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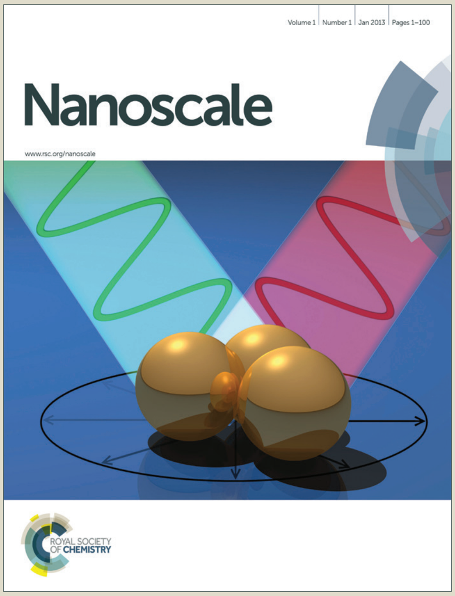

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ARTICLE TYPE

Nano particles of $ZrPO_4$ for green catalytic applications†

Peta Sreenivasulu,[a,b] Chandrasekhar Pendem[b] and Nagabhatla Viswanadham[a,b†]

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Here we report the successful room temperature synthesis of zirconiumphosphate nano particles (ZPNP) using P123 tri co-block polymer for the first time. The samples are characterized by SEM, TEM, XRD, TPD, BET and were employed for the fixation of CO_2 on aniline to produce pharmaceutically important acetanilide, at mild reaction conditions (150° C and 150 Psi CO_2 pressure)

1.Introduction

In recent years development of new compounds and the reproducible preparation of known materials with specific physico-chemical properties is of increasing importance. The main role of a material chemist is to identify the suitable synthesis conditions to obtain the product with the desired composition, structure and properties. In material synthesis, easy, mild, rapid and preferably clean synthetic routes are in demand for the expansion of their applications.

Metal phosphates are important class of inorganic materials, where the amorphous and crystalline forms of the materials have been successfully synthesized and recognized as valuable catalyst materials.[1,2] Aluminum phosphates (AP) and zirconium phosphates (ZP) have attracted enormous interest for their potential applications in many fields.[3-5] The advent of nano size particles provided more insight into the subject of achieving superior catalytic performance by virtue of their properties such as higher surface area, easy-to-access active sites and the ease in separation from the product compared to homogenous catalysts. Recently, much attention has been focused on the development of new preparation methods to produce AP and ZP nano compounds of various morphologies such as nanoparticles,[6] nanoplates [7] and nanocomposites.[8-10] Polymer based precursor methods are generally used for the synthesis of variety of these nanoparticles.[8-14] The lack of ionic nature in the polymers can be overruled by applying the tri block copolymers such as PEO-PPO-PEO (commercial name of Pluronics) that possess both hydrophilic (PEO block moiety) and hydrophobic (PPO block moiety) nature required for effective templating functionality.[15] In aqueous solution, the co-polymer molecules self-assemble to form micelles of various forms and size depending on thermodynamic parameters (entropy or enthalpy driven). Here, the hydrophilic moieties (PEO) form the corona with the surrounding hydrophilic reactant sites, while the hydrophobic blocks (PPO) form the core of the micellar aggregates. However, the tailored synthesis of the nano particles of AP/ZP and their applications to industrially important reactions is still in explorative stage that demands simple and effective synthesis methods to develop catalysts for challenging reactions.

Carbon capture and conversion (CCC) is one of the green and challenging processes that is being attempted recently.[16] The carbon dioxide is thermodynamically stable, being the highest oxidized form of carbon. The CO_2 is either completely reduced to produce hydrocarbons or it is partially reduced to create functional groups such as C=O in the chemical structure.[16-18] The utilization of greenhouse gas CO_2 for the production of industrially important chemicals is of prime importance in energy and environmental catalysis. The catalyst material should possess very special properties such as adsorption and chemical conversion of CO_2 for this purpose. Very little work is done in this direction and recently some attempts have been made in applying nano materials for CO_2 incorporation in the chemical structures. [19-23] However, the catalyst development is still challenging to improve conversion and product selectivity. Acetanilide is the carbonyl derivative of aniline which is important raw material used in drug synthesis. N-acylation of aniline is generally adopted for the production of this molecule. [24, 25] The existing processes involve the use of stoichiometric amounts of activating agents, toxic and corrosive acid chlorides/acetic anhydride, and other coupling reagents which require expensive removal and disposal steps at the end of the reaction. This results in increase of environmental factor (E factor) with decreasing atom efficiency of these processes. [25, 26] Therefore, developing a method which uses fewer catalytic reagents and obviates the need to isolate intermediates would be very desirable for process development. World-leading pharmaceutical companies are looking for efficient catalysts and the development of a general, catalytic, environmentally friendly and scalable synthesis of amides remains elusive.[27] Hence, the introduction of carbonyl group into aniline through CO_2 fixation is a novel route for the utilization of greenhouse gas on one hand and production of pharmaceutically important acetanilide on the other.

Here we report the successful synthesis of ZP and AP nano materials using P123 tri co-block polymer for the first time just at room temperature. So far, no studies have reported on the synthesis of these materials using P123 co block polymer. The materials exhibited excellent CO_2 fixation activity towards the formation of acetanilide directly from aniline using carbonyl functionality from CO_2 and methyl group from methanol at ambient reaction conditions of 150 °C and 150 Psi pressure. The present study is first of its kind to fix CO_2 catalytically for the

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* [a]*AcSIR-Indian Institute of Petroleum Dehradun, India.*
[b]*Catalysis and Conversion Processes Division, Indian Institute of Petroleum, Council of Scientific and Industrial Research, Dehradun-248005, India, Fax: 91-135-2525702, Tel: 91-135-2525856, E-mail: nvish@iip.res.in*

†Electronic supplementary information (ESI) available: Experimental details, wide angle XRD, EDX, IR spectra, GC data etc

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production of acetanilide. It is also first time to reveal the new property of the ZP/AP nano materials to catalyze such reactions and has scope in expansion of their applications. Though the nano particle supported catalysts have been reported for the fixation of CO_2 to produce value added chemicals, most of the studies used metal nano particle supported on oxide supports. The additional advantage of the present method involves in adopting single-step synthesis of AP/ZP nano particles without using any metal-support combination. This is expected to give more stability in activity of the catalyst as the leaching problems associated with metal supported catalysts have been over ruled by these systems.

2. Experimental section

2.1. Materials

Aluminumtri-isopropoxide $[Al(O^iPr)_3]$, Zirconiumacetyl acetonate, ammoniumdihydrogen- phosphate $[NH_4H_2PO_4]$, P123 tri-block copolymer, methanol [CH3OH] and hydrochloric acid [HCl].

2.2. Synthesis of aluminophosphate (AP) and zirconium phosphate (ZP) nanoparticles

The typical synthesis method involves the admixing of 6.102 g of P123 tri-block copolymer, 2.12 g of HCl, 12.21 g of ammoniumdihydrogen- phosphate and 75 g of methanol and treatment of the resultant mixture at 60 °C for 2 hr followed by vigorous stirring of the mixture to obtain the clear solution (solution A). Similarly 28.26 g of zirconium acetylacetonate and 75 g of methanol are mixed and stirred at 45 ºC to obtain another clear solution (solution B). Solution ‘A’ is added to solution ‘B’ in a bit-wise-manner with a continuous stirring for 30 min, during which a milk-like solution was formed from the clear solution of precursors. At this stage, the stirring was stopped and the solution was left for 24 h to settle. The solid material obtained from the solution was washed, collected by filtration, dried and calcined at 500 ºC for 5 hr. Similar procedure is followed for the synthesis of aluminumphosphate with the only difference being the use of aluminumisopropoxide in place of zirconium acetylacetonate. The resultant materials are denoted as ZP (zirconium phosphate) and AP (aluminumphosphate) samples.

2.3. Characterization

Powder X-ray diffraction patterns of the samples were recorded on D8 advance instrument, Bruker, Germany equipped with rotating anode and CuKα radiations. FE-SEM images were recorded on Quanta 200f instrument, Netherland, for obtaining particle morphology.TEM images were recorded on Tecnai-12 model, FEI, Netherland.

2.4 Application of materials for the CO_2 fixation on aniline

The catalyst performance studies of the materials were conducted towards the production of acetanilide from aniline using the green house gas CO_2 as carbonyl source. In a typical reaction procedure, 1 gm of catalyst was added to the reaction mixture of 10 gm of aniline, 2 gm of methanol and 8 gm acetonitrile. The whole mixture was transferred into a 160 ml volume capacity Parr reactor autoclave, sealed tightly and pressurized by CO_2 to 150 Psi. The reaction was conducted at 150 °C for 7 h and the product obtained at the end of the run was filtered and analyzed by GC equipped with an EQUITY column and flame ionization detector (FID). The product is identified by using GC-Mass**.**

3. Results and Discussion

3.1. Properties of Aluminophosphate (AP) and Zirconium phosphate (ZP) nanoparticles

The elemental composition of synthesized AP and ZP samples has been analyzed by EDX analysis, where, the presence of Al, P and O in the AP sample and Zr, P and O in the ZP sample has been identified (ESI Fig.S1). The morphology of the AP/ZP samples was characterized by SEM and TEM. The SEM images of both these samples demonstrated the presence of nano meter range particles (Fig 1). This is further confirmed from the TEM, where both the samples exhibited spherical morphology of nano particles of about ~50 nm size (Fig 1). The nano particles of AP and ZP are denoted as APNP (aluminumphosphate nano particles) and ZPNP (zirconium phosphate nano particles) respectively.

The wide angle XRD patterns suggested the amorphous nature of these materials (ESI Fig.S2). No individual crystalline peak of zirconium phosphate and zirconia was observed in the ZPNP sample calcined at 500 ºC. The ICP results of samples indicated that the ratio of M/P (M= Al or Zr) in these samples is comparable (ESI Table 1). The BET surface area of APNP and

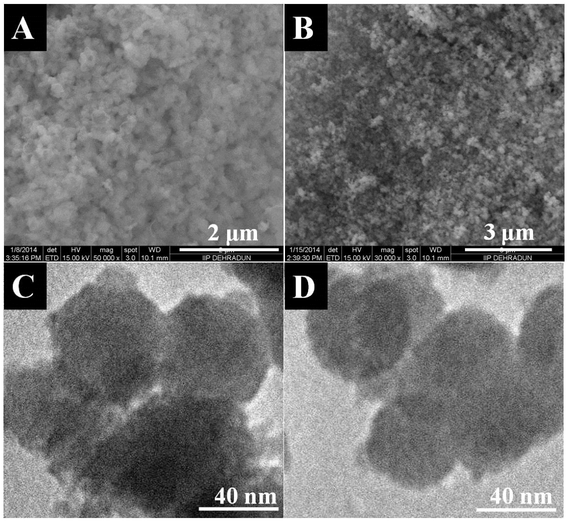

Fig.1. A and B are SEM images and C and D are TEM images of the APNP and ZPNP samples respectively.

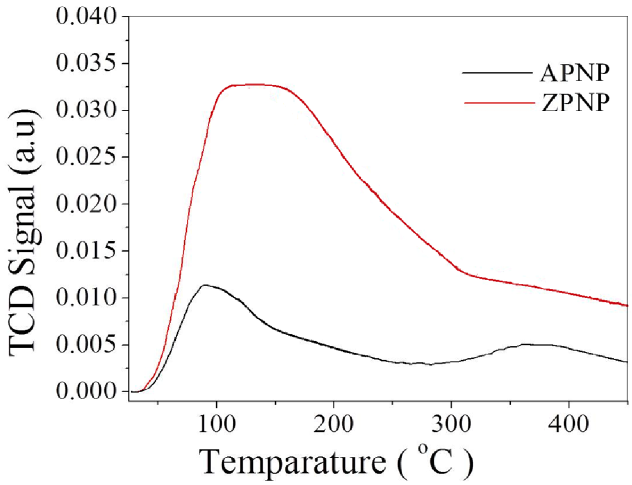

Fig.2. NH_3-TPD spectra of the samples

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ZPNP were 44 and 36 m^2/g, receptively. Both the samples exhibited acidic properties measured by NH_3-TPD (Fig.2). However, the acidity of ZPNP sample is much higher than that of the corresponding APNP sample. This may due to the relatively large difference in ionic charge of Zr and P in this sample (when compared to that of Al and P).

3.2. Synthesis of Acetanilide and Optimization of reaction conditions

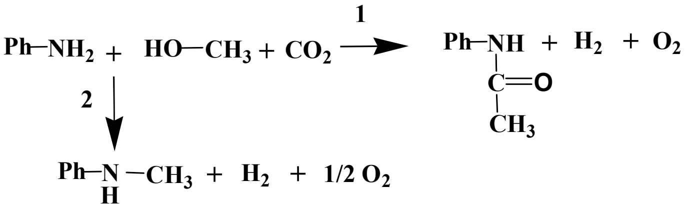
The APNP and ZPNP materials synthesized in the present study have been explored for the fixation of CO_2 into aniline molecule for the production of acetanilide. The influence of the temperature, CO_2 pressure and reaction time was studied. By varying the reaction temperature from 75 °C to 150 °C, a gradual improvement in conversion of aniline (3.1 to 6.0 %) and selectivity of acetanilide (51 to 67%) is observed for the APNP sample (Table 1 entries 1 to 3). The ZPNP sample also exhibited similar trend of increasing conversion of aniline (9.2 to 13.0 %) and selectivity of acetanilide (69 to 85%) at constant CO_2 pressure of 150 Psi (Table 1 entries 8 to 10). However, further increase in reaction temperature (175°C) did not cause any accountable effect on the conversion and selectivity values on both the catalysts (Table1, entries 4 for APNP and 11 for ZPNP). The CO_2 pressure also had a significant influence on the conversion of aniline and selectivity of acetanilide for the both samples. With increasing the CO_2 pressure from 75 to 150 Psi, the aniline conversion and acetanilide selectivity are gradually increased from 2.9 to 6.0% and 50 to 67% respectively for APNP. The ZPNP also exhibited the similar trends of increase in conversion (10.5 to 13%) and acetanilide selectivity (71 to 85%) (Table 1, entries 5, 6, 3 for APNP and 12,13,10 for ZPNP samples) at constant reaction temperature of 150 °C. However, further increase of the CO_2 pressure (175 Psi) did not show any accountable effect on the performances of the catalysts (Table 1, entries 7 for APNP and 14 for ZPNP samples). On both the catalysts, the maximum aniline and acetanilide selectivity was observed at the 7 h reaction time (Table 1, entries 3, 10). The values are increased up to 7 h reaction time and above this reaction time, there is no further increase is observed up to the studied period of 12 h (Table1, entries 18, 19). Overall, the highest aniline conversion of 13% with maximum acetanilide selectivity of 85% was observed at 150 °C, 150 Psi at 7 h reaction time (Table 1, entry 10).

Though the conversions of aniline are limited to 6% and 13% on APNP and ZPNP catalysts (Table 1), the novel property of CO_2 fixation of the catalysts attracts attention from fundamental and industrial research areas. Usually, the reactive absorption of

Table 2: ZPNP catalyst performance on different reaction cycle

Cycles	Aniline Conversion (%)	Products Selectivity (%)	
		N-Methyl Aniline	Acetanilide
1	13.0	15	85
2	13.2	16	84
3	12.0	18	82
4	12.8	21	79
5	12.5	20	80

Temperature= 150 °C, CO_2 Pressure= 150 Psi, Time= 7 hr, Aniline= 10 g, CH3CN=8 g, and Methanol= 2 g



Scheme 1: Schematic presentation of plausible reaction.

Table: 1 Performance of catalysts in CO_2 fixation on aniline

Entry	Catalyst	Temperature (°C)	Time (hr)	Pressure (Psi)	Aniline conversion (%)	Product selectivity (%)	
						N-Methyl aniline	Acetanilide
1	APNP	75	7	150	3.1	49	51
2		125	7	150	4.6	45	55
3		150	7	150	6.0	33	67
4		175	7	150	5.6	36	64
5		150	7	75	2.9	50	50
6		150	7	125	4.7	41	59
7		150	7	175	5.8	34	66
8	ZPNP	75	7	150	9.2	31	69
9		125	7	150	11.2	24	76
10		150	7	150	13.0	15	85
11		175	7	150	12.8	18	82
12		150	7	75	10.5	29	71
13		150	7	125	11.8	22	78
14		150	7	175	12.2	19	81
15		150	1	150	4.5	38	62
16		150	3	150	7.3	35	65
17		150	5	150	10.1	28	72
18		150	9	150	13.0	16	84
19		150	12	150	12.9	15	85
20		150	12	----	1.2	100	0

CH_3CN = 8 g, Aniline = 10 g, Methanol = 2 g, and Catalyst = 1 g.

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acid gases with aqueous amines has been very important in gas purification processes. The most common absorbents used for reactive absorption of CO_2 are aqueous solutions of amines and amine blends. Aqueous solutions of alkanolamines have been widely used in gas purification processes for the removal of acid gases such as CO_2, hydrogen sulfide, carbonyl sulfide, etc.[28-30] The kinetic studies on reactive absorption of CO_2 with aniline in non-aqueous aprotic solvents, namely, acetonitrile, methyl ethyl ketone , toluene and *m*-xylene indicated the vital role of solvents on this reaction.[31] The acetanilide production ability of the present APNP/ZPNP catalyst systems clearly indicates the adsorption and fixation properties of these materials towards CO_2 that eventually reacts with aniline to produce acetanilide in presence of methanol.

The APNP sample exhibited lower aniline conversion of around 6 % with 67% selectivity to acetanilide (Table 1), while the conversion is increased to 13% in case of ZPNP sample. This may be due to the higher acidity and resultant strong adsorption of aniline on the ZPNP sample. This also resulted in the enhanced acetanilide selectivity (85%) on ZPNP when compared to the APNP sample (67%). However, both the catalysts (APNP and ZPNP) exhibited a common phenomenon towards effective conversion of aniline and fixation of C=O functional group from CO_2 into the aniline molecule for the production of acetanilide with good selectivity and reusability. This is further confirmed by a supporting experiment conducted in the absence of CO_2, where there is no formation of acetanilide occurred at similar reaction conditions that confirms the contribution of C=O functional group by CO_2 to the formation of acetanilide (table 2, entry 20). To the best of our knowledge, this is the first of its kind to report the CO_2 fixation activity of the APNP/ZPNP materials for the production of acetanilide. A reference experiment was also conducted in the absence of the catalyst, using CO_2, methanol and aniline, where no reaction was observed to proceed, which confirms the catalytic role of APNP/ZPNP materials. Further, the catalyst material shows its reusability with an excellent catalytic performance even after five reaction cycles (Table 2).

We have also conducted a series of experiments to understand the reaction patyways for the formation of acetanilide on both the catalysts. We have not observed any water formation, but considerable amount of oxygen and hydrogen are appeared in the gas product. It known that acetonitrile forms acetamide in presence of water. [32] The absence of acetamide in the product of the present study clearly rule out the formation of water as byproduct at the present reaction conditions. Further, the reaction was also conducted using toluene / m-xylene as solvents so as to check any contribution of acetonitrile solvent towards the contribution of carbonyl group to the acetanilide. The catalyst exhibited comparable conversions and product selectivitivites (ESI table 2) irrespective to the nature of solvent, that confirms the contribution of CO_2 as the source for carbonyl group in acetanilide. Based on the formation of hydrogen and oxygen in the product, we have proposed the following reaction scheme (Scheme 1) for the formation of acetanilide (Equation 1) and N-methyl aniline (Equation 2). Here acetanilide is supposed to be formed from the reaction of all three reactants, namely, aniline, methanol and CO_2, while the N-methyl aniline is produced from the reaction between aniline and methanol. The former reaction involves the CO_2 fixation while the later does not. In the absence of CO_2, the only product obtained was methyl aniline (entry 20, table 2) that further supports the proposed mechanism (Equation 2). In the presence of catalyst and CO_2, the higher selectivity of acetanilide obtained in the product thus supports that the CO_2 fixation reaction is major (Equation 1) to produce acetanilide and confirms the effective role of catalysts towards the CO_2 fixation reaction.

4. Conclusions

In summary, the present study provides a simple and novel method for the synthesis of an aluminophosphate and zirconiumphosphates nano materials using P123 tri-coblock polymer as organic template, for the first time. The material exhibited promising aniline conversion for the efficient production of acetanilide using green house gas CO_2 as carbonyl source. The process provides a green alternative process to exclude the use of otherwise common harmful reagents such as acid chlorides /acetic anhydride for the acetanilide production. The subject opens up a new property of the metal phosphates as suitable catalysts for selective fixation of CO_2 reactions and has scope in improvement of the catalytic activity through the optimization of the synthesis procedure of metal phosphates for expansion of its applications to other selective fixation of CO_2 reaction.

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