

Laser-assisted Synthesis of Pd/Metal-Organic Framework and Its Application in the Sensing of Ethanol and Methanol Vapors

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ABSTRACT—In this research, palladium nanoparticles (Pd NPs) were first synthesized using laser ablation in the deionized (DI) water environment. Also, metal-organic framework (MOF) was produced using the solvothermal method at a temperature of 150°C. To accumulate Pd NPs on the synthesized MOF, ultrasonic and magnetic stirring methods were used. Different analytical methods were used to investigate the structure and morphology of the synthesized nanocomposite. Also, the sensitivity of the synthesized nanocomposite to ethanol and methanol organic vapors was investigated. The results showed an increase in the response of the MOF in the presence of nanoparticles.

KEYWORDS: Gas sensor, Laser ablation in liquid, Metal-organic frameworks, Organic vapors, Palladium nanoparticles.

I. INTRODUCTION

Organic vapors and hazardous gases pose significant to human health and the environment. Various gases and volatile organic compounds (VOCs) such as NH₃, CO_x, NO_x, aromatic and aliphatic hydrocarbons, ketones, alcohols and aldehydes are emitted into the atmosphere through industrial and human activities, exerting considerable effect on the environment, global climate and human health. Accordingly, the development of gas and VOCs sensors with high selectivity and

sensitivity is imperative for detecting such harmful compounds and safeguard of human health and environment. Sensing materials play a crucial role in gas/VOCs detection systems [1]-[3].

One type of unique crystalline porous material is MOFs which are manufactured through self-assembly of metal ions/clusters and organic ligands. MOFs exhibit remarkable properties such as structural variety, high porosity, large surface area and excellent adsorption. Consequently, they have attracted significant attention for various applications, including gas adsorption/desorption and catalysis. The adjustable pore size, shape and surface environment of MOFs can enhance their selectivity and sensitivity. The porosity of MOFs can also lead to a significant surface area and numerous active sites for accelerating surface host-guest reactions, increasing sensing sensitivity [3], [4]. In addition, MOFs with high specific surface area and pore volumes can effectively adsorb gases and vapors [5]. Composition of MOFs with conductive sensing elements can improve their performance. For example, composition of pristine graphene and MOF can improve the sensing performance where pristine graphene acts as a highly conductive sensing element and MOF with high specific surface area and adsorption capacity

increases sensitivity and selectivity for specific VOCs [6].

Titanium-based MOFs (Ti-MOFs) are a notable category of MOFs, highly regarded due to the beneficial properties of the Ti element such as low toxicity and abundance. Therefore, Ti-MOFs have made significant progress, especially Materials Institute Lavoisier framework (MIL)-125 which is constructed from Ti₈ clusters and dicarboxylate linkers [7]. MIL-125 (Ti)-NH₂ is a common and stable 3D disc-like with large surface area and available metal sites [8]. The crystalline structure of MIL-125 (Ti)-NH₂ is fabricated from the cyclic octamers constructed from octahedral titanium units present at edge or corner [9]. The presence of -NH₂ can improve the aqueous phase stability of MIL-125(Ti) [10]. It shows a significant gases and vapors adsorption ability. Compared with other MOFs such as UiO-66-NH₂ and MIL-101-NH₂, MIL-125 (Ti)-NH₂ showed better performance toward adsorption of VOCs [11].

It was reported that the presence of metallic NPs can improve performance of gas/vapor sensors by increasing electrical conductivity and their spillover influence. In the spillover mechanism of metallic NPs, oxygen molecules can rapidly adsorb and desorb on the substrate and convert to the oxygen species by electrons. Therefore, incorporating metallic NPs can increase reactive oxygen species on the substrate to interaction with gas molecules, improving gas sensor response [12]-[14]. In addition, high surface area of nanoparticles can provide more active surface areas to target gas molecules for interactions and improves sensing performance subsequently. Pd NPs can increase number of chemisorbed oxygens because of their excellent oxygen dissociation catalytically. It was reported that decoration of Pd NPs onto the deposited ZnO nanoroads onto Si/SiO₂ substrate can improve gas sensor response towards C₂H₅OH [15].

There are two principal methods for metallic NPs synthesis, containing of bottom-up methods and top-down methods. The main difference between both the methods lies in the

starting materials used. In top-down methods, bulk materials are utilized as starting material which are reduced to smaller particles through physical, mechanical and chemical approaches. In contrast, atoms or molecules are used as starting materials in bottom-up methods. The choice of appropriate method for metallic NPs synthesis is an important issue due to its strong effect on the morphology, stability and physicochemical features of metallic NPs. Laser ablation is a top-down method, in which laser radiation is utilized to prepare particles in nano size from bulk materials. This method is known as a simple and efficient technique for preparing large content of NPs, in which features of NPs are controllable through adjusting laser parameters [16], [17].

In this study, the synthesized Pd NPs through laser ablation in DI water were supported on MIL-125(Ti)-NH₂ using simple and clean method. The characterization of the prepared nanocomposite indicated that MIL-125(Ti)-NH₂ are formed in the shape of microdiscs with average size of about 1.46 μ m. Small content of Pd NPs were successfully agglomerated on the microdiscs. It was concluded that the presence of Pd NPs can improve the sensitivity and sensing response of MIL-125(Ti)-NH₂ toward methanol and ethanol detection.

II. EXPERIMENTAL SETUP

A. Preparation of MIL-125(Ti)-NH₂/Pd nanocomposite

To synthesis Pd NPs, the laser ablation in deionized (DI) water was employed as a fast and clean method to produce Pd colloidal using a fiber laser (RFLP30Q) operating at a wavelength of 1064 nm, a power of 18 W, frequency of 20 kHz and scan speed of 400 mm/s. Firstly, the Pd target was washed with acetone and DI water, respectively, and then placed in a glass petri dish filled with 10 mL of DI water. The laser beam was focused on a square area (4 mm \times 4 mm) of the target. The color of DI water was changed to black during the laser ablation in liquid (LAL) process, suggesting Pd NPs synthesis. To prevent agglomeration of Pd NPs and reduction in power, the process was stopped every 5 min

irradiation and the product was poured into another glass vessel. After 20 min, Pd NPs with a weight of 0.004 g was produced.

To prepare MIL-125(Ti)-NH₂, the solvothermal process was utilized. Titanium tetrakisopropanolate (TTIP) (3 mmol, 0.852 g) and 2-amino terephthalic acid (NH₂-BDC) (6 mmol, 1.086 g) were prepared in a mixture of methanol (25 mL) and DMF (25 mL) and then stirred for 5 min at room temperature. The obtained solution was then poured into a 60 mL Teflon autoclave and placed at 150 °C for 24 h. The yellow precipitate was collected, washed with DMF and methanol for several times and then dried at 80 °C.

To prepare MIL-125(Ti)-NH₂/Pd nanocomposite, 0.134 g of MIL-125(Ti)-NH₂ was dispersed in 40 mL of DI water through 45 min of sonication and then added to the obtained Pd colloid (3 wt.%). To achieve a uniform suspension, the mixture was stirred for 12 h at room temperature. The obtained suspension was finely dried at ambient conditions. Figure 1 shows a schematic of the MIL-125(Ti)-NH₂/Pd nanocomposite preparation.

Different analytical techniques were used to characterize MIL-125(Ti)-NH₂ and nanocomposite. Morphological investigation of the nanocomposite was performed using scanning electron microscope (SEM) images. X-Ray diffraction analysis (XRD) was also used to evaluate the crystallographic structure of the samples. Fourier-transform infrared spectroscopy (FTIR) was provided information about the chemical bonds and functional groups of the samples.

B. Sensing Test

As reported in our previous study [2], a gold electrode with a thickness of 30 μm, a width of 250 μm and a distance between the electrode fingers of 250 μm placed on a SiO₂/Si substrate was used to detect ethanol and methanol vapors. 0.01 g of the samples (MIL-125(Ti)-NH₂ and nanocomposite) was drop casted on the electrode and dried at room temperature after 24 h.

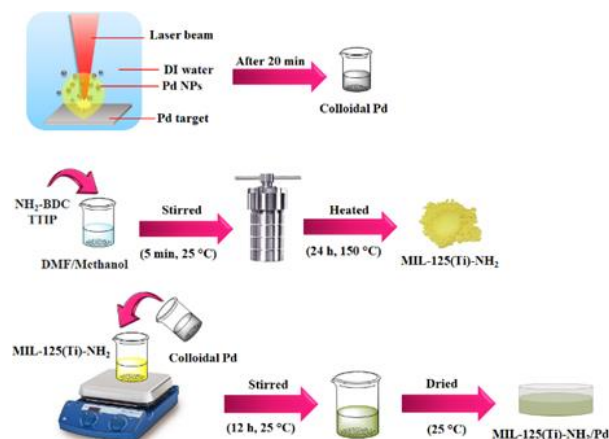


Fig. 1. Schematic representation of the preparation of MIL-125(Ti)-NH₂/Pd.

To test the sensor, an Erlenmeyer flask with one inlet and one outlet was used which was placed on a heater to evaporate methanol and ethanol. One side of the Erlenmeyer flask was connected to the inner chamber where the planer device was placed, and the other side was connected to an air pump. The planner device was also connected to the multimeter to measure the resistance of the samples every second. A volume of 100 ppm of ethanol or methanol was poured into an Erlenmeyer flask and then was placed on a heater with a temperature of 60 °C. The resistance was measured for 30 s. Then the air pump was turned on for 60 s to remove the vapors from the chamber. Figure 2 indicates a schematic of the sensing test setup. The gas response can finely acquire as follow:

$$\left| \frac{R_a - R_g}{R_a} \right| \quad (1)$$

where R_a is the resistance of the layer open to ambient air and R_g is the resistance of the layer exposed to the gas we are considering.

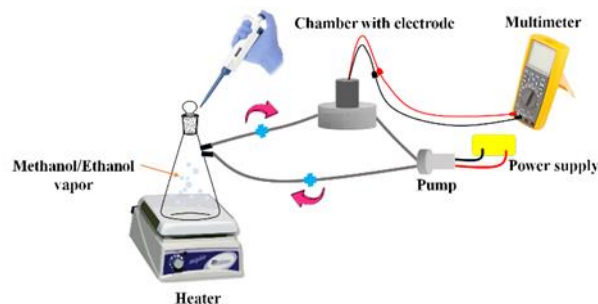


Fig. 2. Schematic representation of the sensing test

III. RESULTS AND DISCUSSIONS

Structure and morphology of the prepared Pd NPs and nanocomposite were evaluated through SEM images, as shown in Fig. 3. According to Figs. 3(a) and 3(b), spherical Pd NPs have been successfully synthesized. The MIL-125(Ti)-NH₂ microdiscs were also produced in varying sizes, as depicted in Figs. 3(c) and 3(d). This structure can provide a high surface area. The average size of these microdiscs was approximately 1.46 μm .

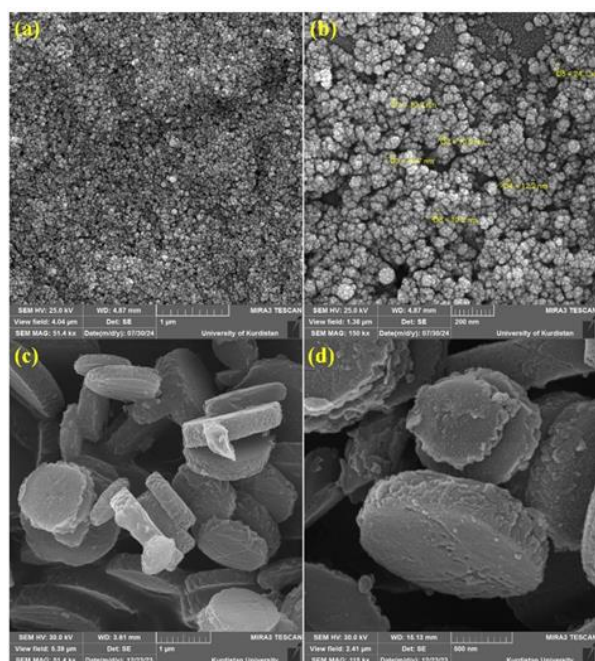


Fig. 3. SEM images of the prepared (a and b) Pd NPs and (c and d) MIL-125(Ti)-NH₂/Pd nanocomposite

Crystal structure of the prepared MIL-125(Ti)-NH₂ and nanocomposite was investigated using XRD patterns, as depicted in Fig. 4. Two sharp peaks located at 6.86° and 9.82° attribute to diffraction of (101) and (002) planes of MIL-125(Ti)-NH₂, respectively. Other peaks with lower intensity have been appeared at 11.73°, 15.47°, 16.67°, 17.98°, 19.64° and 22.66°, corresponding to diffraction of (211), (220), (103), (222), (213) and (004) [18]. The presence of Pd NPs can be confirmed by appearing a new peak at 40.13° attributed to diffraction of (111) (JCPDS 0431-046).

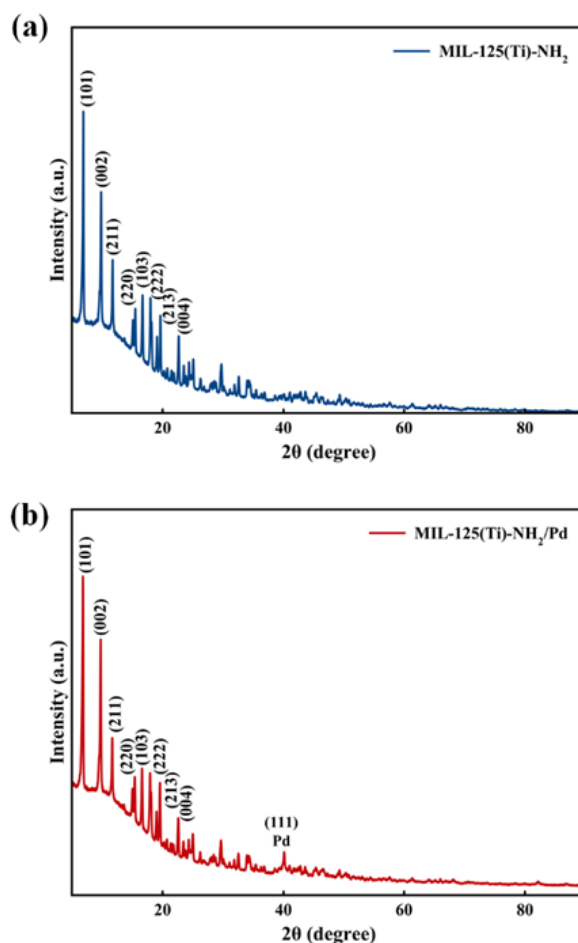


Fig. 4. XRD patterns of (a) MIL-125(Ti)-NH₂ and (b) MIL-125(Ti)-NH₂/Pd nanocomposite.

Figure 5 shows the FTIR spectra of MIL-125(Ti)-NH₂ and MIL-125(Ti)-NH₂/Pd nanocomposite. It is clear that the both samples have almost similar vibration bands. The broad peak in the range of 3687-3129 cm⁻¹ is due to the symmetric and asymmetric stretching of the -NH₂ group and -OH stretching of residual solvents, including methanol and water. The two bands at 1260 and 1662 cm⁻¹ corresponded to the N-C stretching vibration of aromatic amines and the N-H bend vibration, respectively. The vibrations of carboxyl linker are observed as three sharp peaks of 1540, 1439 and 1387 cm⁻¹. A sharp peak at 773 cm⁻¹ is due to the vibration of O-Ti-O bond. The peaks located in the region of 700-400 cm⁻¹ are attributed to Ti-O vibrations [8], [19], [20]. No new peak is created in the spectrum of MIL-125(Ti)-NH₂/Pd after loading Pd NPs.

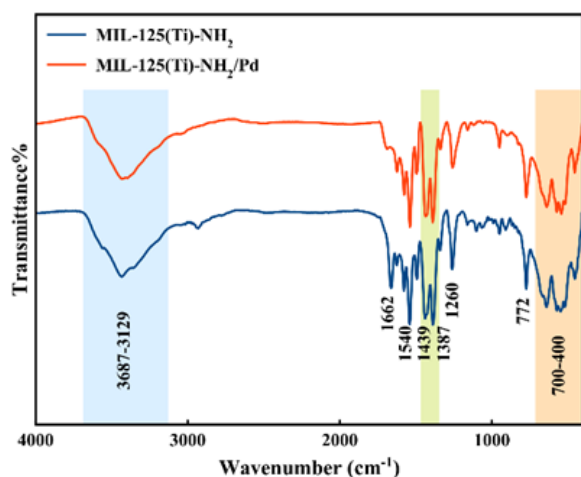


Fig. 5. FTIR spectra of MIL-125(Ti)-NH₂ and MIL-125(Ti)-NH₂/Pd nanocomposite.

Figures 6 and 7 demonstrate the results of the sensor test with ethanol and methanol vapors introduced at concentration of 100 ppm. For more accuracy, five cycles were measured for each vapor, showing very good reproducibility of the sensor. The fluctuations in the graph are also due to the resistance of the material being measured every second, causing the system not to have enough time to stabilize, leading to these fluctuations. Three parameters which are considered important are maximum response, recovery time and response time. The response time is introduced as the time that it takes for a gas meter to display 90% of the gas volume injected into the sensor. The recovery time is the time required for the sensor to return to 90% of the initial original signal after removing the vapor. It was observed that the sensing sensitivity of MIL-125(Ti)-NH₂ was enhanced after adding Pd NPs. The maximum response at 100 ppm for ethanol vapor with MIL-125(Ti)-NH₂ is 19.4, which increased to 26.6 after adding Pd NPs. For methanol at a concentration of 100 ppm with the presence of MIL-125(Ti)-NH₂, this value obtains as 43.5, which increased to 75.1 (an increase of 1.7 times) after loading Pd NPs. In the presence of ethanol vapor, recovery time decreased from 28 s to 25 s by adding Pd NPs. For methanol vapor, loading Pd NPs was also led to reduce the recovery time from 24 s to 21 s. Adding Pd NPs was also caused to reduce in the response time from 12 s to 8 s and 15 s to 7 s for ethanol and methanol vapors, respectively. These results are summarized in Tables 1, 2 and 3. Accordingly, methanol has better interaction with

nanocomposite compared with ethanol. This is attributed to methanol's higher polarity, leading to more interaction between methanol and MIL-125(Ti)-NH₂.

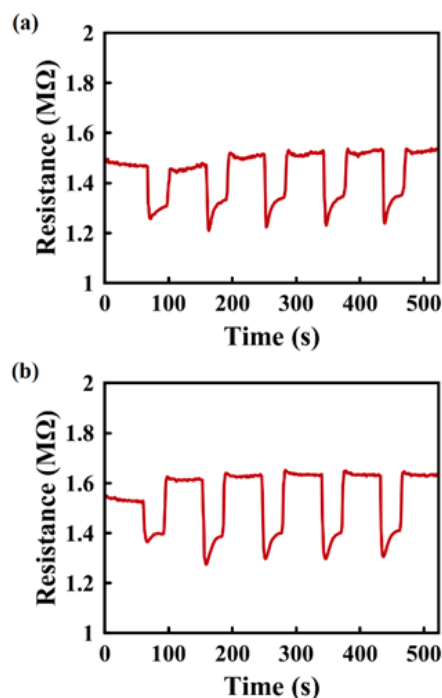


Fig. 6. Response of (a) MIL-125(Ti)-NH₂ and (b) MIL-125(Ti)-NH₂/Pd in volume of 100 ppm of ethanol.

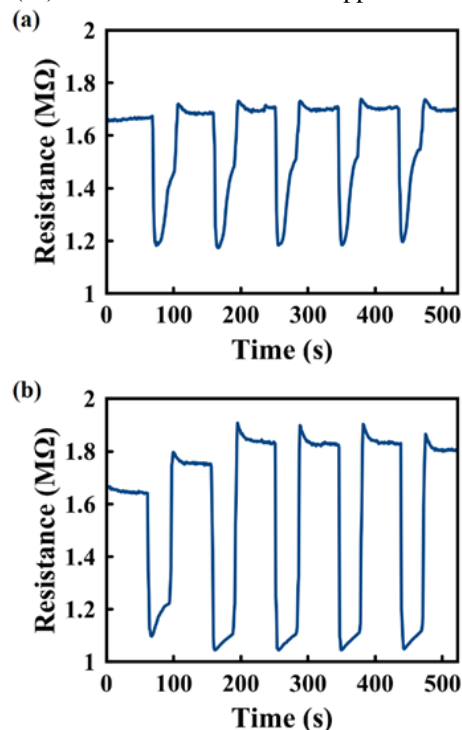


Fig. 7. Response of (a) MIL-125(Ti)-NH₂ and (b) MIL-125(Ti)-NH₂/Pd in volume of 100 ppm of methanol.

Porous structure of MOFs provides high specific surface area, leading to active sites for gas adsorption and transport. In addition, loading Pd NPs can increase the electrical conductivity and improve response of MIL-125(Ti)-NH₂. In addition, the presence of Pd NPs can enhance the response of MIL-125(Ti)-NH₂ through spillover mechanism, in which oxygen molecules can rapidly adsorb and desorb on the MIL-125(Ti)-NH₂. Moreover, the Pd NPs can improve interaction of the adsorbed oxygen species from the exterior and vapor molecules [13].

Table 1. The maximum response of samples in volume of 100 ppm of ethanol and methanol.

| Sample | Gas type | Vapor (%) |
|---------------------------------|----------|-----------|
| MIL-125(Ti)-NH ₂ | Ethanol | 19.4 |
| MIL-125(Ti)-NH ₂ /Pd | Ethanol | 26.6 |
| MIL-125(Ti)-NH ₂ | Methanol | 43.5 |
| MIL-125(Ti)-NH ₂ /Pd | Methanol | 75.1 |

Table 4. Comparison of sensing response of the synthesized MIL-125(Ti)-NH₂/Pd with some other composites including Pd NPs.

| Composite | Methanol vapor concentration (ppm) | Operating temperature | Response | Ref. |
|---------------------------------|------------------------------------|-----------------------|----------|-----------|
| Pd-ZnO | 190-1530 | 200 °C | 85% | [21] |
| Pd-ZnO | 100 | 70 °C | 72.19% | [22] |
| PdO/CeO ₂ | 100 | 200 °C | 6.95 | [23] |
| MIL-125(Ti)-NH ₂ /Pd | 100 | Room temperature | 75.1% | This work |

According to Table 4, the fabricated nanocomposite indicates considerable response toward methanol sensing at a low operating temperature.

The results demonstrate that the sensors exhibit high selectivity, making them suitable for applications where accurate detection of ethanol and methanol is critical. Additionally, the sensitivity and limit of detection (LOD) of the sensors were evaluated, highlighting their effectiveness. To assess the selectivity of the sensors, resistance measurements were taken at various concentrations of ethanol and methanol. The concentrations tested 100 ppm. The selectivity ratio was calculated using the following formula [24]:

$$\text{Selectivity Ratio} = \frac{\text{Response to Gas}}{\text{Response to Interference}} \quad (2)$$

Table 2. The recovery times of samples in volume of 100 ppm of ethanol and methanol.

| Sample | Gas type | Time (s) |
|---------------------------------|----------|----------|
| MIL-125(Ti)-NH ₂ | Ethanol | 28 |
| MIL-125(Ti)-NH ₂ /Pd | Ethanol | 25 |
| MIL-125(Ti)-NH ₂ | Methanol | 24 |
| MIL-125(Ti)-NH ₂ /Pd | Methanol | 21 |

Table 3. The response times of samples in volume of 100 ppm of ethanol and methanol.

| Sample | Gas type | Time (s) |
|---------------------------------|----------|----------|
| MIL-125(Ti)-NH ₂ | Ethanol | 12 |
| MIL-125(Ti)-NH ₂ /Pd | Ethanol | 8 |
| MIL-125(Ti)-NH ₂ | Methanol | 15 |
| MIL-125(Ti)-NH ₂ /Pd | Methanol | 7 |

Table 4 shows comparison of sensing response of the prepared MIL-125(Ti)-NH₂/Pd with some other Pd NPs-based composite.

Since the interference response is considered zero, the selectivity ratio simplifies to the sensor's response to ethanol. Sensitivity was determined by performing a linear regression on the sensor's response to ethanol and methanol concentrations, and the LOD was calculated using the standard deviation of the baseline measurements and the sensitivity [25], [26]:

$$\text{LOD} = \frac{3\sigma}{\text{Sensitivity}} \quad (3)$$

where σ is the standard deviations of the system noise. Table 5 shows the selectivity and LOD results. For the MIL-125(Ti)-NH₂, the sensitivity of the methanol and ethanol vapors were determined to be approximately 0.004 and 0.002 MΩ/ppm, respectively. The limit of detection (LOD) was calculated to be 7 and 15

ppm for methanol and ethanol, respectively. The selectivity ratios indicate that the sensor demonstrated a reliable response to methanol. This consistent distinction between the methanol response and the baseline confirms that the sensor's response is predominantly due to methanol. For MIL-125(Ti)-NH₂/Pd, the

sensitivity of the methanol and ethanol vapors were approximately 0.008 and 0.003 MΩ/ppm, and the LOD were calculated to be 4 and 11 ppm, respectively. The selectivity ratios indicate that the sensor demonstrated a reliable response to ethanol.

Table 5. The selectivity, sensitivity and LOD results of samples in volume of 100 ppm of ethanol and methanol.

| Sample | Gas type | Sensor response (MΩ) | Selectivity | Sensitivity (MΩ/ppm) | LOD (ppm) |
|---------------------------------|----------|----------------------|-------------|----------------------|-----------|
| MIL-125(Ti)-NH ₂ | Ethanol | 0.2 | 1 | 0.002 | 15 |
| MIL-125(Ti)-NH ₂ /Pd | Ethanol | 0.3 | 1.4 | 0.003 | 11 |
| MIL-125(Ti)-NH ₂ | Methanol | 0.4 | 2 | 0.004 | 7 |
| MIL-125(Ti)-NH ₂ /Pd | Methanol | 0.8 | 3.9 | 0.008 | 4 |

IV. CONCLUSION

In summary, a simple and fast method of laser ablation in DI water was employed to synthesis Pd NPs. Furthermore, the produced NPs were supported on the MIL-125(Ti)-NH₂ microdiscs which were prepared using solvothermal method. The formation of MIL-125(Ti)-NH₂ discs is clearly visible in the SEM images. The XRD pattern of nanocomposite confirmed the presence of the (111) plane related to Pd NPs in the synthesized nanocomposite. This nanocomposite was used to detect methanol and ethanol vapors. It was found that the presence of Pd NPs can improve the performance of the sensor. The maximum response time for both methanol and ethanol vapors was reduced by adding Pd NPs. It was probably due to the increasing electrical conductivity and the spillover effect of Pd NPs.

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