₂O : 615-802 H₂O.

Typical procedure for the synthesis of NaAlMCM-41 (SiO₂/Al₂O₃=31.1) involved addition of 0.81 g of Al (OiPr)₃, 0.3 g of NaOH to 30 ml of distilled water and stirred thoroughly under heating at 80°C until a clear solution was obtained. The solution was cooled to room temperature followed by drop wise addition of 4.62 g of 40 wt% aqueous TEAOH. The resultant mixture was stirred for 2 h. In a separate beaker, 12.84 g of TEOS was taken and the sodiumaluminate mixture was added to it drop wise. The resultant mixture was stirred for 3 h and 12.74 g of CTAB (25 wt% in water) was added to it in small quantities. After stirring for 1 h, the pH of the resulting gel was adjusted to 12 using dilute ammonia solution and is transferred
into an autoclave. This is heated at a temperature of 100°C in static conditions for 48 h in an oven. The solid product is recovered by filtration, washed with deionized water and dried in air. All the as-synthesized samples are calcined at 550°C in the presence of static air for 12 h to remove the surfactant. The synthesis was carried out in a Parr Autoclave (600 ml capacity) and the temperature was maintained in an oven.

The calcined catalyst (NaAl-MCM-41) has been converted to H-form (HAlMCM-41) using the following procedure. The dried Na-AlMCM-41 was taken in a round bottom flask containing 10 M aqueous solution of ammonium nitrate and stirred for 24 h at 80-90°C. This procedure was repeated once again and the contents were filtered, dried and calcined at 550°C.

**Fig. 2.1.** Scheme of the autoclave: (1) A cylindrical stainless steel vessel, (2) A Teflon cylindrical beaker, (3) A flat Teflon cover for closing the Teflon beaker, (4) A flat stainless steel cover which was tightened up to part (1) by six screws.
2.3. Vapor phase reaction setup for synthesis of annelated pyridines

All the experiments were carried out in a fixed-bed Pyrex reactor (with 20 mm diameter) with a continuous down flow (Fig. 2.2). The amount of catalyst taken for every reaction was 4 g. The catalyst bed temperature was measured with a thermocouple placed in the middle of the catalyst bed. The reaction mixture was fed from the top using a syring pump (Be Braun, USA). The effluents from the reactor were cooled using ice-cold water and periodically collected at the bottom. Variation of reaction parameters like reaction temperature, feed molar ratio and W.H.S.V will be discussed in results and discussion chapter (chapter 6, section A).

![Diagram of vapor phase reaction setup](image)

**Fig. 2.2.** Vapour phase reaction setup. A-Syringe pump, B-Reactor, C-Furnace, D-Condenser, E-Collector
2.4. *In Situ* ESI-MS experiments

The *in situ* Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a quadrupole time-of-flight mass spectrometer (Q-Star XL, Applied Biosystems/MDS Sciex, Foster city, CA, USA). The typical positive ESI conditions were capillary voltage 5 kV, declustering potential 60 V and focusing potential 220 V; and negative ESI conditions were capillary voltage -4.5 kV, declustering potential -60 V, focusing potential -230 V. The instrument mass resolution was 10000 (FWHM). All the tandem mass spectrometry (MS/MS) were recorded at different collision energies (CE=10, 15 and 20) using nitrogen as the collision gas. The reaction mixture was collected at different time intervals (0, 30, 60 and 90 min) and diluted with two volumes of acetonitrile before introducing into the ESI source through flow injection (10 µl loop; methanol was used as the mobile phase at a flow rate of 30 µL/min).

2.5. *In Situ* $^{13}$C NMR experiments

$^{13}$C NMR experiments were performed on a Bruker AVANCE 500 MHz NMR spectrometer at 25°C.

2.6. Computational study

All the geometry optimization and the frequency calculations have been done using Gaussian 09 program package [5].

2.7. X-ray diffraction studies (XRD)

In the present work, metal ion modified zeolite samples and MCM-41 were recorded on a Philips X-ray diffractometer with FeKα ($\alpha = 1.935$ Å) and CuKα ($\alpha = 1.95418$ Å) as radiation sources with 2θ ranging from 2 to 60°.
2.8. FT-IR analysis

The FT-IR analysis (KBr) of metal ion modified zeolite samples, MCM-41, Nano Beta and Nano ZSM-5 were recorded on “Perkin Elmer Spectrum Gx instrument”. 5 mg of the catalyst sample was mixed with 500 mg of IR grade KBr and finely grinded in mortar and pellets were made with KBr press instrument.

2.9. Energy dispersive X-ray analysis (EDX)

The Si, Al and modified metal ion contents were analyzed by EDX instrument (Hitachi S-520) at an accumulation voltage of 10 KV with system resolution of 98 eV.

2.10. Product identification techniques

2.10.1. Gas chromatography

SHIMADZU-17A and SHIMADZU-14B Gas Chromatographs fixed with an OV-17 and 10% S.E-30 (2 m x 1/8”OD) on a chromosorb W-HP column with a flame ionization detector (FID) and N₂ as carrier gas were used for the quantitative analysis of the products.

2.10.2. \textsuperscript{1}H NMR & \textsuperscript{13}C NMR spectra

The \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra for all the products were recorded on “Varian VXR-Unity-200 MHz and 400 MHz” and “Bruker UXNMR-300 MHz” NMR instruments.

2.10.3. Mass spectra

Mass spectra were recorded on a “VG micro mass 7070H” instrument and a “Fennigan Mat 1020” mass spectrometer.

2.10.4. FT-IR analysis

The IR analysis of the products were recorded on the “Thermo Nicolet Nexus 670 spectrometer” and “Perkin Elmer Spectrum Gx instrument”.

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2.10.5. Elemental analysis (CHNS)

The elemental composition of the products was calculated through CHNS analysis using Vario EL (made by Elementar, Germany) Elemental Analyser.

2.11. References

