European Journal of Chemistry 6 (4) (2015) 488-492

European Journal of Chemistry

Journal webpage: www.eurjchem.com

Phenol removal from aqueous solutions by using H-mordenite and platinum supported H-mordenite

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ARTICLE INFORMATION

DOI: 10.5155/eurjchem.6.4.488-492.1340

Received: 16 October 2015
Received in revised form: 16 November 2015
Accepted: 21 November 2015
Published online: 31 December 2015
Printed: 31 December 2015

KEYWORDS

Phenol
Platinum
H-Mordenite
Wet impregnation
Catalytic wet air oxidation
Advanced oxidation processes

ABSTRACT

H-Mordenite and platinum supported H-mordenite were prepared and tested to remove phenol from aqueous solutions. The supported mordenite was prepared using wet impregnation method. The physicochemical properties of these prepared samples were characterized by several techniques such as SEM, HR-TEM, X-ray diffraction and N_2 adsorption. The effects of temperature, pH, phenol concentration, catalyst amount and UV at 254 nm were studied to obtain the optimum conditions at which best removal occurs. It was seen that the removal using H-mordenite is close to the supported H-mordenite.

Cite this: *Eur. J. Chem.* **2015**, *6(4)*, 488-492

1. Introduction

Phenol is a common raw material to numerous products such as pesticides, pharmaceuticals, phenolic resins and petroleum refineries. However, phenol is one of the hazardous chemicals listed in United States Environmental Protection Agency (EPA) guidelines for 129 priority pollutants; it is listed in number 65 [1,2]. It is a toxic, carcinogenic, and non-biodegradable chemical [3,4].

Catalytic wet air oxidation (CWAO) can be employed to phenol to produce harmless and low-molecular-weight compounds, particularly CO_2 and H_2O [5-7]. Oxidation of phenol can be attained by contacting with aluminosilicate materials particularly mordenite and supported metal mordenite. Mordenite is an aluminosilicate material. It is an inorganic microporous and microcrystalline materials capable of complexing small and medium-sized organic molecules. Supporting with zeolites is found to be a better candidate as compared to other supporting materials due to advantages such as: to solid structure define channels and cavities of molecular dimension, super adsorption capability and special ion-exchange capability of zeolites [8]. The use of zeolitic materials containing metal active species tetrahedrally coordinated into zeolitic framework for catalytic abatement of phenol. Mordenite is hydrophilic molecules because it has low content of Si/Al ratio close to one [9].

The problems of scarcity and the bad use of water have been increased because of the industrial activity, from where effluents with high toxicity and biodegradation difficulties are coming from. For that reason, it is essential to treat these effluents before they are released to the municipal wastewater treatment plants. From the wide variety of chemical processes focused on the treatment of industrial effluents with high content of organic compounds [10], it is found the advanced oxidation processes (AOPs), which develop technologies such as the oxidation of organic compounds, e.g. the catalytic wet air oxidation (CWAO). The improvement of this process is based on the variation either of the catalyst or the oxidant source because they directly affect the operational conditions and cost. The use of catalysts in oxidation processes has been extensively studied; moreover, many of these catalysts belong to the oxidant media in liquid phase but they increase the effluent contamination. For this reason, the present research work proposes to get advantage of the catalytic activity heterogeneous catalysts in the CWPO of phenol. This research aims to study the catalytic activity of the H-mordenite and

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
http://dx.doi.org/10.5155/eurjchem.6.4.488-492.1340

platinum supported H-mordenite toward phenol removal. These catalysts were prepared and characterized using several techniques. Then, different experimental parameters were studied to arrive at the optimal conditions for phenol removal. It is concluded that the removal percent obtained using H-mordenite is close to the removal percent obtained using Pt/ H-mordenite.

2. Experimental

2.1. Materials

Phenol (phenol solution 80%, *w*:*w*, in water) was obtained from BDH Chemicals, England. Buffer solution with ratio of pH = 4 (citric acid), pH = 7 (phosphate) and pH = 10 (boric acid) from Merck were used to adjust the pH of solution. Zeolites (namely) Ammo-Mordenite were supplied by Zeolyst International, USA. Zeolites were either in NH_4^+ (Ammo) or anion form. Hexachloro platinic acid (H_2PtCl_6) as metal precursor obtained from Merck.

2.2. Analyses

The concentrations of the residual phenol were measured using UV-Vis spectrophotometer (UV-VIS-NIR-3101 PC, Shimadzu) at 270 nm. The reaction was done in shaking water bath. Systronic pH meter (Model 331) was used for pH measurements. In order to remove catalyst particles from suspensions before analysis, the suspensions were centrifuged with Type-H-11n and 5000 rpm for 10 min. Scanning electron microscopy (SEM) was carried out using Jeol JSM 5300 Japan. The high resolution transmission electron microscopy (HR-TEM) was carried out with a JEOL electron microscope (JEM-2100), operated at 200 kV, Japan. The X-ray diffraction analysis (XRD) was carried out by PANalytical, X'PRT PRO using Cu-target with Ni-filtered radiation (λ = 1.542 Å), Spectris plc Headquartered in Egham, Surrey, England. The diffraction angle (2θ) was ranged between 2 and 60 °. X-ray fluorescence was done with PANalytical, Epsilon 1 High-stability ceramic side window, 50 µm thin window (Be) for higher intensities and max voltage of 50 kV, ideal for analyzing heavier elements Headquartered in Egham, Surrey, England. The chemisorption measurements were carried out using Micrometritics TPD/TPR 2900 analyser.

2.3. Preparation of the catalysts

2.3.1. Preparation of hydrogen-mordenite

Hydrogen form of mordenite is prepared from the Na-form by exchanging Na^+ ions with 1 M NH_4Cl. Zeolite (10 g) was refluxed with 300 mL of 1 M NH_4Cl under agitation at 80 °C for 12 h. The solid was filtered, washed with deionized water several times, and dried at 120 °C overnight. The ammonium form obtained was calcined at 500 °C for 3 hr in the presence of current air (40 mL/min). High calcination temperatures helped to create the H-form (hydrogen form) of zeolites by decomposing the NH_4-form and removed the organic impurities. Thus, calcinations at the above stated temperatures were enough to convert all the zeolites into H-form [2].

2.3.2. Preparation of Pt/H-mordenite

High dispersed nano-Pt particles containing catalyst was prepared by using hexachloroplatinic acid (H_2PtCl_6) as metal precursor and impregnation with hexadecyltrimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$) as surfactant [11]. These nano catalysts prepared using CTAB as follow;

The molar ratio of CTAB/H_2PtCl_6 is 2 according to the stoichiometric equation (1,2):

$$H_2PtCl_6 \rightarrow 2H^+ + (PtCl_6)^{2-} \quad (1)$$

$$2\ C_{19}H_{42}BrN \rightarrow 2\ C_{19}H_{42}N^{1+} + 2\ Br^{1-} \quad (2)$$

The required volume of the platinum complex solution that be needed to reach the aimed final platinum content (1.0 wt % Pt) was added drop-wise to a suspended solution of 2 g of H-mordenite in 10 mL of deionized water under stirring. The mixture was stirred for 1 h at room temperature. Drying, calcination and reduction processes were carried as mentioned before.

2.3.3. Catalyst characterization

Chemical analysis was carried out to evaluate total silica, alumina and alkali metals by X-ray fluorescence and the ignition loss (I.L.) was obtained by heating to 1000 °C till constant weight. Scanning electron microscopy is a technique used to investigate the morphology of the crystals after coating with thin film of gold to be conductive. All samples were mounted on stubs and gold-coated prior to analysis, to make them electrically conductive. The magnification was about ×2500. The morphology, location and size distribution of Pt particles have been investigated by high resolution transmission electron microscopy. The sample for this analysis were first prepared in a suspension with 30% of ethanol, and the mixture then ultrasonicated for 5 min until the suspension was homogeneous. Afterwards, one drop of this mixture was placed over a copper grid previously covered with collodion and coal for use in the HR-TEM. The structural parameters were determined by X-ray diffraction analysis. The specific surface area for the parent and prepared impregnated samples were determined from N_2 adsorption-desorption isotherms measured at liquid nitrogen temperature (-196 °C). All samples were degassed at 350 °C for 2 h in nitrogen atmosphere prior to adsorption. The chemisorption measurements were carried out by using a dynamic pulse technique with an argon flow of 50 mL/min and pulses of H_2 (99.9995% purity). In order to calculate the metal dispersion, an adsorption stoichiometry of metal/H = 1 was assumed. Dispersion measurements with H_2 pulses were carried out at 60 °C to avoid the spill over phenomenon. Previously, the sample was pre-treated by heating at 15 °C/min in argon flow up to 250 °C and kept constant at this temperature for 20 min. Then, the sample was reduced in situ. Next, the hydrogen was removed by flowing nitrogen for 30 min, the temperature being 10 °C higher than the reduction temperature. Finally, the sample was cooled to the experiment temperature in an argon gas flow. The dispersion measurements with H_2 pulses had an error of ±5% [12].

2.4. Catalytic activity of the catalysts

The catalytic removal of phenol from water was studied by suspending an optimized amount of catalyst (1 g) (H-mordenite:Pt/H-mordenite) in 100 mL of solution containing 100 ppm of phenol in a glass reactor dipped in shaking water bath with temperature controller. The solution was stirred constantly at 150 rpm and 25 °C. The reaction was run for 6 hr. Prior to analysis, 5 mL of the suspension was withdrawn from the reactor and centrifuged for 10 min and the absorbance was measured in 270 nm by using a calibrated UV spectrophotometer [13]. The removal efficiency of phenol was estimated by applying the following equation:

$$\text{Removal \%} = ((A° - A)) / (A°) \times 100 \quad (3)$$

where A° and A are blank (before reaction) and sample absorbance, respectively. Based on the Beer-Lambert's law A° and A are proportional to C° and C which C° and C are the concentration of blank and sample at *t* time [13].

Table 1. Chemical analysis of Na-mordenite, H-mordenite and Pt/H-mordenite.

Components	Na-Mordenite, Wt%	H-Mordenite, Wt%	Pt/H-Mordenite, Wt%
SiO_2	66.760	76.934	76.934
Al_2O_3	10.480	12.829	12.829
Na_2O	7.670	0.511	0.511
CaO	0.351	-	-
Fe_2O_3	0.169	0.499	0.499
MgO	0.119	0.234	0.234
ZrO_2	0.150	-	-
Cl^-	0.099	0.139	0.139
K_2O	0.082	0.087	0.087
Cr_2O_3	0.022	-	-
PbO	0.098	-	-
P_2O_5	-	0.025	0.0025
SO_3	-	0.042	0.042
CuO	-	-	-
ZnO	-	-	-
SrO	-	-	-
NiO	-	-	-
TiO_2	-	-	-
Pt	0	0	1
SiO_2/Al_2O_3 molar ratio	6.37	5.99	5.99
Ignition loss (I.L.) *	14.000	8.700	8.700

* Ignition loss (I.L), as determined by burning one gram sample at 1000 °C till constant weight.

H-Mordenite **Pt/H-Mordenite**

Figure 1. SEM photos for mordenite and Pt/H-mordenite.

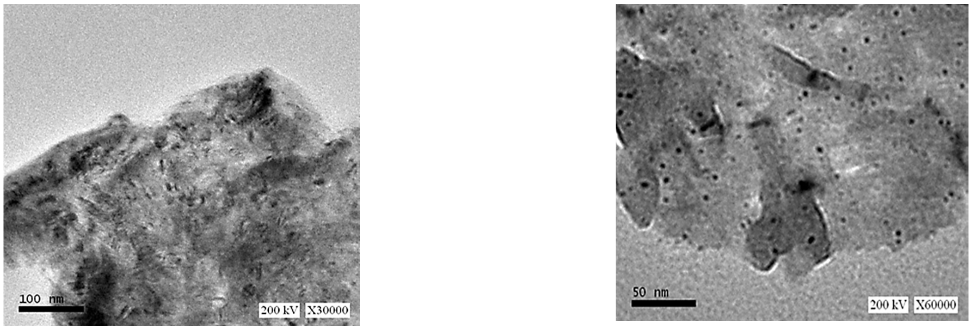

Figure 2. HR-TEM for Pt/H-mordenite.

3. Results and discussion

3.1. Analysis and characterization of the prepared samples

3.1.1 Chemical analysis

The results of chemical analysis of zeolites are presented in Table 1. It is clear that the silica/alumina ratio (SiO_2/Al_2O_3 = ~6.37) for mordenite in conformity with the published value [14]. The low content of Na_2O in the H-forms of mordenite indicates the high exchangeability of Na-mordenite and with ammonium chloride solution.

3.1.2. Scanning electron microscopy (SEM)

Scanning electron microscopy for the samples is represented in Figure 1. H-mordenite appears as corn flake-like crystals with a fluffy appearance revealing its extremely fine plate-like structure [15]. Pt crystallites are noticeable in sample Pt/H-mordenite.

3.1.3. High Resolution Transmission electron microscopy (HRTEM)

The morphology, location and size distribution of Pt particles have been investigated by HR-TEM. The HR-TEM micrographs of Pt/H-mordenite catalyst are shown in Figure 2. HR-TEM pictures of the platinum catalyst with a content of 1 wt. % confirmed high metallic dispersion of the platinum catalysts.

3.1.4. X-Ray diffraction analysis

Pt/H-mordenite was analyzed by X-ray powder diffraction technique.

Table 2. Textural properties for catalysts *.

Sample	S_{BET}, m²/g	V_m, cc/g	r, Å
H-Mordenite	321.830	0.092	11.963
Pt/H-Mordenite	353.084	0.093	12.644

* SBET, surface area Vm, the monolayer capacity is the volume of gas required to cover the whole surface of the solid with a unimolecular layer in cm³/g.

The diffraction pattern is shown in Figure 3. The pattern of Pt-containing catalyst shows good dispersion of Pt on the surface of the support.

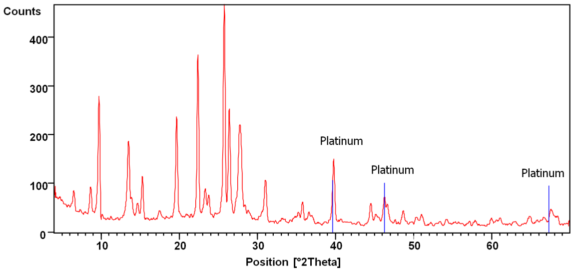

Figure 3. XRD pattern of Pt/H-mordenite.

3.1.5. N_2 adsorption-desorption isotherms

N_2 Adsorption-desorption indicates the values of specific (Brunauer-Emmett-Teller) BET surface area (SBET), together with the total pore volumes (Vm) and average pores radius (r, Å) after application of BET equation, summarized in Table 2 [16]. It was seen that Pt loading has insignificant effect on the surface textural characteristics. This could be related to distribution of the Pt particles on the surface of H-mordenite which has high surface area (321 m²/g).

3.1.6. Metal dispersion

The dispersion of metal particles over the support is an important parameter to be controlled since it determines the quantity of metal particles available on the support surface to participate in a reaction. The metal dispersion for Pt/H-mordenite is 31.95%.

3.2. Preliminary study of phenol removal

Preliminary tests including phenol removal in aqueous solution on H-mordenite and Pt/H-mordenite are represented in Figure 4. The two samples can remove phenol despite of low efficiency. The poorest removal for mordenite is possibly due to its hydrophilic nature and lower SiO_2/Al_2O_3. The ring dimension is small (0.26 × 0.57 nm), this is also a reason for low removal since phenol molecular size is higher (0.6 nm) [2]. The phenol removal efficiency using H-mordenite was 43.6% within 3 h in case of using Pt/H-mordenite the removal was 43.9% within 3 h. Hence, no significant increase in the removal was observed in case of loading by Pt, because that the surface area for Pt/H-mordenite is close to the surface area of the parent H-mordenite.

3.3. Effects of removal parameters

The first parameter measured used in this study was temperature which was 30-50 °C, Figure 5. As can be seen, temperature showed quite significant impact on phenol removal process using either H-Mordenite or Pt/H-Mordenite. The highest removal was at 50 °C.

On the other hand, fixed phenol solutions were put in oxidation at different pH values 3, 5, 7 and 9. Figure 6 showed that the maximum removal value for H-mordenite was 11.6% obtained at pH = 7. In case of Pt/H-mordenite, the maximum removal value was 13.1% obtained at pH = 9.

The removal of phenol was studied over a wide range of initial concentration from 25 to 200 ppm. Figure 7 shows variation of phenol concentration for each catalyst. Removal efficiency of phenol decreased with increasing phenol concentration for all catalysts. This can be explained in the term of the saturation of the limited number of active sites of the catalyst. The active sites for catalytic reaction remain the same at fixed catalyst dosage [17].

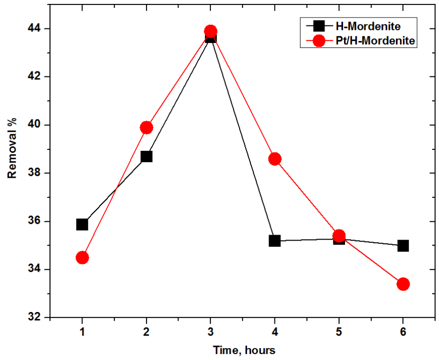

Figure 4. The effect of the time on the phenol removal in aqueous solution on H-mordenite and Pt/H-mordenite.

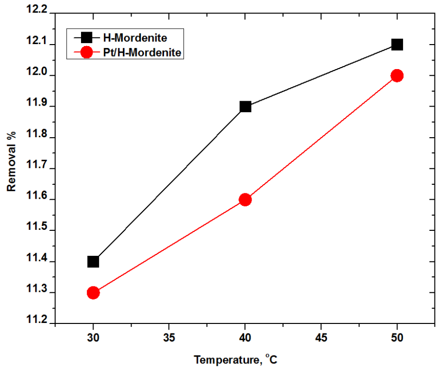

Figure 5. The effect of temperature on phenol removal in aqueous solution on H-mordenite and Pt/H-mordenite.

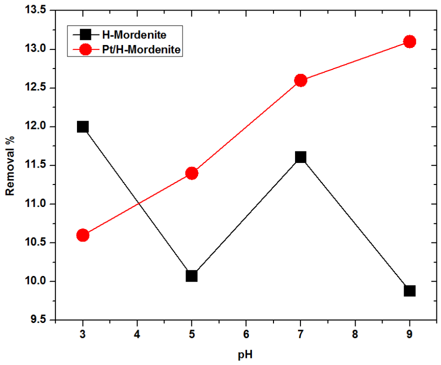

Figure 6. The effect of pH on phenol removal in aqueous solution on H-mordenite and Pt/H-mordenite.

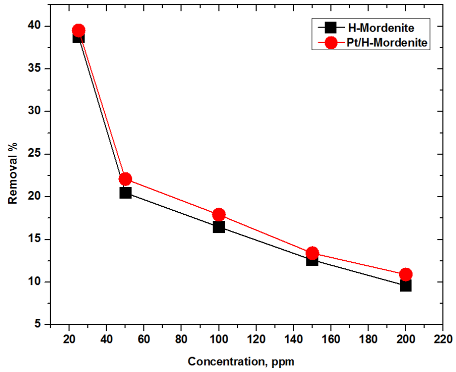

Figure 7. The effect of initial concentration on phenol removal in aqueous solution on H-mordenite and Pt/H-mordenite.

Figure 8 shows the effect of catalyst loading (0.2-0.5 g) on phenol removal. High catalyst dose in solution would result in higher phenol removal, because increasing the amount of catalyst will increase the adsorption and also the available active sites to initiate the oxidation [7]. The optimum loading for all catalysts were 0.5 g. The highest removal of phenol using H-mordenite was 37% while this value increased to 38.1% in case of using Pt/H-mordenite.

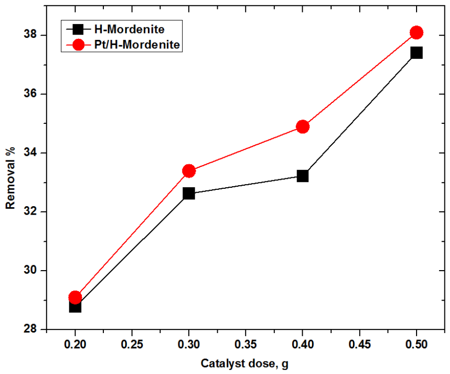

Figure 8. The effect of catalyst dose on phenol removal in aqueous solution on H-mordenite and Pt/H-mordenite.

The photocatalytic removal of phenol using H-mordenite and Pt/H-mordenite was studied at the optimum conditions for each catalyst from the previous experiments. The reaction was done in a quartz reactor. A Hg lamb of wavelengths greater or equal to 254 nm positioned above removal experiment was positioned above the shaker to supply irradiation process. UV at 254 nm can remove low concentrations of phenol. This wavelength is in the region of maximum germicidal effectiveness and is highly effective in phenol removal by generating OH radicals in the solution (OH radicals are formed when this radiation strips the hydrogen atoms from water molecules). The energy of this wavelength (470 kJ/mol) is higher than the bond energy of O-H (462.8 kJ/mol), C-O (357.7 kJ/mol), C-H (413.0 kJ/mol), so these bonds probably break upon UV irradiation [18]. We can see that the percent of removal increased to 41% using H-mordenite. In case of using Pt/H-mordenite the percent of removal increased to 41.2%.

4. Conclusions

The present study illustrates the removal of phenol by using H-mordenite and Pt/H-mordenite. It was seen that the loading with platinum is not effective in phenol removal because that Pt loadings have insignificant effect on the surface textural characteristic, which is related to distribution of the Pt particles on the surface of H-mordenite which has high surface area. In case of using H-mordenite, the optimum conditions at which the best removal of phenol occurs were 0.5 g of catalyst, pH = 7, 50 °C, 100 ppm of phenol and irradiation with UV (254 nm) within 3 hr. Also, the loading with platinum have the same conditions but at pH = 9.

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