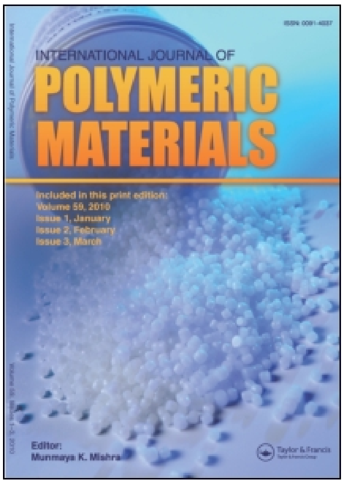

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Ceria-Supported Vinylpyridine Polymers: Synthesis, Characterization and Application in Catalysis

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A simple, one-step synthesis of 4-vinylpyridine polymer crosslinked with 2% divinylbenzene [poly(4vp-dvb)] anchored with ceria nanocrystals via in situ reactions that involve simultaneous formation of the polymer and ceria nanocrystals is presented. The polymer support is formed by free radical suspension polymerization of the monomers, while ceria nanocrystals are generated from $CeCl_3 \cdot 7H_2O$ *by the homogeneous precipitation method in a single pot. The polymer supports were characterized by XRD, TEM, SEM, ESCA, and TGA and then tested for their ability as heterogeneous recyclable catalysts in a Biginelli reaction. The catalytic activities of these supports were found to be far superior to the two-step conventional one and simultaneous microporous bead counterparts. Reusability is an added advantage over the other regularly used cerium-based catalysts in aqueous media. The significant increase in the catalytic activity is due to the higher Ce/N ratio and predominance of well-defined and more reactive exposed planes of ceria nanocrystals on the new supports. Such catalysts are of great importance due to environmental, practical and economical concerns.*

Keywords: ceria nanocrystals, heterogeneous catalysis, vinylpyridine polymers

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INTRODUCTION

Synthesis and characterization of nanosized metal–polymer composites have been particularly gaining importance due to their potential applications as biomedical, electronic, and optical devices and as heterogeneous green catalysts [1], in particular due to the modern organic synthesis scenario. The intrinsic advantages of such green catalysts lie in reactions that are often very clean, high-yielding and involve simpler product isolation and reusability. Metal nanoparticles when supported on polymers remain homogeneously dispersed and avoid agglomeration that otherwise occurs due to high surface energy of the particles. Thus, there is a large potential for the development and application of metal nanoparticles with tailored physical and chemical properties in both materials science and catalysis.

Cerium oxide-based catalysts are widely used as effective oxidation systems due to their unique properies such as redox, oxygen release and storage abilities. They are reported to have enhanced catalytic activity when immobilized on suitable substrates [2,3]. Vinylpyridine polymers are reported to immobilize metal nanoparticles through the tertiary nitrogen. These polymers were found to be suitable for catalytic applications mainly due to their good thermal and chemical stabilities [4–6].

During the fabrication of metal nanoparticles on polymer supports, the main focus is on the control of their size, shape, extent of dispersion, percentage of immobilized metal content and the type of interaction between the metal and the support. These properties and the method of preparation play an important role in the behavior of these catalysts. Generally, such polymer supports are synthesized in two or three steps wherein the polymer and metal particles are prepared separately, followed by mechanical mixing or generating the metal/metal oxide particles in situ on the polymer by vapor deposition, chemical reduction/oxidation, and radiolytic or photolytic methods [7,8]. We have also reported a two-step process for the preparation of the poly(4vp-co-dvb)/ceria nanocomposite by the wet chemical method [9]. The main drawback of such methods is lack of homogeneous distribution of the particles in the polymer matrix and long processing times. Therefore, there is a need for finding novel methods to synthesize nanocomposites, overcoming the drawbacks and also simplifying lengthy processes to a one-step reaction. The most popular among them were radiolytic and photolytic methods where simultaneous formation of polymer and metal nanoparticles take place [10,11]. However, reports using chemical methods for

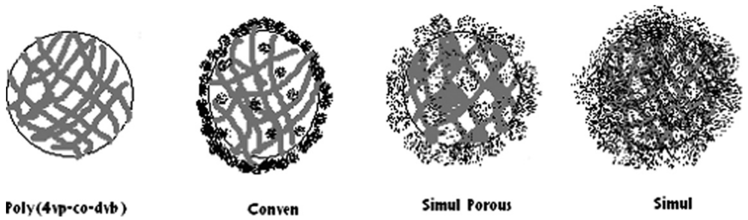

FIGURE 1 Schematic representation of a) poly(4vp-co-dvb) and different forms of CeO_2@Poly(4vp-co-dvb), b) **conven**, c) **simul porous**, and d) **simul**.

one-step reactions have been limited. Nakao [12] reported the preparation of bulk solid solutions of noble metals in poly methylmethacrylate (PMMA). But, the procedure is limited to only those metals that are soluble in monomers or monomer solutions.

In this article, the symbol @ will stand for the words “embedded in.”

Here, we report a simple one step synthesis of CeO_2@Poly(4vp-dvb) supports where polymer and metal oxide nanocrystals are formed simultaneously resulting in a nanocomposite (**simul**) (see Figure 1). The free radical suspension polymerization of monomer and oxidation of the metal source take place in an aqueous medium [13]. The composites were found to have not only near monodisperse and homogeneously well-dispersed metal nanocrystals, but also had increased content of the metal particles in comparison to the microporous nanocomposite beads (**simul beads**) and the conventionally (**conven**) prepared counterparts. The resulting heterogeneous catalysts were then used in three component condensation reactions, such as Biginelli reaction, in an aqueous medium. A comparatively enhanced catalytic performance of the new method over the others has been reported.

EXPERIMENTAL

Materials

4-vinylpyridine (4VP), divinylbenzene (DVB), t-amylperoxy-2-ethylhexane carbonate (Luperox 101) and 2,5-bis(tert-butylperoxy)-2,5–dimethylhexane (Lupersol TAEC) were purchased from Aldrich Chemicals, USA. Polyvinylpyrrolidone (K-30) (PVP), cerium trichloride heptahydrate ($CeCl_37H_2O$), sodium hydroxide (NaOH), cyclohexane, cyclohexanone and reagent grade methanol were procured from SD Fine Chemicals, India. 4VP was purified by distillation under vacuum prior to use while the others were used as obtained without further purification.

Instrumentation

The size and morphology of nanosized ceria particles supported on the polymer were investigated by scanning electron microscope (SEM) and XRD analysis, and the size of metal particles was measured by transmission electron microscope (TEM). A broad absorbance band for the composites covering the band for pyridine ring of the pure copolymer at 230 nm and ceria nanoparticles at 365 nm was observed in UV-VIS spectroscopy. Identification of the free N1s peak from the copolymer and the metal coordinated nitrogen peak of the nanocomposities and the oxidation state of cerium was done using XPS. TEM observation was conducted on a Technai-12 (model) instrument and observed at an acceleration voltage of 100 KV. To obtain the microscopic images of cerium oxide nanoparticles, a drop of the dilute dispersion was deposited by slow evaporation on a copper grid covered with a formal carbon membrane. SEM studies were performed on Hitachi 5S 520 scanning electron microscope under high vacuum, 0.1 torr and high voltage of 1.2 kV, by mounting the gold-coated samples on aluminium stubs with double-sided adhesive tape. XRD analysis was done on a Rigaku Dmax – γ_A X-ray diffractometer using Cu-K_α radiation ($\lambda = 1.54178$ Å). XPS measurements were made on a KRATOS AXIS 165 X-ray photoelectron spectrometer instrument using monochromatic Al K_α radiation. Survey scan (0-1000 eV binding energy range) was used to identify the surface elemental compositions of the samples. The X-ray gun was operated at 15 kV voltage and 20 mA. Survey and high-resolution spectra were collected using 80 and 40 eV pass energy respectively. The pressure in the analyzer chamber was $\sim 1.33 \times 10^{-6}$ Pa. Ultraviolet-visible (UV-VIS) spectra were measured on a Cintra 10e-UV spectrophotometer. Thermogravimetric analysis was performed using an 851 Mettler Toledo TGA instrument. The samples were heated from room temperature to 700°C at a scan rate of 10°C per min under a nitrogen purge at a flow rate of 100 ml/min.

Synthesis of Poly(4vp-co-dvb)

The copolymer was prepared by suspension copolymerization method using 4vp and 2 mol% dvb (on 4vp). Into a four-neck resin kettle, fitted with a half moon Teflon blade agitator, nitrogen purge adaptor and a reflux condenser containing 2.5% (by weight) PVP distilled aqueous solution, a mixture of 4vp, dvb and 2% Lupersol TAEC initiator (w/w on monomers) was added dropwise while operating the blade agitator at 650 rpm at room temperature. The nitrogen purge was continued throughout the reaction. The bath temperature was raised to 89°C and maintained for 1 h before increasing further to 100°C. The second initiator, 1% Luperox 101 (w/w based on monomers) was then added to the reaction mixture. The reaction was allowed to proceed for 5 h with continuous agitation. The copolymer was filtered and washed thoroughly with hot water to remove the water-soluble PVP, followed by methanol to remove the linear polymer and traces of unreacted monomers. The off-white colored copolymer microspheres were dried overnight under vacuum at 65°C and stored.

Synthesis of CeO_2@Poly(4vp-dvb) by Conventional Two-Step Method

1 g of the poly(4vp-co-dvb) and $CeCl_3$ $7H_2O$ (5.0 mol% of the monomers) were dispersed in 100 ml of distilled water whose pH was adjusted to 10 by addition of 0.1 M NaOH. A shift in the pH towards acidic was balanced by the constant addition of 0.1 M NaOH in order to maintain pH 10 until a color change to reddish orange was noticed, which turns yellow after 24 h. The reaction mixture was left for a total time period of 72 h under constant stirring for complete metal–polymer bond formation. The composite of ceria nanoparticles supported on the copolymer was then filtered and washed thoroughly with distilled water until neutral. The ceria-supported polymer thus obtained was dried under vacuum at 100°C.

Synthesis of CeO_2@Poly(4vp-dvb) by Simultaneous Single-Step Method

The nanocomposite was prepared by suspension copolymerization method using 4vp and dvb (2 mol% on 4vp). Into a four-neck resin kettle, fitted with a half moon Teflon blade agitator, nitrogen purge adaptor and a reflux condenser containing 2.5% (by weight) PVP, a distilled aqueous solution of cerium trichloride heptahydrate (5 mol% on monomers) was taken. A mixture of 4vp, dvb, and 2% Lupersol TAEC initiator (w/w on monomers) was added dropwise while operating the blade agitator at 650 rpm at room temperature. A nitrogen purge was continued throughout the reaction. A basic pH of 10 was maintained using 0.1 N NaOH for 30 min in order to obtain nanosized ceria particles. The bath temperature was raised to 89°C and maintained for 1 h before increasing further to 100°C. The second initiator, 1% Luperox 101 (w/w based on monomers), was then added to the reaction mixture. The reaction was allowed to proceed for 5 h with continuous agitation. The ceria nanoparticles supported on the copolymer thus formed was filtered and washed thoroughly with hot water, to remove the water soluble PVP, followed by methanol to remove the linear polymer and traces of unreacted monomers. The yellow-colored composite was dried overnight under vacuum at 65°C.

Synthesis of Microporous CeO_2@Poly(4vp-dvb) by Simultaneous Single-Step Method

A mixture was prepared of 4-vinylpyridine (4vp), 2 mol% divinylbenzene (dvb) 1% of AIBN (Azobis isobutyronitrile) in 50% of porogen agents (cyclohexanone and cyclohexane) with respect to monomer mixture. This total reaction mixture was added drop-wise to an aqueous solution containing 2.5% w/w of polyvinylpyrrolidone (PVP) and 5 mol% of cerium trichloride heptahydrate ($CeCl_3 \cdot 7H_2O$) (on monomers) stirring at 650 rpm under nitrogen purge. For the formation of ceria nanoparticles and stabilization of the suspension, a pH of 10 was maintained in the medium for 24 h. The yellow-colored poly(4vp-co-dvb)/ceria nanocomposite was then washed with hot distilled water followed by methanol to remove the water-soluble PVP, 4vp homopolymer and unreacted monomer, and dried under vacuum at 100°C.

Biginelli Reaction

To a mixture of benzaldehyde **1** (4.7 mol, 500 mg), methyl-3-cyclopropyl-3-oxo-propionate **2e** (4.7 mmol, 670 mg), urea **3** (7.1 mmol, 425 mg) and ceria nanoparticles (0.47 mmol, 650 mg) were added 5 ml of distilled water and the reaction mixture was stirred for 10 h at 80°C. After cooling to room temperature, ethylacetate was added to the reaction mixture and filtered through a Buckner funnel. The organic layer was separated, washed with water, dried over sodium sulphate, and then concentrated under reduced pressure. The crude product was recrystallized by hexane ethylacetate mixture to afford the pure product.

Spectral Data for Selected Compound 4e

White solid, mp.113–115°C; IR (KBr) ν_{max} 3245, 1735, 1647; ^1H NMR (300 MHz, $CDCl_3$): δ 0.80–1.04 (m, 4H), 3.04 (m, 1H), 3.60 (s, 3H), 5.34 (sd, 1H), 6.55 (br s, NH), 7.15–7.31 (m, 5H); LS MS: m/z 273.2 (M + 1).

RESULTS & DISCUSSION

Synthesis of CeO_2@Poly(4vp-dvb) Supports

The polymer supports reported earlier were synthesized in two steps. The new supports were synthesized in a single pot with two reactions taking place simultaneously that are noninterfering with one another. Lanthanide cations (Lewis acids) accept the pair of electrons from N atom of the 4vp monomer to form a covalent coordination bond.

$$\mathrm{CeCl_3 \cdot 6H_2O + 4vp + dvb + initiators \xrightarrow[NaOH]{H_2O} CeO_2@Poly(4vp\text{-}dvb)}$$

Polyvinylpyrrolidone (PVP), used as a colloidal stabilizer for the polymerization reaction, was found to play a dual role of simultaneously stabilizing the fine suspension of monomer in water as well as the dispersion of ceria nanoparticles by controlling the particle–particle interaction and preventing agglomeration [14]. Another advantage of the method is the presence of sodium hydroxide in the medium, which enhances the metal–polymer complexation of the weakly basic 4vp leading to precipitation of metal oxide nanoparticles not only on the surface but also inside the polymer microparticles. It is also reported that a basic pH of the aqueous suspension lowers the adsorption capacity of PVP on to ceria nanoparticles, leaving no scope for the formation of PVP/ceria nanocomposite [15]. These factors are the important reasons for the formation of poly(4vp-co-dvb)/ceria composite with well-dispersed crystalline ceria nanoparticles, which is not found in the conventionally prepared one. Synthesis of microporous beads of the same polymer using the simultaneous method was done in order to test the effect of porosity on the catalytic performance.

Characterization of CeO_2@Poly(4vp-dvb) Supports

The broad peak at $2\theta = 17^\circ$ seen in Figure 2a is attributed to the copolymer with amorphous nature. The intensity of the polymer peak decreases on composite formation. All the CeO_2@Poly(4vp-dvb) show additional diffraction peaks at $2\theta = 28.5, 33.0, 47.5$ and 56.5° that correspond to the major reflections of crystal faces 111, 200, 220 and 311, respectively, of metallic crystalline CeO_2 with a fluorite (CaF_2) structure [16]. However, the intensity and the sharpness of the peaks vary from one another. The peaks increase in intensity from **conven** (1b) to **simul** (1c) with **simul-porous** (1d) falling in between. This indicates that the crystallinity of the ceria nanoparticles is higher in **simul**, with an average size of 15–20 nm as estimated by Scherer's equation. Broadening of the peaks in case of **simul porous** and more for the **conven**, suggests the presence of smaller ceria particles. The XRD of the recycled **simul** polymer nanocomposite (shown as inset in Figure 2) had shown all the ceria peaks with almost the same intensity as that of the freshly prepared one.

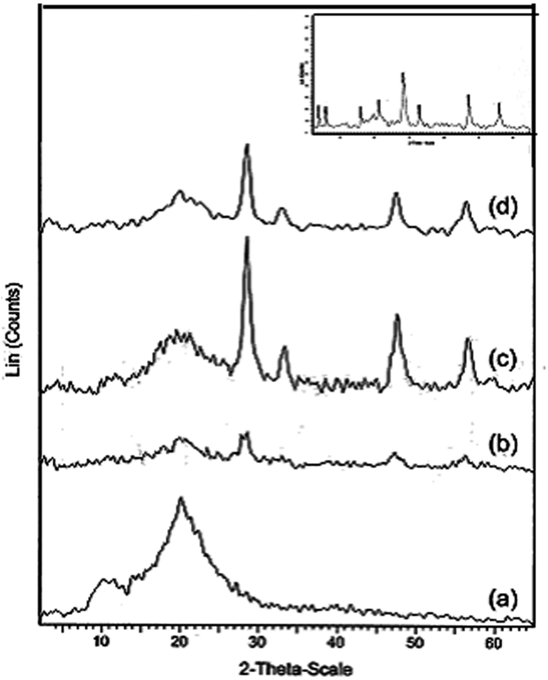

FIGURE 2 XRD patterns of a) poly(4vp-co-dvb) and CeO_2@Poly(4vp-co-dvb), b) **conven**, c) **simul** beads, d) **simul** and **simul** recovered after Biginelli reaction in the inset.

The morphology of all three forms of nanocomposites is shown in comparison to the virgin polymer in SEM images (Figure 3). The images include the plain polymer microparticle (a,b), with a clear surface, while the composites show the presence of ceria nanoparticles on the polymer. The difference between the three forms of CeO_2@Poly(4vp-dvb) is evident with metal content decreasing in the order **simul** > **simul porous** > **conven**. Figure 4 presents the TEM images of **conven** and **simul** forms of the composite with an inset of their corresponding SAED (selected area electron diffraction) patterns. The morphology of the conventional composite shows that ceria particles are not well-dispersed in the polymer matrix and show polycrystallinity, whereas, **simul** in Figure 4b shows near monodisperse, nanocrystalline CeO_2 particles that are homogeneously dispersed throughout the polymer and the size matches with that found in XRD. The SAED pattern indicates that the ceria nanoparticles are single crystalline, suggesting a face-centered cubic structure. The shape of the particles was predominantly octahedral

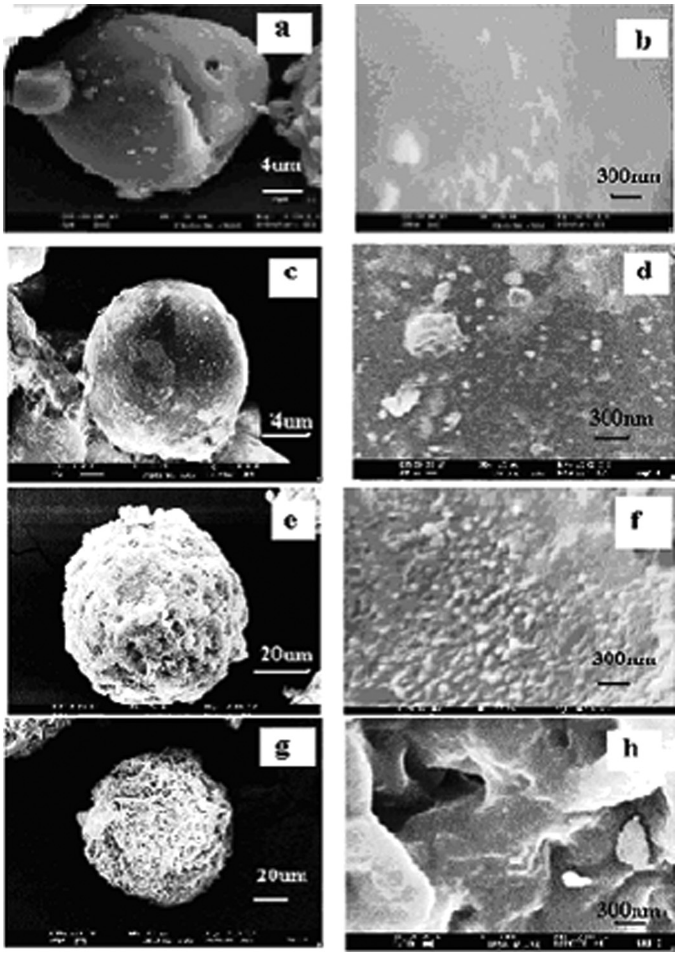

FIGURE 3 SEM images of a and b) poly(4vp-co-dvb), CeO_2@Poly(4vp-co-dvb), c and d) **conven**, e and f) **Simul**, and g and h) **Simul porous**.

with 12 edges parallel to {110} directions and 8 {111} surfaces and some are truncated octahedral enclosed by 8 {111} and 6 {001} surfaces [17]. The EDAX values obtained from the SEM images for cerium element were found to be tenfold higher for the **simul** composite (8.9%) than that in **conven** (0.8%), with **simul porous** showing (3.8%).

The binding energies of the N 1s peaks for the pure polymer and the ceria supports are shown in Figure 5. The free N 1s peak for the polymer appears at 398 eV, which on metal complexation shows an

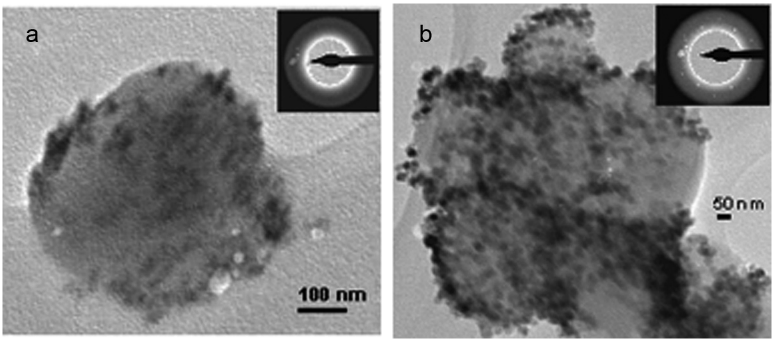

FIGURE 4 TEM photographs of CeO$_2$@Poly(4vp-co-dvb), a) **conven** and b) **simul**.

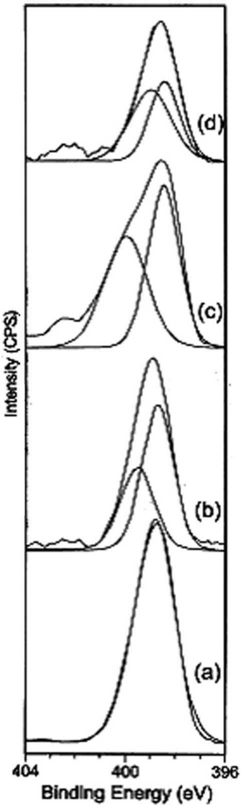

FIGURE 5 XPS of N 1 s peaks of coordinated and free nitrogen for a) poly(4vp-co-dvb) and CeO$_2$@Poly(4vp-co-dvb), b) **conven**, c) **simul**, and d) **simul porous**.

additional peak for the bound N 1s at 400 eV for all the composites. It has been reported earlier that the quaternary N, coordinated to a metal, normally appears at 401 ev [5]. All the supports have shown an additional peak in the range of 399 to 400 eV with maximum shift and intensity for the **simul**. The amount of coordinated N in the support indicates the Ce/N ratio, which is directly proportional to the intensity of the coordinated peak.

The thermogravimetric analysis was done to evaluate the thermal stability of the nanocomposites and determine the total metal content in the polymer. Shown in Figure 6 are the TGA curves of the poly(4vp-co-dvb) and its nanocomposites (**simul, simul porous** and **conven**). The pristine polymer decomposes completely at 405°C and the conventional one displayed a similar single-stage degradation at 410°C, indicating an improvement in the thermal stability. However, **simul** and **simul porous** have shown a two-stage degradation pattern lowering the initial degradation temperature to 370°C and 386°C, respectively. The char yield was found to be 4% higher for the **simul** and 3% higher for the **simul porous** than the **conven**. The reason for the two-stage degradation in both the simul forms of

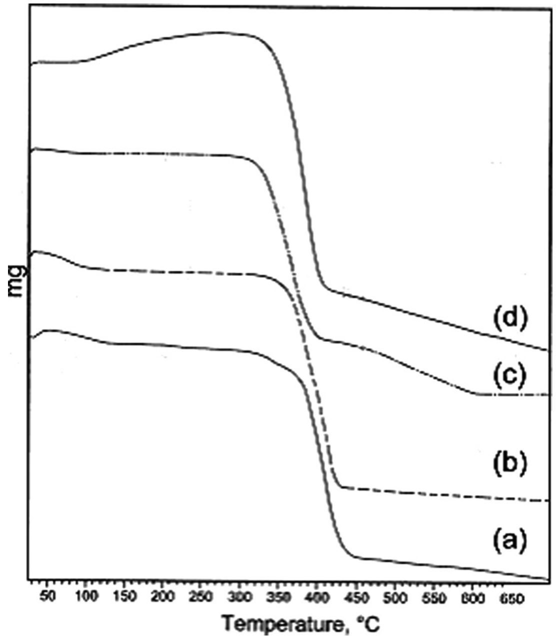

FIGURE 6 TGA graphs of a) poly(4vp-co-dvb) and CeO_2@Poly(4vp-co-dvb), b) **conven**, c) **simul**, and d) **simul porous**.

the composite is probably due to the enhancement in the rate of scission of head-to-head linkages [18] of the composite, thereby reducing the degradation temperature due to an additional heat transfer. The complexation of cerium oxide leads to stronger crosslinking thereby causing a second-stage degradation up to 600°C for the scissions. The degradation pattern is similar to that of the one for the thermooxidative method reported for a Cu-complexed polymer. SEM and TEM results also support higher thermal stability and high charyield of the **simul** than **simul** beads, presenting a narrow size distribution and evenly dispersed metal nanoparticles in the polymer. The morphology is of raspberry type with the metal mostly present on the surface of the beads proposed for the **conven** composite. This is supported by the difference in the degradation pattern.

Crosslinked vinylpyridine polymers have been considered as promising supports for metals and are used as heterogeneous catalysts in organic synthesis [19]. These polymers are known as functional resins because the pyridine ring bearing the tertiary nitrogen atom endows them with distinct features. All the three forms of CeO_2@ Poly(4vp-dvb) were tested for their efficacy as heterogeneous catalysts for the synthesis of dihydropyrimidinones. Under similar conditions of the reaction, the yields were found to be maximum (89%) for the **simul** form in comparison to others. The catalytic activity of the dispersed ceria on the support is influenced by a number of factors, namely, size, shape, extent of dispersion, relative amount of metal present, chemical nature of the support and the strength of interaction between the support and the metal. In **conven** the raspberry type of morphology has all the metals mostly located on the surface of the bead, which are highly accessible for the reaction, but has lower metal content resulting in lower yields (80%). Similarly, the **simul porous** are microporous in nature and have the possibility for the reaction medium to enter the pores and interact with the metals present inside the beads. These beads had slightly higher metal content than **conven** and therefore gave better yields (84%). The behavior could also be attributed to coverage of inside ceria particles by the polymer, which were not accessible to the reaction, and this is clearly seen in the SEM image of Figure 3. The significant increase in the catalytic activity of the **simul** form is due to the higher Ce/N ratio and predominance of well-defined and more reactive exposed planes of ceria nanocrystals on the supports.

CONCLUSIONS

A simple and easy preparation technique for synthesis of CeO_2@Poly (4vp-dvb) in a single step has been demonstrated for the first time.

The advantages of the new method are: a nanocomposite with higher percentage of ceria nanoparticles, well-defined crystallinity and narrow size distribution, that are uniformly dispersed in the matrix. In addition, the process involves simple operation in one pot with no need for surfactants, and could be extended to other metals that are monomer-insoluble. All the three forms of composites were used as heterogeneous catalysts in Biginelli reaction for the synthesis of dihydropyrimidinones and have proved recyclability. The **simul** form resulted in higher yields than the others because of its enhanced properties, like greater Ce/N ratio, near monodisperse ceria particles, and their single crystalline nature. Such polymer supports are useful as eco-friendly catalysts and render several advantages over their homogeneous counterparts.

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