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Comparative Study of Rate Constant of Metallophthalocyanines as Nitrogen Dioxide Sensor

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ABSTRACT

Cobalt Phthalocyanine (CoPc), Copper Phthalocyanine (CuPc), Zinc Phthalocyanine (ZnPc) and Iron Phthalocyanines (FePc) are synthesized by chemical reaction from phthalic anhydride and urea. After characterization of materials by XRD, UV Visible and FTIR, sensor samples are prepared in the form of pellets. The change in electrical resistance due to exposure of samples to different concentrations of nitrogen dioxide (NO_2) of the samples is studied. All samples are studied at room temperature. Response curves of the samples are plotted and best fitted with the chemisorptions kinetics to determine rate constant. The rate constants for different NO_2 concentrations and different materials are compared. ZnPc showed highest response rate than CuPc and CoPc and FePc.

Key words: Metal Phthalocyanine, Gas Sensor, Nitrogen Dioxide, Rate constant.

INTRODUCTION

The main issue of public health is the degradation of the air quality in industrial and highly dense fuel vehicle areas. It is due to unavoidable emission of toxic air pollutants [1]. The combustion of diesel generates suspended particulate matter (SPM), nitrogen oxides (NO_x), sulphur dioxide, polycyclic aromatic hydrocarbon (PAH) and also carbon monoxide (CO). Highly pollutant and toxic gas like NO_2 in an environment has become important as a result of increased automobile fuel

vehicles and production in the chemical industries [2]. Phthalocyanines (Pcs) and structurally related compounds are of interest in gas sensor applications. In earlier paper Chakane et el. studied NO_2 sensor using metallophthalocyanine (MPc) coated on porous silicon [3]. The family of MPc has been found to be highly reactive with strong oxidizing gases such as NO_2 [4]. CuPc, CoPc, ZnPc, FePc are belongs to this family of organic molecular solids. Their composition consists of hydrogen, carbon, nitrogen and substituted metal atom arranged into a macrocycle. Their semiconducting properties are exploited for gas sensing applications. The gas sensing principle is based on the change of conductivity upon the adsorption of gas species at the surface. The conductivity of p-type MPcs increases on the adsorption of oxidizing molecules, because of the increase of the hole carriers induced by the formation of charge transfer complexes at the surface of phthalocyanines [5]. The response characteristics study in this work shows that the rate of change of sensitivity is different for different concentrations of NO_2 gas. The response rate increases with increase in NO_2 gas concentration in the air surrounding the sample. The rate of change of sensitivity is expressed in form of the equation in terms of rate constant. The response characteristics are best fitted with the equation to determine rate constant. The comparative study of the determined rate constants respective to various NO_2 concentrations and different sensor materials is discussed in this paper.

METHODOLOGY

Synthesis procedure of MPcs involves mixing of phthalic anhydride, urea and metal salt taken in the weight proportion of 4:4:1 along with the catalyst ammonium molybdate. These precursors are crushed together and mixed properly. The mixture is then heated with constant stirring. Reaction took place at about 200°C– 250°C. The residue is crushed to a fine powder. Un-reacted precursors are removed by several times washings with methyl alcohol and distilled water. The powder is then air-dried under IR lamp and uniformly crushed to make fine and uniform granules. Synthesized MPcs were characterized by bulk XRD, UV-Visible absorption spectra and FTIR spectroscopy. Samples in the form of pellets were prepared for studying the gas response. The synthesized MPc material was compacted into the pellets of 13 mm diameter using press technique. Three parameters viz. pressure, time weight of MPc material were optimized. Electric contacts were made by coating silver paste on either surface of the pellet.

Gas exposure tests of prepared sensor samples were performed in a controlled environment at room temperature using specially designed glass chamber to obtain data toward the detection of NO_2 mixed with atmospheric air. Electrodes from sample were connected to keithley-2000 electrometer in order to measure sample resistance. Electrometer is interfaced to computer through RS-232 port provided at the back panel of electrometer. Software provided by keithley is used to monitor the resistance in the domain of time.

RESULTS AND DISCUSSION

CuPc, CoPc, ZnPc and FePc sensor samples were exposed to 0.5 volume % concentration of NO_2. The resistance is monitored with 30 seconds interval and the response is plotted. The response of CuPc samples with different NO_2 concentration is shown in Figure 1 in terms of instantaneous sensitivity S(t) given by equation 1.

$$S(t) = \frac{\left(R_a - R_g\right)}{R_a} \times 100\% \qquad (1)$$

Where, R_a and R_g are initial resistance and resistance in the presence of gas of the sample respectively.

It is seen from the response graph shown in figure 1 that the response rate is different phthalocyamines for same NO_2 gas concentrations. The variation of electric current or resistance during the doping stage of the sensing period is given by kinetic model based on gas adsorption/desorption theory. The derived general form of it is expressed as equation 2 [6].

$$S(t) = S(1 - e^{-b\,t}) \qquad (2)$$

Where, S (t) is instantaneous value of sensitivity, S is steady state value of sensitivity, b is rate constant in the doping stage and t is time. In order to determine the rate constant b, equation 2 can be modified as,

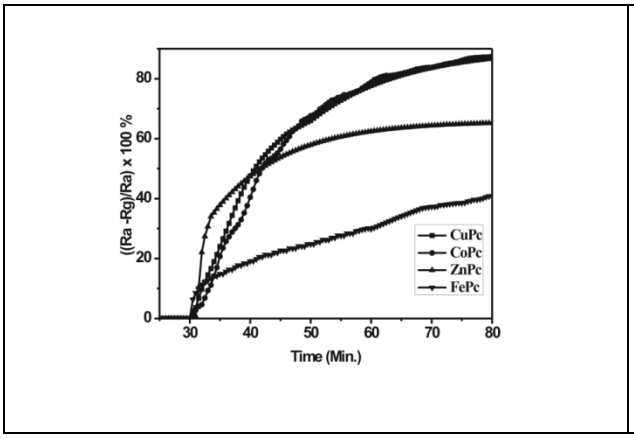

Figure 1: Response of CuPc, CoPc, ZnPc and FePc pellets to 5000 ppm NO_2.

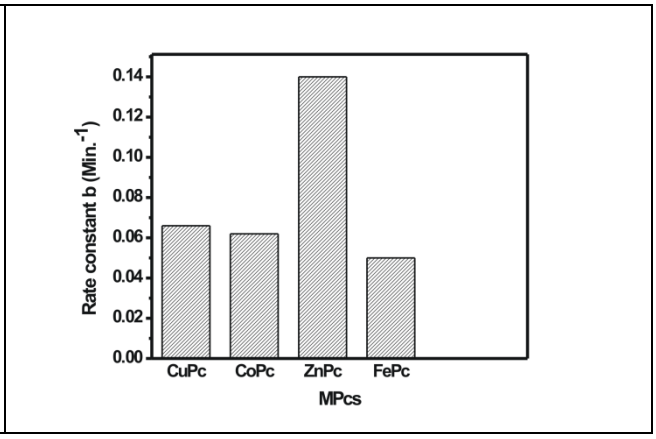

Figure 2: Rate constant for CuPc, CoPc, ZnPc and FePc pellets to 5000 ppm NO_2.

$$\ln\left(\frac{S}{S-S(t)}\right) = b\,t \qquad (3)$$

The slope of graph of $\ln\left(\frac{S}{S - S(t)}\right)$ versus t will give the value of rate constant b. The rate constant b is related to the rate constant of adsorption (K_a) and desorption (K_d) as $b = K_a C_0 + K_d$. C_0 represents the bulk concentration of NO_2 present in the test chamber. The comparative values of rate constant b are plotted in the following graph.

It is seen from figure 2 that the value of rate constant of ZnPc pellet is highest and that of FePc is smallest. Hence ZnPc shows highest response rate. Further studies are needed to study the adsorption and desorption process which is responsible for response rate.

CONCLUSION

The time dependence of the response of MPc sensors to NO_2 changes with MPc material. ZnPc showed highest response rate, the sensitivity of which is smaller than CuPc and CoPc. Hence the materials having small sensitivity can be used as gas sensors if initial short time exposure to the gas is taken into account.

Conflicts of interest: The authors stated that no conflicts of interest.

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