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Communication A novel and effective Zn/PEI-MCM catalyst for the acetylene hydration to acetaldehyde

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E-mail addresses: <u>db_tea@shzu.edu.cn</u> (B. Dai), <u>zhangjinli@tju.edu.cn</u> (J. Zhang) **Graphical Abstract**



The introduction of PEI can enhance the metal-support interaction to make the better metal dispersion and more active sites, and the charge transfer from N atom to Zn species, especially for the Zn/P-MCM-12 catalyst with about 88% C_2H_2 conversion and 85% selectivity.

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ABSTRACT

Article history: Received Received in revised form Accepted Available online <i>Keywords:</i> Polyethyleneimine Modified MCM-41 Acetylene hydration Zinc catalyst High activity	MCM-41 material was modified by polyethyleneimine (PEI) using ultrasonic assisted impregnation method with different PEI loading (P-MCM- x , $x = 0.15$ wt%). The synthesized P-MCM- x materials and corresponding Zn/P-MCM- x catalysts were characterized by FTIR, XRD, TEM, BET, XPS, TGandH ₂ -TPR, as well as their catalytic performance in the hydration of acetylene was investigated. The results showed that the modified materials retained the				
	the higher catalytic performance than that of Zn/MCM catalyst, especially for the Zn/P-MCM- x displayed the higher catalytic performance than that of Zn/MCM catalyst, especially for the Zn/P-MCM- 12 catalyst with about 88% C ₂ H ₂ conversion and 85% selectivity, and the optimal content of PEI is 12 wt%. More importantly, the introduction of PEI enhanced metal-support interaction to make the better metal dispersion and more active sites, and the charge transfer from N atom to Zn species. These all would be responsible for the high activity of the modified Zn catalysts in the acetylene hydration.				

Acetaldehyde is widely used as a chemical intermediatefor the production of peracetic acid, acetic anhydride, butylene glycol, and so on [1, 2]. The hydration of acetylene to give acetaldehyde has attracted increasing attentionbecause it provides a more promising route for the industrial production of acetaldehyde, and it profits from the vast domestic coal reserves and the increase in oil prices [3]. A stoichiometric amount of mercuric sulfate hasbeen employedunder strongly acidic conditions for the hydrationof acetylene. However, this catalytic process generates toxic waste containing mercury, which results in severe environmental problems [4]. Therefore, environmentally friendly non-mercury-containingcatalysts have been widely investigated over recent decades.

Numerous transition metal ions, such as Cu^{2+} , Ag^+ , Cd^{2+} , and Zn^{2+} , which were either in aqueous solution or in the solid state in the form of their oxides, phosphates, molybdates, phosphomolybdates, and tungstates, exhibited initial activityin the hydration of acetylene [5-13]. Notably, the catalytic activity

in the hydration of acetylene decreased in the order of Cd > Zn >Pb [11]. Unfortunately, although the Cd-based catalysts showed the excellent catalytic performance for the hydration of acetylene, the toxicity of cadmium limited their application in the reaction. In addition, the activezeolite catalysts containing transition metal ions were easily deactivated because the metal ions were reduced (such as Cu^{2+} , Ag^+ , Hg^{2+}) or/and carbonaceous depositswere formed. In view of this, zinc-based catalysts would be likely to constitute potential replacementsforcadmium-based catalysts preserved the relatively high initial activity in the hydration of acetylene [11].

Inprevious studies, the particularly potential support MCM-41 has been used in the acetylene hydration due to its exceptional properties [14-16], such as the well-organized mesoporous structure, large surface area, excellent thermal stabilities and facile surface modification. However, almost no active sites, almost neutral of surface charge and single Si-OH groups of the MCM-41 caused to the poor activity and stability [17-20]. Therefore, it is essential for the surface modification through introducing the reactive organic functional groups to bond or anchor more metal on the mesoporous MCM-41 surface to enhance the catalytic performance. It is well known that the polyethyleneimine(PEI) is a cationic hydrophilic polymerwith a large amount of charge density, particularly, the high amine density, good solubility and functionality has been employed in the preparation and surface modification for the materials [21-27]. As a result of these excellent properties, the unique PEI has always applied invarious systems to play different roles. For instance, the PEI modified nanocomposites could enhance adsorption capacity as a functionalized adsorbents and the modified PEI-MOFs materials could effectively separate CO₂ and phosphate sequestration [28-30]. Additionally, PEI also could be served as a stabilizer to capture nanoparticles [31]. Notably, the adhesion between compounds and carriers surface can be improved by adding the PEI [32-34]. Moreover, PEI also could be used to prepare multifunctional fluorescent carbon dots profiting from its picturesque proton sponge mechanism [35].

Hence, inspired by the excellent properties of PEI with ahigh density of charge, a series of PEI modified MCM-41 materials with different PEI contents were synthesized by using the ultrasonic assisted impregnation method. And then thePEI modified MCM-41 materialscapturedzinc active compound as catalysts for acetylene hydration to acetaldehyde. In this work, we explored thenature of the structure and introduction of amine functional groups for the as-synthesised materials as well as the influence on the catalytic performance in the acetylene hydration. Interestingly, the PEI modified Zn catalyst showed the high catalytic performance in the acetylene hydration. Allofthe samples were characterised by FTIR, XRD, BET,H₂-TPR, TEM, XPS, and TGA.

In this work, the parent MCM-41 was synthesised by using the traditional hydrothermal treatment method [36, 37]. Typically, 1.82 g cetyltrimethylammoniumbromide was mixed with a solution containing 0.2 mol/L of sodium hydroxide at 40°C for 2 h. Then, the tetraethyl orthosilicate was slowly added to the mixture under vigorous stirring for 2 h. The obtained solution was transferred to a Teflon autoclave and placed in drying oven at 110°C for 72 h. The white solid was filtered and washed

thoroughly with deionised water until pH 7 was reached. The powder wasthen dried at 60 $^{\circ}$ C and calcined at 500 $^{\circ}$ C for 6 h with airflow to obtain the MCM-41 material.

Then, the PEI modified MCM-41 material was prepared by the ultrasonic assisted impregnation method. A certain amount of PEI was dissolved in deionised water, and then obtained PEI solution was added dropwise into the MCM-41 material under the ultrasonicirradiated for 8 h with argon at ambient temperature. Finally, the obtained mixture was dried at 100°C overnight to gain PEI modified MCM-41 material, named P-MCM. Notably, the synthesizedPEI modified MCM-41 materials contained different PEI contents: 4 wt%, 6 wt%, 10 wt%, 12 wt%, and 15 wt%, called after P-MCM-4, P-MCM-6, P-MCM-10, P-MCM-12, and P-MCM-15.

The corresponding Zn/P-MCM-x (where x = 4, 6, 10, 12 and 15) catalysts were synthesised using thewet impregnation technique with deionised water as a solvent. Briefly, a stoichiometric amount of ZnCl₂solutionwas added to the P-MCM-x powder dropwise under magnetic stirring. The resulting suspension was stirred for 10 h in the environmental condition and then evaporated to dryness before the powder was further dried for 18 h at 100 °C to form the Zn/P-MCM-x catalysts. The same procedure was followed to prepare the corresponding Zn/MCM catalyst for comparison. The content of ZnCl₂ was 10 wt% in all catalysts.

The synthesised PEI modified MCM-41materials and corresponding Zn catalysts were carried out by a series of characterization techniques. Fourier-transform infrared spectroscopy (FTIR): IS10 FT-IR spectrometer with wavelength range of 500-4000 cm⁻¹.X-ray diffractometry(XRD): Bruker D8 X-ray diffractometer. Transmission advanced electron microscopy (TEM): a JEM 2010 electron microscope.X-ray photoelectron spectroscopy(XPS): an Axis Ultra spectrometer with a monochromatised Al-Ka X-ray source. Brunauer-(BET): a Micromeritics Emmett–Teller ASAP 2020. Temperature-programmed reduction (TPR): anAutoChem 2720 instrument. Thermogravimetric (TG)analysis:over the temperaturerange of 50-1000°C with the heating rateof 20°C/minand a nitrogen flow rate of 10 mL/min.

In brief, the catalytic performance was tested using 2 mL catalyst in the fixed-bed glass microreactor (i.d. of 10 mm) for the hydration of acetylene. Firstly, in order to eliminatetheair atmosphere of the reactor, the nitrogen was continued to purge for 30 min. Then, when the temperature of reactor reached to 240 °C, the reactant water vapourwas injected the reactor by using a peristaltic pump. After 0.5 h, the other reactant acetylene was poured into the system to react with water vapour. Finally, the reaction products were detected by the gas chromatograph (GC-2014C). In addition, acetylene conversion(X_A) and selectivity to acetaldehyde(S_{AA}) are the performance indicators for the Zn catalyst, and the calculation equation is as follows:

$$X_{\rm A} = \frac{\Phi_{\rm A0} - \Phi_{\rm A}}{\Phi_{\rm A0}} \times 100\%$$
$$S_{\rm AA} = \frac{\Phi_{\rm A}}{1 - \Phi_{\rm A}} \times 100\%$$

Where Φ_{A0} and Φ_A are the volume fraction of the initial and remaining acetylene, respectively.

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Fig. 1 showed the FTIR spectra of P-MCM-*x* materials. It is clearly observed that the special groups of MCM-41 framework were still well retained after the introduction of PEI, which can be confirmed by the special features at 800, 956, 1238 and 1386 cm⁻¹corresponding to Si–O–Si symmetric stretch, Si–O–H stretching vibration, Si–O–Si asymmetric stretch and -OH inplane bending vibration of MCM-41 [38]. In addition, it is reported that the features at 1553-1646 cm⁻¹ and 1468 cm⁻¹ could be classified as bending of -NH₂ and symmetric bending of NH₃⁺ in the silica samples doping by PEI [39, 40]. Thus, at this stage, it could be considered that the PEI has been successfully doped into the MCM-41 framework from the FTIR result.

The thermal stabilities of P-MCM-*x* samples were performed by the TG experiments, and the results are plotted in Fig. 2. Firstly, as shown in Fig. 2, the first step of weight loss below 200 °C could be attributed to the removal of moisture molecules and/or desorption of organic molecules on the surface of P-MCM-*x* samples. Then, the middle of weight loss at the temperature range of 200-400 °C would be related to the decomposition of amine groups anchored to the framework. Moreover, the last step of slight weight loss might be belonged to the release of surfactant molecules in the samples. Meanwhile, the corresponding DTG curves were observed two obvious peaks at 50-150 °C and 300-400 °C in the Fig. S1 in Supporting information. The first peak could be due to the adsorb water or/and organic molecules loss; the second peak would be caused by the decomposition of amine groups.







Fig. 3. N₂ adsorption-desorption isotherms of P-MCM-x samples.

In addition, the structure parameters (including surface area, pore volume and pore diameter) of P-MCM-x samples are listed in Table S1 in Supporting information. In comparison with the parent MCM-41, the decrease of surface area and pore volume would confirm that the PEI has been successfully doped into the MCM-41 framework. Although the reduction of structure parameters of PEI modified MCM-41 due to the organic species plunged into framework and limited the accessible to N2, the P-MCM-x samples also have high surface area to seize active sites to catalyze reaction. In addition, the N₂ adsorption-desorption isotherms of P-MCM-x samples in Fig. 3 could suggest that the samples retained the mesoporousstructure because of the type IV isotherm. Furthermore, it is feasible that the further decrease of structure parameters after the zinc species deposition on the surface of P-MCM-x samples, and the mesoporous structure was not destroyed but with the poor ordered pore channels for the Zn/P-MCM-x samples (shown in Table S1 and Fig. S2 in Supporting information). Notably, these features also could be observed from the small-angle XRD patterns in Fig. 4.



Fig. 4. Small-angle XRD patterns of P-MCM-x samples.

The diffraction peaks located around 2.4°, 4.1° and 4.8° of P-MCM-*x* samples corresponding to the (100), (110) and (200) planes, respectively, which is the symbol of mesoporous structure with a hexagonal ordered pores [38]. However, after the zinc species deposition, the peak intensity reduced and only one diffraction peak located at 2.4° was found for the Zn/P-MCM-*x* samples (shown in Fig. S3 in Supporting information). These indicated that the addition of PEI and zinc species reduced the ordered pore channels, which is consist with the BET results. Interestingly, from the Table S1, the δ (wall thickness) value increased with the content of PEI for the P-MCM-*x* samples due to the decrease of pore diameter after PEI incorporation into MCM-41. As expected, the δ value of Zn/P-MCM-*x* samples is higher than that of P-MCM-*x* samples, which might suggest that most of zinc species deposited on the entrance and a portion of

species entered into the inside pore channels of P-MCM-x samples.



Fig. 5. Acetylene conversionduring the hydration of acetylene catalyzed by Zn/P-MCM-*x* catalysts.

Moreover, the synthesized Zn/P-MCM-x catalysts were used to catalyze the hydration of acetylene, and the reaction conditions were as follow: reaction temperature is 240°C, reactants ratio is 4 (water vapour is more), and gas hourly space velocity is 90 h⁻. From the catalytic activity results in Fig. 5, the Zn/MCM catalyst displayed a high initial activity, which was continuously deactivated from 83.5% to 30.0% witha C_2H_2 conversion loss of about 64.1% after 14 h, indicating the poor catalytic activity and stability, as well as the selectivity to acetaldehyde for the Zn/MCM-41 catalyst in the acetylene hydration reaction. Surprisingly, the Zn/P-MCM-x catalysts showed the higher catalytic activity and stability than that of the Zn/MCM-41 catalyst in the same reaction conditions. Specific contentsare as follows: the C2H2 conversion loss of Zn/P-MCM-4, Zn/P-MCM-6, Zn/P-MCM-10, Zn/P-MCM-12, and Zn/P-MCM-15 catalysts was 19.6%, 17.8%, 8.0%, 7.5% and 9.0%, respectively. In other word, the catalytic activity increased with the content of PEI, but further increase in PEI amount the C₂H₂ conversion was not continue to increase but decreased. Obviously, the Zn/P-MCM-12 displayed the better catalytic activity with aC2H2 conversion of about88% and selectivity to acetaldehyde of about85% (shown in Fig. S4 in Supporting information). Therefore, the catalytic activity results indicated the addition of PEI could enhance the catalytic activity and stability of Zn catalyst in the hydration of acetylene, and the optimal content of PEI is 12 wt%.



To explore the influence of PEI modification on the Zn catalyst, the following experiments were conducted. Firstly, the H_2 -TPR was used to reveal the strength of interaction between the metal and support and the reducibility of metal catalysts and the

results are shown in Fig. 6. It is clearly found that a reduction peak at temperature of around 380°C for the Zn/MCM-41 catalyst. For the representativeZn/P-MCM-12 catalyst, there are two obvious reduction peaks at the temperature of 337°C and 475°C, except for the reduction peak of P-MCM-12 material. It might be speculated that the low temperature of reduction peak could be attributed to the reduction of zinc species dispersed on the support externalsurface, and the other reduction peak might be belonged to the reduction of the zinc species that entered into the inside pore channels with strong interaction between the P-MCM-12 support. These obvious changes could suggest that the metal-support interaction has been strengthened after the incorporation of PEI, which may be one of the reasons for the high activity of Zn/P-MCM-*x* catalysts in the acetylene hydration reaction.



Fig. 7. TEM images of fresh Zn/P-MCM-x catalysts.



Fig. 8. TEM images of spent Zn/P-MCM-x catalysts.

Then, the TEM micrographs and particles size distribution of fresh and spent Zn/P-MCM-*x* catalysts are shown in Figs. 7 and 8. The apparentblack/darker dots and a broad particles size distribution could be observed from the fresh Zn/MCM-41 catalyst with an average particle size of 8.1 nm. Else, the average particle size of spent Zn/MCM-41 catalyst expanded to 13.3 nm with the conspicuous agglomeration. In other word, the poor metal dispersion and particles agglomerated may be one of the reasons of Zn/MCM catalystdeactivation in the acetylene hydration. However, it turns dust into glory after the PEI introduced, as shown in Fig. S5(Supporting information), the Zn species and N species uniformly distributed on the MCM-41 indicated that the PEI was successfully introduced into the MCM-41framework.On one hand, the metal particles showed a good dispersion on the outer surface and the average particle size never exceeded 5 nm with a narrower particles size distribution of the fresh Zn/P-MCM-x catalysts. On the other hand, the absence of apparentagglomeration of the spent Zn/P-MCM-xcatalysts suggested that the addition of PEI could prevent the particles agglomerated during the reaction. These would be responsible for the high catalytic performance of the Zn/P-MCM-x catalysts in the acetylene hydration.



Fig. 9. The high-resolution XPS spectra for the N 1s (A) and the Zn 2p (B) of the catalysts.

Lastly, in order to measure the chemical state and surface composition of the representative Zn/P-MCM-12 catalyst, the XPS experiment was performed. From the Fig. S6 (Supporting information), the obvious peak at the binding energy of 400.0 eV indicated that the presence of the nitrogen (N 1s) of the Zn/P-MCM-12 catalyst [41], which confirmed that the PEI has been doped into the MCM-41 framework due to the N atoms derived from the PEI. More importantly, the N 1s peak (Fig. 9A) has been fitted well by two peaks with the binding energies of 400.0

Table1

Surface atomic composition (%) and binding energies of catalysts.

eV and 402.2 eV (listed in Table 1) for the fresh Zn/P-MCM-12 catalyst. Some studies have been pointed out that the N 1s peak at higher binding energy (400-402 eV) could be related to the adsorption of metal ions (Mⁿ⁺) [42-44], which would cause to the positive polarization. Therefore, in this study, the N 1s peak at low binding energy could be attributed to the N of the amino group, the other N 1s peak would originate from the charged ammonium, such as -NH3+ or -NH2-M2+ [45, 46]. However, after the reaction, the N 1s consisted of three peaks and the binding energies slight reduced indicated that the metal-support interaction appeared during the reaction. It is well known that the N atom derived from the amino group has a free electric pair, which could be formed the coordination bonds with the metal ions and resulted to the increase of metal electron density to obtain more active sites. This can be further confirmed by the Zn 2p_{3/2} XPS spectra for the Zn/P-MCM-12 catalyst (Fig. 9B). As shown in Table 1, the binding energies of $Zn 2p_{3/2}$ peaks in Zn/P-MCM-12 catalyst is lower than that of Zn/MCM-41 catalyst, indicating that the Zn species obtained the electrons from the PEI modified support caused to the lower Zn 2p_{3/2}binding energies. These could imply that the stronger interaction between Zn²⁺ and amino group from the PEI modified support, as well as for the spent Zn/P-MCM-12 catalyst. In addition, the elemental compositions in Table 1indicated the addition of PEI could enrich more Zn species and present the Zn species loss (Zn loss of 13.8% is obvious lower than that of Zn/MCM-41 catalyst). Therefore, the stronger metal-support interaction, more active sites and lower Zn loss would be also responsible for the high catalytic performance in the hydration of acetylene.

Surface atomic composition (70) and omening chergies oreatarysts.										
Samples -	Composition (At %)		Binding energy (eV)							
	Ν	Zn	С	Zn 2p _{3/2}	Zn 2p _{3/2}	N 1s				
Fresh Zn/MCM-41	/	3.13	10.56	1023.2	1024.0	/	/			
Spent Zn/MCM-41	/	2.27	11.69	1023.1	1023.6	/	/			
Fresh Zn/P-MCM-12	3.73	3.78	10.98	1022.6	1023.2	400.0	402.2			
Spent Zn/P-MCM-12	2.46	2.96	25.72	1022.0	1022.5	399.8	400.9	401.9		

In this work, a simple ultrasonic assisted impregnation method was used to synthesize PEI modified MCM-41material with different PEI amount. FTIR results suggested that the PEI has been successfully doped into the MCM-41 framework. The TD-DSC results confirmed the good thermostability of P-MCMx materials. BET and XRD indicated that the P-MCM-x materials retained the mesoporous structure with hexagonal pores. In the activity tests, the corresponding Zn/P-MCM-x displayed the higher catalytic performance than that of Zn/MCM-41 catalyst in the hydration of acetylene. Notably, the Zn/P-MCM-12 catalyst showed the better activity with aC2H2 conversion of about88% and selectivity to acetaldehyde of about85%, suggested the optimal content of PEI is 12 wt%. Furthermore, the H₂-TPR results implied that the addition of PEI could enhance the interaction between metal and support that related to the high activity of Zn/P-MCM-12 catalyst. The better metal dispersion and narrower particles size of Zn/P-MCM-x catalysts can be verified by the TEM, as well as the fact that the introduction of PEI prevented the particles agglomerated. More importantly, the XPS results confirmed the strong metal-support interaction and the charge transfer from N atom to Zn species. Else, the incorporation of PEI not only enriched more active sites but also restrained the Zn species loss during the reaction. These all would be responsible for the high activity of the modified Zn catalysts in the acetylene hydration. We believe that this work would be as a basic research to develop and design the powerful metal catalysts in the hydration of acetylene to acetaldehyde for industrial applications.

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