

Synthesis of Gamma Alumina for Catalyst Support Using Yeast Cell as Pore Forming Agent Using Regression Model

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Abstract: The porous gamma alumina Al_2O_3 has a wide range of many applications, for example, the catalyst carrier. The powder of alumina was prepared from recrystallization of alum and the effect of yeast cell addition as pore forming agent was studied to form porous γ -alumina. The weight percentage of yeast cell added to prepare of porous gamma alumina are (5, 10, 15 and 20%) and the gel casting method was used for preparation of porous gamma alumina. The result showed that the gel-casting method by using yeast cell as pore forming agent is one of the successful method to obtain porous γ -alumina that used as catalyst carrier because the improvement of the amount of porosity with high compressive strength and increase the pore volume and high surface area. The apparent porosity obtained was in the range 12.51-82.25% with compressive strength range from 44.22-7.89 MPa. The porosity increased and decreasing in compressive strength with increasing the percentage ratio of the yeast cell. This result was confirmed by using a regression analysis, R^2 was (82.29%) and R-adj was (77.86%). The R^2 (94.06%), R-adj (92.58%) according to the regression analysis.

Key words: Al_2O_3 -catalyst support, yeast cell-gel casting, regression analysis, compressive strength, alumina, powder

INTRODUCTION

A porous material having high specific surface area such as γ -alumina is useful as a catalyst carrier supporting a catalyst substance, a filter, thermal insulation, filtration liquid or metal molten, hot-gas purifier and in biomedical (Aswad and Saud *et al.*, 2017). Catalytic supports are inactive materials for most of the reactions that supported catalysts will be used for it or totally low activity materials (Derouane *et al.*, 2012). The catalyst carrier is used in the petrochemical industry field and the adsorptive filtering material is used for water/waste liquid treatment (Yu *et al.*, 2017). Pore volume, pore volume distribution and surface area are the key properties which related to the adsorption capability. The increase pore volume and high specific surface area were needed for catalyst support this is because it gives large area per unit mass of catalyst for the chemical reaction (Chaturvedi *et al.*, 2012)

The speed of chemical reaction is commonly improved at a surface, especially when the materials such as platinum are existing. Consequently, utilizing porous materials is as a substrate and media to encouragement the chemical reactions (Webber, 2014). The textural characteristics of the alumina carrier have a significant role in regulating the efficiency of alumina

dependent heterogeneous catalysts. The pore size distribution in the catalyst support is essential significance in the development of a promising catalyst (Kumar *et al.*, 2001). Porous γ -alumina was commonly used as an adsorbent and catalyst support, the structure and chemical characteristics of alumina play a significant role in the catalytic support application. These characteristics can be enhanced by the addition of impregnate which has a specific effects on both the selectivity and the reactivity of the surface area in the catalytic reactions and also may be the services as an adsorbent (Qadeer and Ikram, 2005).

Because of porous alumina were varied possible utilizations in catalysis, the synthesis of meso-porous alumina with large pore volume and high surface area has enticed much attention (Chang and Jang, 2014). There are varied methods to preparation meso porous alumina such as pressing, freeze casting, sol-gel, slip casting and gel casting. Gel casting methods is utilized to prepare reticulated ceramic materials that were needed for catalyst support. The stages of gel-casting method involve premixing, casting, drying and sintering (Guo, 2011).

Essentially the most significant physical properties of a catalyst is its specific surface area. The surface area of a porous catalyst is practically completely consists of the

surface of pores that are present in all catalyst particle (Thommes *et al.*, 2015). Pore volume is also important factors that effect on the quantities of catalyst cursors which is presented on the catalyst supports (Rostrup-Nielsen, 2006). Surface area was measured by BET (Brunauer-Emmet Tailer) and gas adsorption. The purpose of this research is to show which of the variables contributing in the forming of porous gamma alumina support has an effect on the physical and mechanical characteristic.

MATERIALS AND METHODS

Alum ($KAl(SO_4)_2 \cdot 12H_2O$) as raw material for prepared alumina. Yeast cell as pore forming agent and agar was used to formed gel.

Preparation of alumina powder: Alumina powder was synthesis by recrystallization of alum in these methods the source was alum. The recrystallization of alum method was used to prepare the alumina powder, according to following steps.

Alum solution was prepared by dissolving the proper amount of the alum in 100 mL of water was put on the magnetic stirring with speed of 1200 rpm for 2 h then aged for 3 h. At ambient temperature after that the white precipitate look like whiskers was filtrated and washed with the deionized water for the several times. The product powder was dried at 100°C and calcined at 700°C to obtain γ -alumina.

Preparation of (porous alumina) samples: Porous alumina sample were prepared by gel casting method using different percentages of agar solution (5, 10, 20 wt.%). Prior to use the agar in gel casting, the main characteristics of the agar gel were identified. These include the gelation temperature and the minimum agar to water ratio. The gelation temperature is necessary to find out the casting temperature of the slurry in the gel casting process while the minimum agar to water ratio is important to get green sample that can be safely handled after the gelation.

For preparing the gel casting slurries, the agar solution was prepared by dissolving the agar in distilled water (agar to water ratio was found to be 0.4 wt.%) with helping of microwave treatment for 1min using power of 900 W and frequency of 2450 MHz and the solution was then transferred to water bath at 55°C. The desired amount of alumina was added to the agar solution at 55°C under sonication and mixing with speed of (1600 rpm) for 15 min. After that the slurry was poured in PVC Molds and then cooled down to 10°C in refrigerator. The alumina

gel demolded and aged at room temperature for 24 h and dried in a convection oven at 55°C., the green samples sintered at 900°C.

Characterization: The phase of alumina powder was evaluated using X-Ray Diffractometer (XRD 6000, Shimadzo, Japan) in the Ceramics Laboratories/College of Material Engineering/Babylon University) at room temperature using $Cu\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) with scanning speed of 5°/min from 20-70° of 2 (Bragg angle) and an applied power of 40 kV/30 mA.

Particle size distribution was determined using (Bettersize 2000, laser particle size analyzer instrument Ltd., China). Small amount of powder added to the distribution medium (water) under mixing and sonication in order to determine the particle size distribution curve. Tests were done in (Babylon University, College of Material Engineering, Ceramics and Building Materials Department). Infrared (FTIR) spectra of samples were recorded using (Shimadzu 1800, Japan) to evaluate molecular structure of functional group in inorganic materials. Tests were done in Babylon University, College of Material Engineering, Polymer Department. The FTIR study has been carried out to characterize the gamma alumina powders. The FTIR spectra were recorded on an infrared spectrophotometer with KBr pellets in the range 400-4000 cm^{-1} with (KBr: sample weight ratio of 100:1). Tests were carried out at room temperature.

All the samples were polished and then coated with thin layer of gold by sputtering deposition process (EMITEC K 350 UK) before scanning using FE-SEM instrument which is available in the Universiti Teknologi Malaysia in Johor Bahru/Malaysia). FE-SEM test were done in order to identify the morphologies of the porous gamma alumina. The pore size distribution and surface area was measured by Brunauer-Emmett-Teller (BET) which are available in the Universiti Teknologi Malaysia/Johor Bahru/Malaysia) for porous in range (20 \AA to below~1500 \AA).

RESULTS AND DISCUSSION

Characterization of alumina powder: Figure 1a was shown the XRD pattern of the γ - Al_2O_3 . The obtained diffraction data are fully matching the JCPDS card No. (00-29-0063) reported for γ - Al_2O_3 . All the peaks were indications to γ - Al_2O_3 with strongest reflection at $2\theta = 66.8^\circ$. Figure 1b shows the particle size of gamma alumina powder after by calcaintion at 900°C for 2 h. It can be noticed that the powder has single model distribution with an average particle size 4.26 μm .

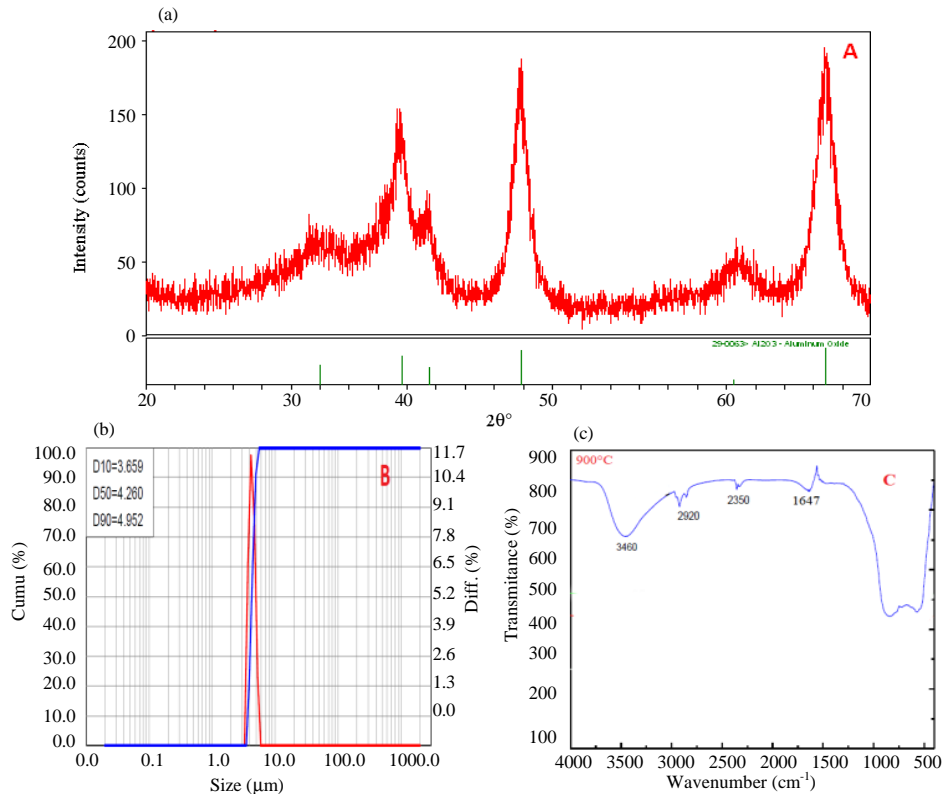


Fig. 1: a) XRD patterns of alumina powder; b) Particle size analysis for alumina powder and c) FTIR for the gamma alumina prepared powder by recrystallization of alum

Figure 1c shows the FTIR for gamma alumina powder. The IR spectra of prepared powders that calcined at 900°C for 2 h. The common bands exist in Fig. 1c such as the broad band of Al-O-Al was around 500 and 900 cm^{-1} , the broad band of OH group was centered around 3226-3480 cm^{-1} , The peak at 2920 is due to CH stretching vibrations of alkane groups. The band at 1647 cm^{-1} is due to stretching vibrations of H_2O band (Dey, 2014).

Characterization of porous alumina sample

Physical and mechanical properties: Figure 2a displays the effect of additives (yeast cell) upon the property of apparent porosity for the porous alumina samples. It is generally observed that the rise of additive will be caused increment in the value of apparent porosity, regardless of the additive type. The forming process was produced a contrast in porosity the gel casting technique had given a preference in porosity value (82%) with the yeast cell additive. Figure 2b depicts the relationship between the increments of additives with the apparent density of the porous alumina samples. It is due to the fact that the density of the porous alumina is inversely related with the

porosity. So as the additives ratio is further increased, the density values of the samples are rapidly decreased. It has been observed that the behavior of the density of the samples follows the same trend as explained in the porosity article.

On the other hand, the compressive strength changes with the variation of amount of additive (yeast cell) and also effected by the pore size, pore morphology and interconnectivity of pores. Figure 2c explains the relation between compressive strength and yeast cell addition. There is decrease in the compressive strength from 28.41 to 53.3 MPa with the increase of the yeast cell ratio from 5-20 wt.%. Table 1 also shows experiments variables (amount of additive yeast cell) with it results include (apparent porosity, apparent density and compressive strength).

A prediction model for the apparent porosity was established by taking the apparent porosity as the dependent variable and the input variables (ratio of yeast cell) as independent variables. Model by regression is used based on 6 experiments for a one factors and 6 levels as shown in Table 1 using Minitab Software. Regression equation:

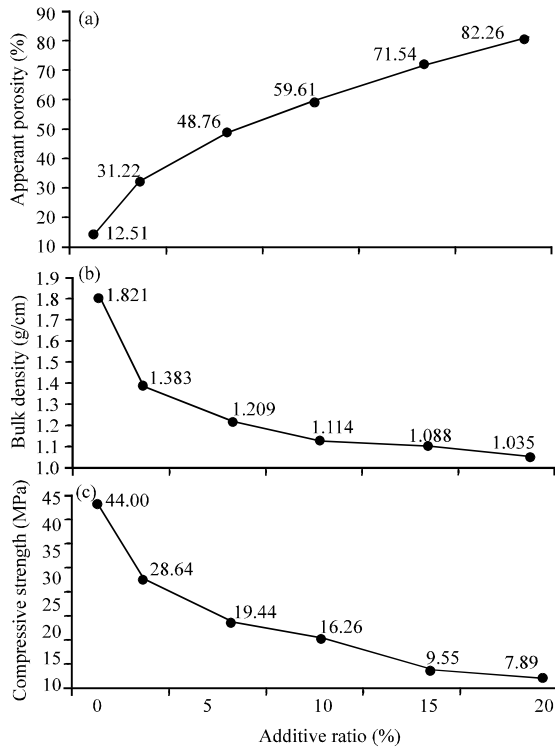


Fig. 2: The additive ratio of yeast cell with: a) Apparent porosity; b) Bulk density and c) Compressive strength

Table 1: Experiments variables (amount of additive yeast cell)

Yeast cell (wt.%)	Apparent porosity (%)	Bulk density (g/cm³)	Compressive strength (MPa)
0	12.51	1.821	44.22
2	31.22	1.383	28.64
6	48.76	1.209	19.44
10	59.61	1.114	16.26
15	71.54	1.088	9.55
20	82.26	1.035	7.89

Table 2: Regression equation analysis of porosity

Term	Coef.	SE coef.	t-values	p-values	Vif
Constant	22.20	4.62	4.80	0.009	
X(1)	3.259	0.409	7.69	0.001	1.00

$$\text{Apparent porosity} = 22.20 + 3.259x \quad (1)$$

where, X_1 = The ratio of yeast cell. The R^2 (94.06%), R-adj (92.58%) and the regression equation analysis are given in Table 2.

The prediction model for bulk density is made by taking bulk density as dependent variable. While, the ratio of the yeast cell as an independent variable (input) as follows regression equation:

$$\text{Bulk density} = 1.555 - 0.0317x$$

Table 3: Regression equation analysis of Bulk density

Term	Coef.	SE coef.	t-values	p-values	Vif
Constant	1.555	0.121	12.90	0.000	
X(1)	-0.031	0.0107	-2.97	0.041	1.00

Table 4: Regression equation analysis of compressive strength

Term	Coef.	SE coef.	t-values	p-values	Vif
Constant	35.15	4.20	8.38	0.001	
X(1)	-1.602	0.372	-4.31	0.013	1.00

Table 5: Total pore volume, BET surface area, Langmuir surface area, Isotherm type and BJH adsorption average size (°A)

Sample	Total pore volume (°A)	BET surface area (m²/g)	Langmuir surface area (m²/g)	Isotherm type	BJH adsorption average size (°A)
	387.34	116.57	125.77	2	50.24

where, $x(1)$ is the ratio of yeast cell. The R^2 (68.73%), R-adj (60.92%) and the regression equation analysis are given in (Table 3).

The prediction model for bulk density is made by taking bulk density as dependent variable. While, the ratio of the yeast cell as an independent variable (input) as follows regression equation:

$$\text{Compressive strength} = 35.15 - 1.602x(1)$$

where, $x(1)$ is the ratio of yeast cell. The R^2 (82.29%), R-adj (77.86%) and the regression equation analysis are given in Table 4.

FE-SEM results: Figure 3 shows the FE-SEM micrographs of the porous γ -alumina samples sintered at 900°C with heating rate of (1.5°C/min) for a soaking time of 2 h. These image belong to the sample with of (10 wt.%) and lowest agar ratio (0.7 wt.%). The FE-SEM image showed that the sample which have been prepared by gel casting method have large pore size distribution. Also, the distribution of the porosity is found to be homogeneity between agar and the powder. This may belongs to the use of ultrasonic waves to break weak agglomerations and disperse the particles in the suspension, containing pores that caused by combustion of yeast cell and agar at 600°C.

Brunauer-Emmett-Teller (BET): The value of the pore volume, specific surface area, pore size distribution, BJH adsorption average size of green body sample with (10% wt. of yeast cell) that prepared by gel casting method shown in Table 5. The result was showed that the N_2 adsorption/desorption isotherms corresponding confirm type 2 isotherm with a hysteresis loop located at the relative Pressure (P/P_0) range of (0.15-1) with average pore size 50.24°A which represent to mesoporous. The pore

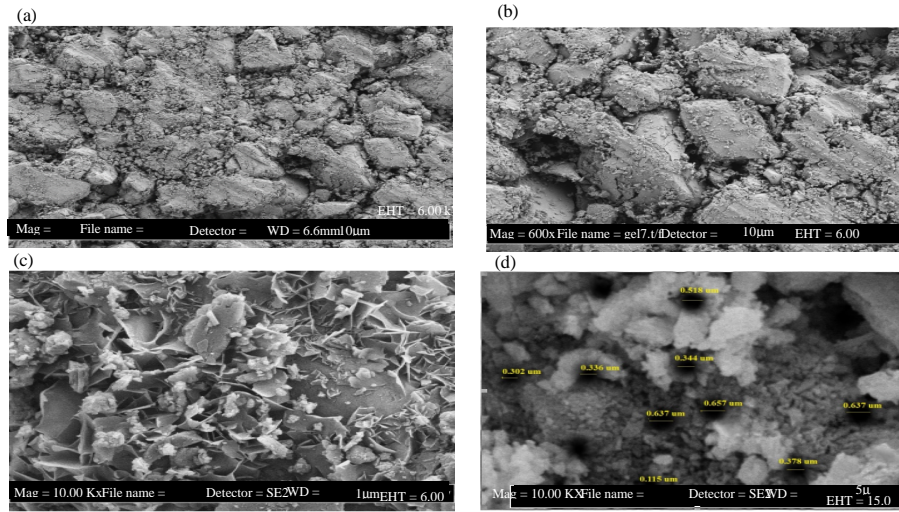


Fig. 3: a-d) The FE-SEM micrographs of the porous γ -alumina sintered at 900°C with different magnification

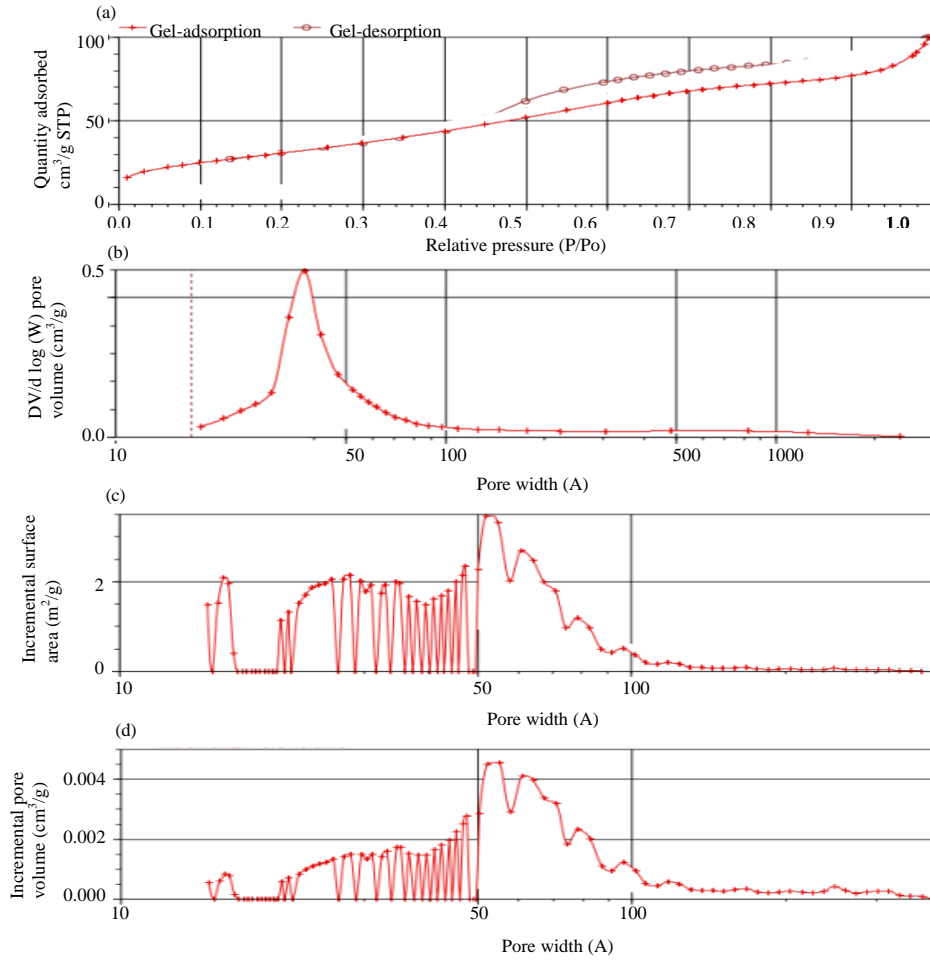


Fig. 4: BET result of porous alumina prepared by gel casting of sample with 20 wt.% and calcined at 900°C : a) Isotherm linear plot; b) BJN desorption $dV/d \log (w)$ pore volum; c) Incremental surface area vs. Pore width and d) Incremental pore volum vs. Pore width

volume and BET increased due to the burn of yeast cell and agar out of the green bodies. At low sintering temperature show high adsorption that indicate to large surface area .The adsorption capacity of the synthesized samples decreases with the increases of the sintering temperature (Fig. 4).

CONCLUSION

Alumina powder was prepared via. recrystallizations of the alum and high purity gamma alumina powder with a hexagonal structure was successfully formed by calcination at 900°C for 2 h. The specific signatures of γ -AlO powders by a blend of X-ray diffraction and FTIR spectroscopy. The meso porous alumina was successfully prepared using Gel casting method and yeast cell as pore forming agent .The apparent porosity obtained was in the range 12.51-82.25% with compressive strength range from 44.22 -7.89 MPa .

The increase in porosity and decrease compressive strength as an increased in the percentage ratio of the yeast cell increased. The adding of yeast cell to the γ -alumina powder during the preparation stage of the porous alumina samples is effective method for enhancement of pore volume (porosity) and BET Area (Specific surface area) of the γ -alumina samples which can be used as catalyst support. The regression analysis was given a results, apparent porosity = $22.20+3.25 \times 1$, R^2 (94.06%), R -adj (92.58%). Bulk density = $1.555-0.0317 \times 1$, R^2 (68.73%), R -adj (60.92%). While compressive strength = $35.15-1.602 \times 1$, R^2 (82.29%), R -adj (77.86%). Consequently, from the general overview, the increase in sintering temperature will caused the reduction in porosity because of the increase in the yeast weight.

REFERENCES

Aswad, A.P.D.M.A. and A.N. Saud, 2017. Preparation of macro-porous alumina via organic additive and characterizations physical properties by using a Genetic Algorithm method. Proceedings of the 2017 IEEE 1st International Conference on Recent Trends of Engineering Science and Sustainability, May 17-19, 2017, IEEE, Baghdad, Iraq, pp: 1-5.

Chang, H. and H.D. Jang, 2014. Controlled synthesis of porous particles via aerosol processing and their applications. *Adv. Powder Technol.*, 25: 32-42.

Chaturvedi, S., P.N. Dave and N.K. Shah, 2012. Applications of nano-catalyst in new era. *J. Saudi Chem. Soc.*, 16: 307-325.

Derouane, E.G., V. Parmon, F. Lemos and F.R. Ribeiro, 2012. Principles and Methods for Accelerated Catalyst Design and Testing. Vol. 69, Springer, Berlin, Germany, ISBN:978-1-4020-0721-7, Pages: 518.

Dey, S., 2014. Synthesis and application of α -alumina nanopowders. MSc Thesis, National Institute of Technology, Rourkela, Odisha.

Guo, X., 2011. Gel casting of high strength ceramics. Master Thesis, Department of Materials and Manufacturing Technology, Chalmers University of Technology, Goteborg, Sweden.

Kumar, M., B. Lal, A. Singh, A.K. Saxena and V.S. Dangwal *et al.*, 2001. Control of mesoporosity in alumina. *Indian J. Chem. Technol.*, 8: 157-161.

Qadeer, R. and S. Ikram, 2005. Cobalt impregnated alumina: Nitrogen adsorption study at 77 K. *Tur. J. Chem.*, 29: 101-106.

Rostrup-Nielsen, J., 2006. The 40 years in catalysis. *Catal. Today*, 111: 4-11.

Thommes, M., K. Kaneko, A.V. Neimark, J.P. Olivier and F. Rodriguez-Reinoso *et al.*, 2015. Physisorption of gases with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.*, 87: 1051-1069.

Webber, J.B.W., 2014. Accessible catalyst pore volumes, for water and organic liquids as probed by NMR cryoporometry. *J. Basic Principles Diffus. Theory Exp. Appl.*, 22: 1-8.

Yu, L., M. Han and F. He, 2017. A review of treating oily wastewater. *Arabian J. Chem.*, 10: S1913-S1922.