Australian Journal of Basic and Applied Sciences, 9(12) Special 2015, Pages: 114-121

ISSN:1991-8178

Australian Journal of Basic and Applied Sciences

Journal home page: www.ajbasweb.com

A Two-Step Process for Industrial Scale Production of Nano Heterometallic Catalysts

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ARTICLE INFO

Article history:
Received 22 February 2015
Accepted 20 March 2015
Available online 25 April 2015

Keywords:
Heterometallic Catalysts MOFs,, Thin Films, Optimization, Porosity

ABSTRACT

Background: Heterometallic crystalline particles with controlled size and morphology are widely used in many industrial applications. Different synthesis approaches are used to achieve specific crystal morphology and desired quantity of heterometallic catalysts. Among them, precipitation followed by thermal decomposition is one of the most prominent option to produce heterometallic catalysts and their nano particles even at industrial scale. **Objective:** In this work, a newly developed two-step process was employed for the synthesis of heterometallic nano particles (NPs) via Metal Organic Frameworks (MOFs). **Results:** The crystalline products were synthesized and characterized by FTIR, FeSEM, EDX and XRD. The yield of Ni, Zn and Al clusters were above 81%, 80% and 78% respectively, while the yield of Ni-Zn, Zn-Al and Ni-Zn-Al complexes were 85%, 78.5% and 77% respectively. Apart from higher yield, thin films deposited by AACVD on the stainless steel (SS) and fluorine-doped tin oxide (FTO) coated glass substrates showed high homogeneity and smooth features.
Conclusion: This study opens an avenue for the production of industrial-scale catalysts with specific size and morphology.

To Cite This Article: Mushtaq Ahmad, A.R. Abdul Aziz and Sohail Ahmed, A Two-Step Process for Industrial Scale Production of Nano Heterometallic Catalysts. ***Aust. J. Basic & Appl. Sci.,*** *9(12): 114-121, 2015*

INTRODUCTION

Heterogeneous catalysis has important role in many chemical, pharmaceutical and refinery processes. Approximately ninety percent of chemical processes utilize heterogeneous catalysts and the value created by utilizing catalysts is approximately three orders of magnitude higher than the amount invested in them(Czaja *et al*. 2009, Fechete *et al*. 2012). Moreover, morphology, size and selectivity of the catalysts are the essential considerations for almost all the industrial catalytic processes and are usually accomplished by employing polymetallic catalysts of nano porous structures (Gomez and Tigli 2013, Guo *et al*. 2013). Uniform porosity can be possible by fabricating highly ordered structures, in which channels/pores are the part of the building blocks (i.e., repetitive units). These unique structures of the polymetallic catalysts are beneficial for various industrial applications (Czaja *et al*. 2009, Morozan and Jaouen 2012, Li and Xu 2013, Montes *et al*. 2014).

Numerous methods of synthesizing heterometallic catalysts and their nano particles (NPs) have been recently reported (Patete *et al*. 2011, Dai *et al*. 2014). Polymetallic catalysts and their nano particles (NPs) can be synthesized in solution (Chae *et al*. 2010, Yin *et al*. 2012) in vapors or gas phase (Noei *et al*. 2011) in a matrix (Qian and Yang 2008, Zhang *et al*. 2012) or supported on a substrate (Tahir *et al*. 2010). All these synthesis techniques can be classified into two main categories; physical and chemical (Liu *et al*. 2014). Physical techniques are mainly based on the mechanical alloying of the materials. Both categories were also employed to synthesize nano size polymetallic NPs. Physical methods are effective to produce catalysts even at room temperature without toxic solvent or reducing agents (Ferrando *et al*. 2008). However, these methods need complicated equipments and their accessories with their huge maintenance cost. Moreover the morphology of the synthesized NPs and their narrow size distribution are not possible to control. Therefore chemical methods (e.g., thermal decomposition, chemical reduction, crystallization and electrochemical method) attracted the attention of researchers as attractive alternates (Moezzi *et al*. 2012, Guo *et al*. 2014, Hosoya *et al*. 2014). These are easy to perform and the synthesized polymetallic catalysts with desired size and morphology which are the main requirements of the NPs or their clusters to be used as catalyst (Salavati-Niasari *et al*. 2011). Each chemical method has specific advantages (Sankar *et al*. 2012). However, chemical methods

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mostly require toxic solvents and reducing agents as well as a synthesis process that is often energy and time consuming (Parveen *et al*. 2012). Moreover, adsorption of the surfactants on the active sites of the NPs is also a common problem, which reduces their effectiveness in industrial applications. In addition to these, several metallic NPs or their clusters are easily prone to oxidation (Parveen *et al*. 2012). So, compromise is made either on the quality of the crystalline material or its cost, when it is produced at industrial scale.

To overcome these problems and induced specific properties, several researchers have focused MOFs derived materials. MOFs have shown excellent potential due to their high surface areas, controllable structures and versatile electrochemical properties (Burrows 2011). In addition, these methods have significantly improved the efficiency, stability and the reusability of heterometallic catalysts for the heterogeneous processes (Yang *et al*. 2011). Significant advances in the development of MOFs for clean energy applications are also reviewed and special emphases are shown to the applications of MOFs as platforms for hydrogen production and storage, fuel cells, Li-ion rechargeable batteries and solar cells (Burrows 2011, Li and Xu 2013, Cukrowski *et al*. 2014). Present study offers preparation of bimetallic and trimetallic nano particles via thermal decomposition of MOFs. This work is the extension of our previous work (Unpublished and under review) in which Zn-Al bimetallic nano particles were synthesized using newly developed 2-step process. Influence of the independent process variables such as temperature (0C), time (hr) and stirring speed (rpm) were assessed and optimized. Results were highly engorging. A great improvement in crystal morphology and yield were achieved. In this work, addition of Ni into Zn-Al composite has been carried out using 2-Step process. In the first step, monometallic, bimetallic and trimetallic complexes of Ni, Zn and Al were prepared and characterized. 2,2'-bipyridine was used as ligand to interlink metal atoms while continuous stirring is applied to control crystal size distribution (CSD) inside the crystallizer. In the second step, AACVD method was employed to produce nano particles.

The main focus was the on the development of the process that can produce a wide range of heterometallic crystalline catalysts and their NPs with desired crystal size and enhanced porosity. Major part of the production process (precipitation) was carried out at low temperature (35-38 0C) and atmospheric pressure, without releasing toxic fumes. Therefore, the process is environmentally friendly. Moreover, synthesis process was divided into two parts to optimize time, energy and product cost. 2-proapnol and DMF were effectively used for monometallic and polymetallic systems to produce desire materials. Availability of ligand, solvents and their data were also considered here. A wide range of reliable data regarding 2,2'-bipyridine and its complexes is available (Nazir *et al*. 2011, Parveen *et al*. 2012, Cukrowski *et al*. 2014). Solvents; ethanol, 2-proapnol and DMF are also available at commercial scale. Temperature range of the major operational part (crystallization) is very low as compared to other process. All these make this an attractive process for the production of a variety of catalysts. Moreover, with the addition and employment of efficient solvent recovery system, developed process would be the more cost effective and environmentally safe. This study explores new avenues for the industrial scale production of heterometallic complexes, catalysts and special alloys for a variety of industrial applications.

Experimental Details:

Materials:

In this study, analytical grade reagents were used without further purification. Aluminium chloride, Nickel chloride hexahydrate, Zinc chloride, 2,2´-Bipyridine, N,N-Dimethylformamide (DMF), 2-Propanol and Ethanol were purchased from MERCK. The prepared bimetallic and trimetallic clusters and thin films were confirmed by characterizing them using FTIR, EDX, FeSEM and XRD.

Synthesis of [Zn(bpy)]Cl2, [Ni(bpy)]Cl2 and [Al(bpy)3]Cl3:

Stoichiometric ratios; mentioned in the standard methods (Parveen *et al*. 2012) were used to synthesize all of the mano-metallic complexes. 3.13g of ZnCl2 and 7.0g of 2,2'-bipyridine ligand were dissolved in 2-propanaol 10 mL and 100 mL separately and dropwise mixed in a round bottom lab scale crystallizer with a flow rate of 0.33 mL/min. Solution stirred for 2 hours and temperature was maintained at 36-38 oC. Fine crystals of Zn-complex were separated, washed with ether to remove impurities. The yield was 80%.

Similar environment was employed for [Ni(bpy)]Cl2 and [Al(bpy)3]Cl2. 6.4g of 2,2'-bpy ligand and 2.6g of NiCl2.H2O were used to synthesize [Ni(bpy)]Cl2 while 2.5g of AlCl3 and 8.8g of 2,2'-bpy ligand were used to synthesize Al(bpy)3Cl3.

Fine crystals of [Ni(bpy)]Cl2 and [Al(bpy)3]Cl3 were separated, washed with ether to remove impurities. The yields were 81% and 78% respectively.

Synthesis of Bimetallic Complexes:

0.8g of Zn-complex and 0.5g of Ni-complex were dissolved in 10 mL DMF solvent separately and dropwise mixed in a round bottom lab scale crystallizer with a flow rate of 0.33 mL/min. Solution stirred for one hour and temperature was maintained at 36-38 oC. Fine crystals of Zn-Ni-complex were separated, washed with ether to remove impurities.

The yield was 85%.

Similar conditions were employed for the synthesis of bimetallic complexes of the Zn-Al. For this system, 0.8g of Zn-complex and 0.5g of Al-complex were used and fine crystals of Zn-Al-complex separated, washed with ether to remove impurities. The yield was 78.5%.

Synthesis of Trimetallic Complex:

0.52g of Zn-Complex, 0.48g of Ni-Complex and 0.40g of Al-complex were dissolved in 10 mL DMF solvent separately and dropwise mixed. Solution stirred for one hour and temperature was maintained at 38oC. Fine crystals of Zn-Ni-Al-complex were separated, washed with ether to remove impurities. The yield was 77%.

Deposition of Thin Films by AACVD:

Thin films were deposited by AACVD on a stainless steel (SS) and fluorine-doped tin oxide (FTO) coated glass substrates. Substrates were washed with distilled water, ethanol and acetone. 10mg of Zn-Ni-Al-complex was dissolved in 10mL DMF solvent. The well mixed solution was poured into a round bottom flask, placed in the sonicator bath (PIFCO air humidifier) fitted with the assembly for thin film formation. SS substrate was kept first followed by FTO coated glass substrates. Small mist/aerosol produced in the solution, directed toward the furnace, kept at 400oC. Argon was passed through the aerosol mist at a flow rate of 1mL/min, to force the aerosol droplets into the reactor chamber. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. Depositions were conducted for 40 mints for the formation of thin film. After that aerosol line was closed, and furnace was allowed to cool up to 40oC before substrate and films were removed from the reaction chamber for structural studies.

Similar procedure was adopted for Zn-Al thin film on SS substrate. However, for Zn-Al bimetallic system, only SS substrate was used. Thin films of Zn-Ni-Al and Zn-Al, showing high homogeneity and smooth feature were analyzed through FeSEM, EDX and XRD. EDX analysis (Table 1.) confirms presence of Zn, Ni and Al oxides in the thin films. FeSEM and XRD results have further supported the results in term of crystallinity and nano-size.

Characterization:

The metal-bipyridine complexes were characterized using FTIR, EDX, FESEM and XRD. FTIR studies were made on Perkin Elmer instrument (model no. FTIR-Spectrum 400) and FeSEM was made on FEI QUANTA 450FEG. EDX was recorded on EDX-Oxford instrument (model no. X-Max-Assy) having accelerating voltage of 5KV. The identity of the phase and the degree of crystallinity of the crystalline materials and the deposited thin films were investigated using a PANalytical X-ray diffractometer model EMPYREAN with primary monochromatic high intensity Cu-Kα (λ =1.54060 A°) radiation. A range of 2θ (from 10.00 to 90.00) was scanned.

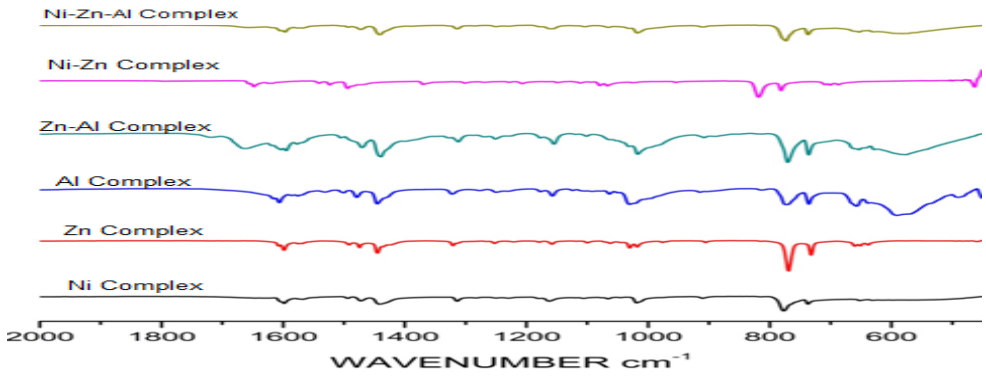

Fig. 1: IR Spectra of Monometallic and Polymetallic Complexes.

RESULTS AND DISCUSSIONS

The formation of complexes occurred due to metal-ligand bridging (---C-N-M-N-C---). The infrared spectra for [Zn(bpy)2]Cl2, [Ni(bpy)2]Cl2, [Al(bpy)3]Cl3, Ni- Zn -complex, Zn-Al-complex and Ni-Zn-Al-complex were analysed and comparison was made with free 2,2'-bipyridine spectra (NIST). A range between 2000-450 cm was given focus. Figure 1 represents several shifts and differences. For example, in free 2,2'-bipyridine stretching vibrations at 1553 and 1579 cm-1 appear for ν(C=C) and ν(C=N) respectively. In monometallic and polymetallic complexes, these vibrations appeared in the range 1561–1563 and 1592–1595 cm-1, respectively. The characteristic pyridine ring breathing frequency at 991 cm-1 is shifted by 21–29 cm-1 to higher frequencies in the complexes. Blending mode (for ring-H, out-of-plane) in the uncoordinated bipyridine, was reported at 753 cm-1, but the same was observed at 766 cm-1for [Zn(bpy)2]Cl2, 777 cm-1 for [Ni(bpy)2]Cl2, 772 cm-1 for [Al(bpy)]Cl , 771 cm forNi-Zn-complex and 774 cm forNi-Zn-Al-complex. Besides these, new

bands in the range 813–816 and 1313–1319 cm-1 were also appeared. These results reveal that the ligand is coordinated to the metal atom (Laïk *et al*. 2007).

EDX analysis of the particles showed presence of carbon, nitrogen and chlorine containing coordinated ligand. During decomposition these coordinated ligand atoms were removed from the metal complex in the presence of argon flow, which has provided inert atmosphere and also wiped out the decomposed by-products from the reaction zone. Table 1 summarizes the metals with their organic or oxides clusters.

Table 1: EDX Analysis of the Clusters and Thin Films

Catalyst Clusters	Weight composition (%)						
	Ni	Zn	Al	O	C	Cl	N
$[Ni(bpy)_2]Cl_2$	15.35	-	-	1.50	53.95	16.06	12.98
$[Zn(bpy)_2]Cl_2$		15.96		0.00	53.50	14.95	12.59
$[Al(bpy)_3]Cl_3$	-	-	4.76	2.96	62.20	17.09	12.99
Ni-Zn-complex	3.9	6.74	-	2.06	61.47	13.84	12.03
Zn-Al-complex	-	7.84	5.10	0.81	55.52	17.76	12.02
Ni-Zn-Al-complex	4.58	4.48	3.69	4.65	57.48	15.46	9.69
Zn-Al (Thin Film on SS)	-	68.00	3.00	31.60	-	-	-
Zn-Ni-Al (Thin Film on SS)	1.50	76.33	7.26	14.96	-	-	-
Zn-Ni-Al (Thin Film on FTO Glass)	11.1	3.7	0.10	20.4	-	-	-

The morphology of the bimetallic and trimetallic clusters was investigated using FESEM. Samples were collected from their magma solutions, dried and then analyzed without dispersion of the crystalline particles. Figure 2 and Figure 3 illustrate the understandable features of these complexes. The particles in polymetallic clusters (Figure 3) have better defined boundaries as compared to monometallic cluster (Figure 2). In all clusters, particles have shown tendency of sintering together to make linked microporous structures. Figure 4 shows the Zn-Al thin film grown on both SS substrate by AACVD. The FeSEM results reveal that grown particles are mesoporous nano balls.

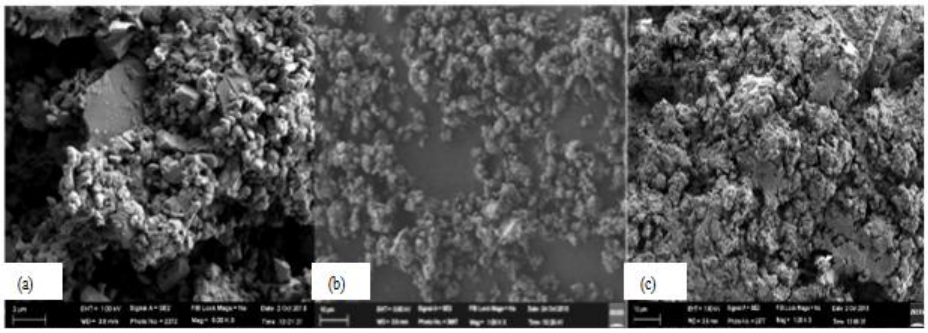

Fig. 2: Ni (a), Zn (b) and Al (c) Monometallic Complexes.

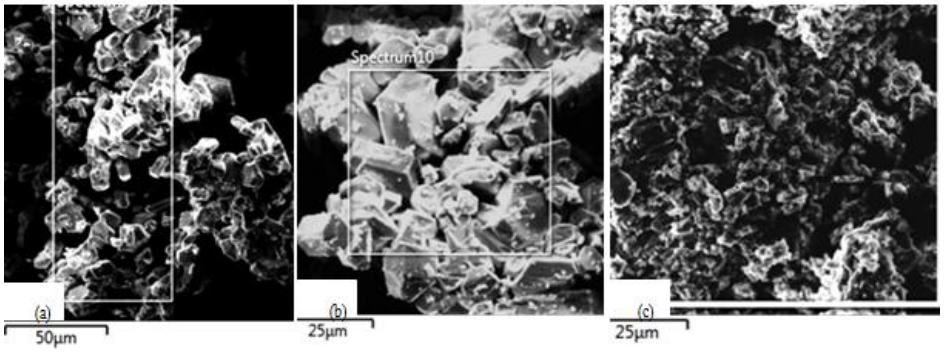

Fig. 3: Zn-Ni (a), Zn-Al (b) and Zn- Ni-Al (c) Heterometallic Complexes.

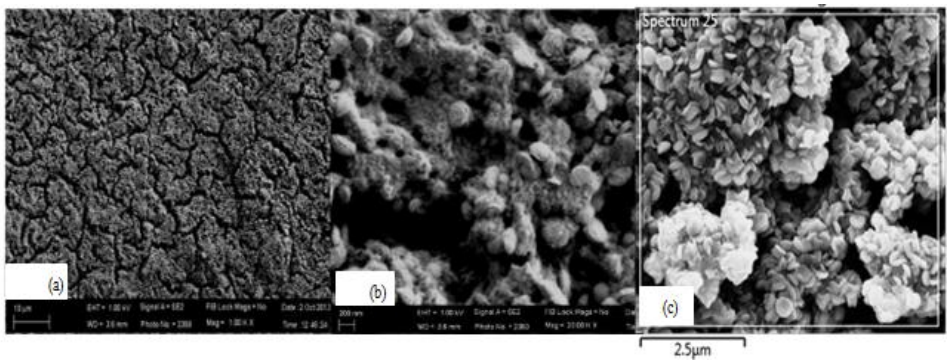

Fig. 4: FeSEM Images (a & b) and Electron Image (c) of Zn-Al Thin Film Supported On SS Substrate.

For trimetallic films, deposition pattern of the nano particles of the metal atom on SS substrate was slightly different as compared with FTO substrate (Figure 5 and Figure 6). Addition of Ni atoms caused the growth of needle like crystals instead of nano balls. However, material of construction and location of the substrate also affected the particle size and quality of the crystalline material. In this case, Zn-deposition was noted more on the SS substrate (placed first), followed by FTO glass substrate, while the deposition of Ni was increased at FTO glass substrate. Average particle size of the SS- substrate based film was also greater than other

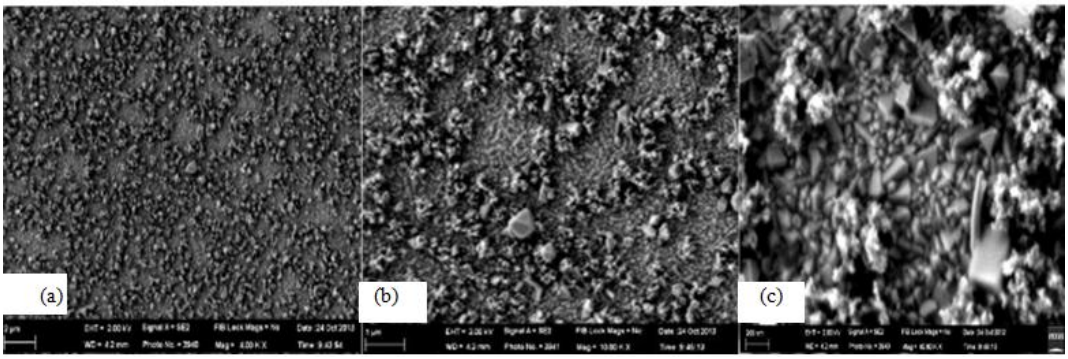

Fig. 5: Zn-Ni-Al Thin Film Supported On FTO Glass Substrate.

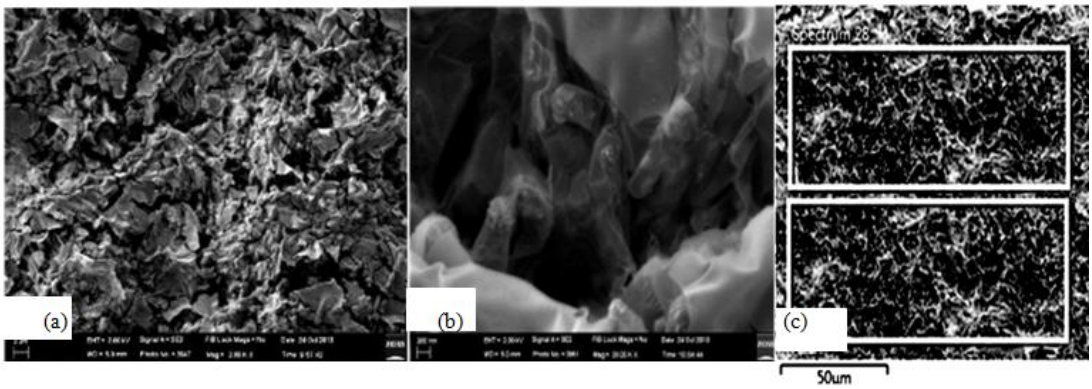

Fig. 6: Zn-Ni-Al Thin Film on SS Substrate.

The identity of the phase and the degree of crystallinity of the crystalline materials and the deposited thin films were examined by scanning a range of 2θ from 10.00 to 90.00. Figure 7 shows the XRD patterns of the [Ni(bpy)2]Cl2, [Zn(bpy)2]Cl2, [Al (bpy)3]Cl3, Ni-Al-complex and Ni-Zn-Al-complex. No clear evidence of the presence of metal (Ni, Al and Zn) salts can be observed, this is due to both the fact that reactants have completely reacted with ligand to form the complex phase and that the unreacted quantities are very small as to be detected by XRD (Buitrago-Sierra *et al*. 2012).

Figure 8 shows the XRD patterns of thin films, deposited on SS and FTO glass substrate. For bimetallic system, the presence of spinel phase Al2O9Zn6 (Ref. Code 00-051-0037), characterized

by three intense peaks at 2 = 32.15, 34.38 and 36.63 and other less intense peaks at higher 2 values, is clearly evidenced. These peaks increase in intensity with increasing the ZnO (Ref. Code 01-079-0207) loading (Buitrago-Sierra *et al*. 2012). The broadness of the peaks indicates a small crystal size of the spinel phase.

For trimetallic system, presence of Al2Ni0.4O4Zn0.6 (Ref. Code 01-080-1685) characterized by two intense peaks at 2 = 31.30, 36.90 and other less intense peaks at higher 2 values, is clearly evidenced. The presence of the Ni0.8OZn 0.2 (Ref. Code 01-075-0271), characterized by two intense peaks at 2 =37.28, 43.30 and other less intense peaks at higher 2 is also detected. It may be due to the insufficient amount of Al atoms required to produce Al2Ni0.4O4Zn0.6. The XRD results confirmed that particles in all the samples were highly crystalline. The broadness of the XRD peaks was used to calculate the average crystalline size using the Debye–Scherrer equation. The results showed that the particles in all the tested samples were nano sized with size between 112.8 and 105 nm (Zhang *et al*. 2012). However, in FeSEM study, cluster's morphology and porosity were given the main focus. Moreover, oxygen content can be minimized by employment of the inert atmosphere; passing argon gas during crystallization, deposition and cooling the thin films.

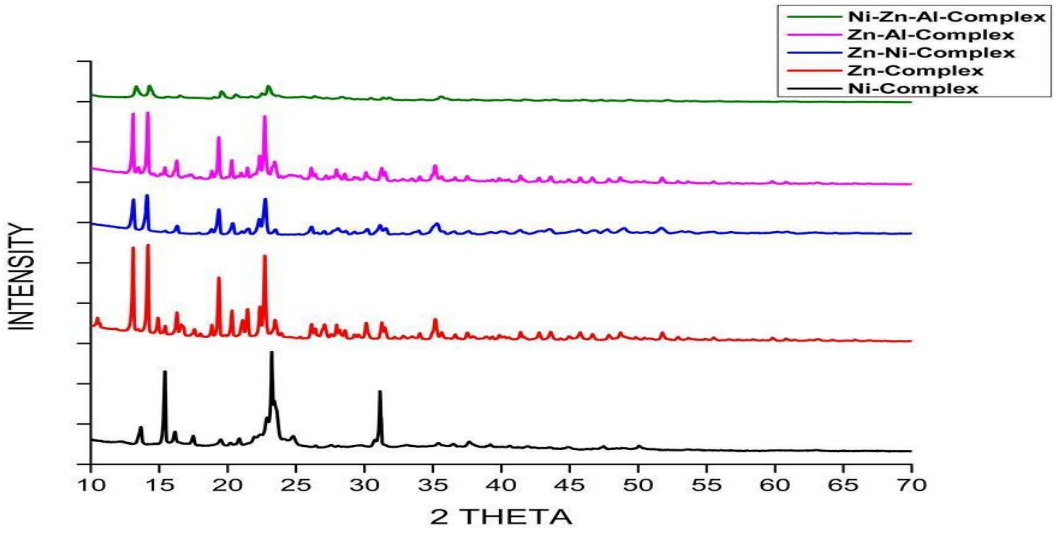

Fig. 7: XRD Patterns of Monometallic and Heterometallic Complexes.

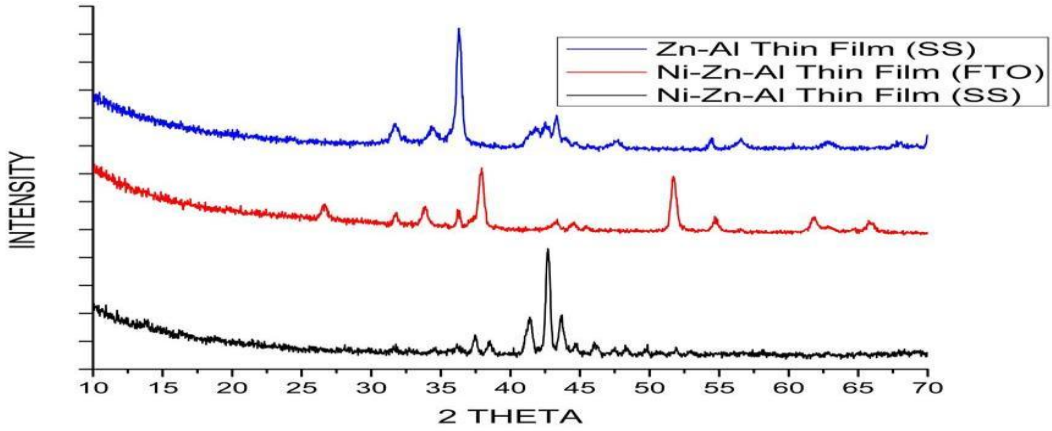

Fig. 8: XRD Patterns of Thin Films.

In addition to better crystal morphology, narrow crystal size distribution; yield of the synthesized materials was remarkable. Figure 9 illustrates the percent yield of the crystalline material produced by the proposed process. Ni and Zn clusters have shown better yield (above 80%), while Al-cluster was the least in production (77%).

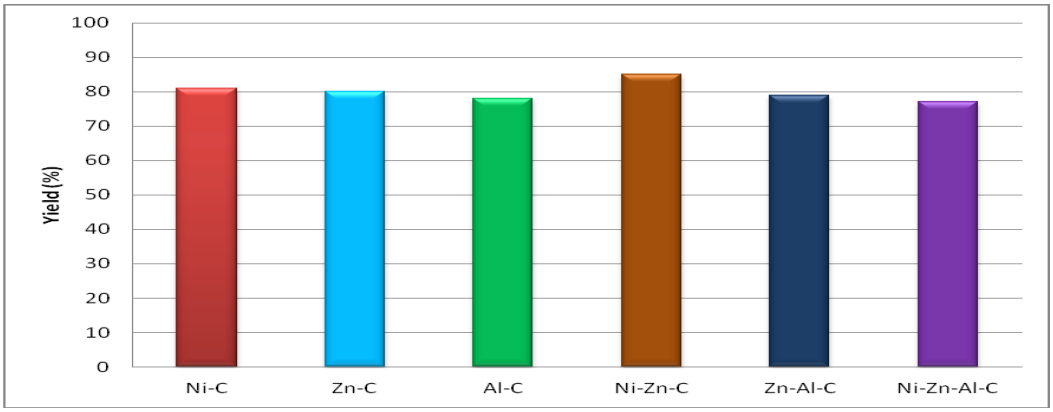

Fig. 9: Yield of the Crystalline Materials.

It might be due to the loss of ultra fine particles during filtration stage. With efficient filtration systems, yield can be increased up to 85-90%. From the results it is clear that 2-Step process has shown excellent potential for the production of a wide range of industrial catalysts and composite materials

Conclusions:

A 2-step process was used for the synthesis of heterometallic MOFs and their thermal decomposition to form nano sized clusters. In the first stage, precipitation process was effectively employed to produce monometallic and polymetallic complexes. 2,2'-bipyridine was used as the ligand to interlink metal atoms (Ni, Zn and Al). In the second stage, heterometallic complexes were thermally decomposed to produce nano clusters. The crystalline products were characterized by FTIR, FeSEM, EDX and XRD. The developed process was found to greatly improve the size, morphology and porosity of the crystalline materials.

The yield of Ni, Zn and Al clusters were above 81%, 80% and 78% respectively, while the yield of Ni-Zn, Zn-Al and Ni-Zn-Al complexes were 85%, 78.5% and 77% respectively. Addition of Ni metal-atoms to Zn-Al composites changed the size and morphology of the crystalline particles. Thermal decomposition of Zn-Al complex produced mesoporous nano balls. However, Zn-Ni-Al complex caused formation of needle like crystals.

The synthesized materials can be used in a variety of industrial applications. In addition, availability of ligand (2,2'-bipyridine), solvents (ethanol, 2-proapnol and DMF) and their relevant information in the literature make this 2-step process an attractive process for the production of a variety of catalysts and special alloys.

ACKNOWLEDGEMENTS

This research is supported by a Post- graduate Research Fund (PPP) with project number PG115-2012B from the University of Malaya.

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