Characterization of Heterogeneous Catalysts for Glycerol Catalytic Conversion

Steven Zhou and Jason Yang
X-Catalysis Group
Email: info@x-catalysis.com
Website: x-catalysis.com
Journal of X-Catalysis Group, **2017**, 1(12), pp 31-38

Abstract:

Catalyst characterization, if properly utilized, can be both the cornerstone of the science of catalysis and the catalyst in its own right for industrial progress. Glycerol, also called glycerine or glycerin, is a simple polyol compound. The glycerol backbone is found in all lipids known as triglycerides. It is widely used in the food industry as a sweetener and humectant and in pharmaceutical formulations. In the present work, various characterization techniques for catalytic conversion of glycerol are discussed and reviewed. It is concluded that in situ and opera-do characterization techniques provide insight into catalytic glycerol conversion for valuable chemicals and biofuels production.

1 Introduction

Most catalysts of practical importance are highly porous and possess large specific surface areas. Although the catalytic activity may be only indirectly related to the total available surface, evaluation of the surface area is generally considered to be an important requirement in catalyst characterization. [1, 2] In addition, it is necessary to assess the pore size distribution in order to investigate whether the molecular transportation and reaction pathways are affected by changes in the pore structure. [3, 4, 5]

It must be kept in mind that the recorded values of surface area, porosity, pore size and pore volume are likely to depend on the experimental methods used, as described in Figure 1 [6] In the case of a highly porous catalyst, no experimental technique should be expected to provide absolute values of these parameters and the choice of a particular procedure should take into consideration the nature of the catalyst or support and its application. [7, 8] Since methods are most often used to determine the effective (or apparent) surface area and pore size distribution, most attention must be given to these procedures. [9, 10] It is not always easy to distinguish between roughness and porosity. In principle, a simple convention is to refer to a solid as porous if the surface irregularities are deeper than they are wide. [11] It is also convenient to regard the area of a rough or macropore surface as the external surface area and the area of the micropore or mesopore walls as the internal area.

Glycerol is generally obtained from plant and animal sources where it occurs as triglycerides. Triglycerides are esters of glycerol with long-chain carboxylic acids. The hydrolysis, saponification, or transesterification of these triglycerides produces glycerol as well as the fatty acid derivative. [12] Typical plant sources include soybeans or palm. Animal-derived tallow is another source. Approximately 950,000 tons per year are produced in the United States and Europe; 350,000 tons of glycerol were produced per year in the United States alone from 2000 to 2004. [13, 14] Production will increase as the EU directive 2003/30/EC are implemented, which required the replacement of 5.75% of petroleum fuels with biofuel across all member states by 2010, as glycerol is a byproduct in the production of biodiesel. [15, 16] It was projected in 2006 that by the year 2020, production would be six times more than demand. Glycerol from triglycerides is produced on a large scale, but the crude product is of variable quality, [17] with a low selling price of as low as 2-5 U.S. cents per kilogram in 2011. [18, 19] It can be purified, but the process is expensive. [20] Some glycerol is burned for energy, but its heat value is low. [6] Crude glycerol from the hydrolysis of triglycerides can be purified by treatment with activated carbon to remove organic impurities, alkali to remove unreacted glycerol esters, and ion exchange to remove salts. High purity glycerol ($>$ 99.5%) is obtained by multi-step distillation; vacuum is helpful due to the high boiling point of glycerol (290 $^{\circ}$C). [21]

2 SEM and TEM

Transmission Electron Microscope theory of image formation, resolution and contrast in the TEM can be found in general treatises on electron microscopy and in review articles. The point-to-point resolution in TEM is not limited by the wavelength of electrons, but by spherical aberrations of lenses, stability of voltage and mechanical vibrations. [22, 23, 24] However, in the case of catalytic materials, the detection of small particles is mainly limited by contrast effects due to the presence of two or more solid phases.

In the STEM, the electron beam is focused by lenses placed before the specimen to obtain a very small electron probe directed on to the specimen. The interaction between the electron probe and the atoms in the small irradiated volume of the specimen gives rise to different types of signals, which are recorded by specific detectors and which can be used for imaging or for analytical purposes. As the electron probe is scanned over the specimen, the intensity of one of these signals is detected, amplified and visualized on the screen of a cathode-ray tube (CRT) which is scanned synchronously with the scanning coils in the microscope column.

3 BET and Chemisorption

Physisorption (physical adsorption) is a general interfacial phenomenon and, unlike chemisorption, occurs whenever a gas (the adsorptive) is brought into contact with the surface of a solid (the

adsorbent). [25] The matter in the adsorbed state is known as the adsorbate, as distinct from the adsorptive, which is the adsorbable gas. The forces involved in physisorption are the same as those responsible for the condensation of vapors and the deviations from ideal gas behavior. They always include the long-range London dispersion forces and the short-range intermolecular repulsion. These combined forces give rise to non-specific molecular interactions. [26] Various types of specific interactions come into play when polar molecules are adsorbed on ionic or polar surfaces, but the process is still regarded as physisorption unless there is some form of chemical bonding. [27]

In spite of its theoretical limitations, the BrunauerEmmettTeller (BET) method continues to be widely used for evaluating the surface area of catalysts and supports. It is now generally agreed that the BET theory was based on an oversimplified model of physisorption.

In its original form, the BET theory was essentially a multilayer extension of Langmuir kinetic treatment of monolayer adsorption on an array of identical sites. Thus, the Langmuir concept of the ideal localized monolayer was extended to include the formation of either an infinite or a finite number of adsorbed layers. The molecules in the first layer were assumed to act as sites for the second-layer molecules, which in turn provide sites for the adsorption of molecules in the higher layers. [28] Equilibration is attained at a given temperature when the rate of condensation (i.e. adsorption) is equal to the rate of evaporation (i.e. desorption).

Particle size can be measured by chemical and physical methods. Chemical methods are based on measurements of the amount of gas chemisorbed on the surface of particles. Provided that some assumptions are made on the stoichiometry of adsorption and on the nature of atomic planes exposed on the surface, the surface area and the particle size can be obtained. [29, 30, 31] This technique is limited to metals but it is widely used since it does not require any expensive equipment or special skills.

4 XPS, XRD and EXAFS

X-Ray Photoemission Spectroscopy (XPS) X-ray photoemission spectroscopy (XPS) is certainly among the most widely used methods for surface chemical analysis. It provides the possibility to analyze quantitatively the chemical composition in the surface region and to identify different chemical states of an element. The surface sensitivity of XPS has also been used to obtain information about the dispersion and size of supported particles. [32, 33] For a given amount of supported material, the extent to which the substrate is covered (and therefore its signal reduced) depends on the dispersion of that material, its signal intensity and also on its size relative to the mean free path of the corresponding photoelectrons.

X-ray diffraction (XRD, sometimes also called WAXS: wide-angle X-ray scattering) is one of the most important techniques for catalyst characterization. For most catalysts XRD is limited to powder pattern identification of crystalline phases. For zeolites, and catalysts with good crys-

tallinity, long range order exists, and XRD can give a complete description of their structure. In all cases, the possible presence of amorphous phases should be taken into account in interpretation. The technique can be complemented by line broadening analysis which gives valuable information on the size of individual crystallites. Variations of ratios between lines indicate either order imperfections along certain crystallographic directions or spontaneous [34] orientation of the crystallites in the sample holder. [35]

The oscillations which occur in the X-ray absorption coefficient in the energy range of 50-1000 eV above an absorption edge contain information on the distances between the absorbing atom and its surrounding coordination spheres, the number of surrounding atoms, the identities of the absorber and its neighbors and the dynamic and static disorder in the internuclear distances. The distance to the first coordination shell can be determined to within 1-2 pm, particularly when elements of higher atomic number are involved; for succeeding shells accuracy falls to 10-20 pm. [36, 37, 38] Uncertainty in coordination numbers is greater, being about 20% for the first shell. (The RED technique gives interatomic distances directly and accuracy does not fall sharply beyond the first shell.) The major advantage of EXAFS is that the short-range chemistry it reflects can be examined separately around each type of atom, a facility which is particularly useful for the study of multimetallic catalysts and which is not available with RED.

5 Concluding Remarks

In the present work, various characterization techniques for catalytic conversion of glycerol are discussed and reviewed. It is concluded that in situ and opera-do characterization techniques provide insight into catalytic glycerol conversion for valuable chemicals and biofuels production.

6 Acknowledgments

This work was supported X-Catalysis Group (x-catalysis.com).

References

[1] Zhang, Xinghua, Wang, Tiejun, Ma, Longlong, Zhang, Qi, Yu, Yuxiao, and Liu, Qiying, “Characterization and Catalytic Properties of Ni and NiCu Catalysts Supported on ZrO_2-SiO_2 for Guaiacol Hydrodeoxygenation,” *Catalysis Communications*, volume 33, pp. 15–19, 2013

[2] Zeng, Zhenhua and Greeley, Jeffrey, “Characterization of Oxygenated Species at Water/Pt(111) Interfaces from {DFT} Energetics and {XPS} Simulations,” *Nano Energy*, volume 29, pp. 369 – 377, 2016

[3] Xiao, Yang, Greeley, Jeffrey, Varma, Arvind, Zhao, Zhi-Jian, and Xiao, Guomin, "An Experimental and Theoretical Study of Glycerol Oxidation to 1,3-Dihydroxyacetone over Bimetallic Pt-Bi Catalysts," *AIChE Journal*, volume 63, no. 2, pp. 705–715, 2017

[4] Zaheer, Muhammad A., Zill, Jeremias C., Matysik, Jorg, Glaser, Roger, and Dvoyashkin, Muslim, "In Situ and in Operando Characterization of Mixing Dynamics in Liquid-Phase Reactions by ^{129}Xe NMR Spectroscopy," *ChemPhysChem*, pp. n/a–n/a, 2017

[5] Yohe, Sara L., Choudhari, Harshavardhan J., Mehta, Dhairya D., Dietrich, Paul J., Detwiler, Michael D., Akatay, Cem M., Stach, Eric A., Miller, Jeffrey T., Delgass, W. Nicholas, Agrawal, Rakesh, and Ribeiro, Fabio H., "High-pressure Vapor-Phase Hydrodeoxygenation of Lignin-Derived Oxygenates to Hydrocarbons by a PtMo Bimetallic Catalyst: Product Selectivity, Reaction Pathway, and Structural Characterization," *Journal of Catalysis*, volume 344, pp. 535 – 552, 2016

[6] Shi, Hui, Lercher, Johannes A., and Yu, Xiao-Ying, "Sailing into Uncharted Waters: Recent Advances in the in Situ Monitoring of Catalytic Processes in Aqueous Environments," *Catal Sci Technol*, volume 5, pp. 3035–3060, 2015

[7] Xiao, Yang, Xiao, Guomin, and Varma, Arvind, "A Universal Procedure for Crude Glycerol Purification from Different Feedstocks in Biodiesel Production Experimental and Simulation Study," *Industrial Engineering Chemistry Research*, volume 52, no. 39, pp. 14291–14296, 2013

[8] Weckhuysen, Bert M., Rosynek, Michael P., and Lunsford, Jack H., "Characterization of Surface Carbon Formed During the Conversion of Methane to Benzene over Mo/H-ZSM-5 Catalysts," *Catalysis Letters*, volume 52, no. 1, pp. 31–36, 1998

[9] Xiao, Yang, Gao, Lijing, Xiao, Guomin, and Lv, Jianhua, "Kinetics of the Transesterification Reaction Catalyzed by Solid Base in a Fixed-Bed Reactor," *Energy Fuels*, volume 24, no. 11, pp. 5829–5833, 2010

[10] Watkins, Dereca, Nuruddin, Md., Hosur, Mahesh, Tcherbi-Narteh, Alfred, and Jeelani, Shaik, "Extraction and Characterization of Lignin from Different Biomass Resources," *Journal of Materials Research and Technology*, volume 4, no. 1, pp. 26 – 32, 2015

[11] Xiao, Yang, Gao, Lijing, Xiao, Guomin, Fu, Baosong, and Niu, Lei, "Experimental and Modeling Study of Continuous Catalytic Transesterification to Biodiesel in a Bench-Scale Fixed-Bed Reactor," *Industrial Engineering Chemistry Research*, volume 51, no. 37, pp. 11860–11865, 2012

[12] Wang, Dingjun, Lunsford, Jack H., and Rosynek, Michael P., "Characterization of a Mo/ZSM-5 Catalyst for the Conversion of Methane to Benzene," *Journal of Catalysis*, volume 169, no. 1, pp. 347 – 358, 1997

[13] Varma, Arvind and Xiao, Yang, "Catalytic Deoxygenation of Bio-oils Using Methane," *US Patent*, volume Publication No. 20170029712, 2017

[14] Valerio, Oscar, Horvath, Tessa, Pond, Christopher, Misra, Manjusri, and Mohanty, Amar, "Improved Utilization of Crude Glycerol from Biodiesel Industries: Synthesis and Characterization of Sustainable Biobased Polyesters," *Industrial Crops and Products*, volume 78, pp. 141 – 147, 2015

[15] Saucedo, Jose A., Xiao, Yang, and Varma, Arvind, "Platinum-Bismuth Bimetallic Catalysts: Synthesis, Characterization and Applications," *The Summer Undergraduate Research Fellowship SURF Symposium*, 2015

[16] Thompson, J. C. and He, B. B., "Characterization of Crude Glycerol from Biodiesel Production from Multiple Feedstocks," *Applied Engineering in Agriculture*, volume 22, no. 2, pp. 261–265, 2006

[17] Xiao, Yang and Varma, Arvind, "Insight into Pt-Bi Bimetallic Catalysts for Tuning Selectivity and Improving Stability," *International Symposia on Chemical Reaction Engineering ISCRE 24*, 2016

[18] Sun, Xiao-Feng, Sun, Fowler, Paul, and Baird, Mark S., "Extraction and Characterization of Original Lignin and Hemicelluloses from Wheat Straw," *Journal of Agricultural and Food Chemistry*, volume 53, no. 4, pp. 860–870, 2005

[19] Smirnov, A.A., Geng, Zh., Khromova, S.A., Zavarukhin, S.G., Bulavchenko, O.A., Saraev, A.A., Kaichev, V.V., Ermakov, D.Yu., and Yakovlev, V.A., "Nickel Molybdenum Carbides: Synthesis, Characterization, and Catalytic Activity in Hydrodeoxygenation of Anisole and Ethyl Caprate," *Journal of Catalysis*, volume 354, no. Supplement C, pp. 61 – 77, 2017

[20] Xiao, Yang and Varma, Arvind, "Kinetics of Glycerol Conversion to Hydrocarbon Fuels over Pd/H-ZSM-5 Catalyst," *AIChE Journal*, volume 63, no. 12, pp. 5445–5451, 2017

[21] Shu, Yuying and Ichikawa, Masaru, "Catalytic Dehydrocondensation of Methane Towards Benzene and Naphthalene on Transition Metal Supported Zeolite Catalysts: Templating Role of Zeolite Micropores and Characterization of Active Metallic Sites," *Catalysis Today*, volume 71, no. 1-2, pp. 55 – 67, 2001

[22] Xiao, Yang and Varma, Arvind, "Catalytic Deoxygenation of Guaiacol Using Methane," *ACS Sustainable Chemistry Engineering*, volume 3, no. 11, pp. 2606–2610, 2015

[23] Sardar, Kripasindhu, Playford, Helen Y., Darton, Richard J., Barney, Emma R., Hannon, Alex C., Tompsett, David, Fisher, Janet, Kashtiban, Reza J., Sloan, Jeremy, Ramos, Silvia, Cibin, Giannantonio, and Walton, Richard I., "Nanocrystalline Cerium-Bismuth Oxides: Synthesis, Structural Characterization, and Redox Properties," *Chemistry of Materials*, volume 22, no. 22, pp. 6191–6201, 2010

[24] Xiao, Yang and Varma, Arvind, "Kinetics of Guaiacol Deoxygenation Using Methane over the Pt-Bi Catalyst," *Reaction Chemistry Engineering*, volume 2, no. 1, pp. 36–43, 2017

[25] Saaid, Ismail Mohd, Mohamed, Abdul Rahman, and Bhatia, Subhash, "Activity and Characterization of Bimetallic ZSM-5 for the Selective Catalytic Reduction of NO_x," *Journal of Molecular Catalysis A Chemical*, volume 189, no. 2, pp. 241 – 250, 2002

[26] Romann, T., Vaartnou, M., Janes, A., and Lust, E., "In Situ Infrared Spectroscopic Characterization of a Bismuth-Ethanol Interface," *Electrochimica Acta*, volume 53, no. 28, pp. 8166 – 8171, 2008

[27] Xiao, Guomin, Li, Haoyang, and Xiao, Yang, "Applications of Chemical Simulation Softwares in the Course of Transport Phenomena," *Chemical Industry Times*, volume 51, pp. 53–59, 2012

[28] Quispe, Cesar A.G., Coronado, Christian J.R., and Jr., Joao A. Carvalho, "Glycerol: Production, Consumption, Prices, Characterization and New Trends in Combustion," *Renewable and Sustainable Energy Reviews*, volume 27, pp. 475 – 493, 2013

[29] Xiao, Yang and Varma, Arvind, "Conversion of Glycerol to Hydrocarbon Fuels via Bifunctional Catalysts," *ACS Energy Letters*, volume 1, no. 5, pp. 963–968, 2016

[30] Queiroz, R. M., Pires, Luiza H. O., de Souza, Ruth C. P., Zamian, J. R., de Souza, A. G., da Rocha Filho, G. N., and da Costa, C. E. F., "Thermal Characterization of Hydrotalcite Used in the Transesterification of Soybean Oil," *Journal of Thermal Analysis and Calorimetry*, volume 97, no. 1, p. 163, 2009

[31] Xiao, Yang and Varma, Arvind, "Experimental and simulation study of crude glycerol purification from different feed stocks in biodiesel production," *Abstract of Papers of the American Chemical Society*, volume 246, 2013

[32] Nishimura, Shun, Takagaki, Atsushi, and Ebitani, Kohki, "Characterization, Synthesis and Catalysis of Hydrotalcite-Related Materials for Highly Efficient Materials Transformations," *Green Chem*, volume 15, pp. 2026–2042, 2013

[33] Mihut, Corina, Descorme, Claude, Duprez, Daniel, and Amiridis, Michael D., "Kinetic and Spectroscopic Characterization of Cluster-Derived Supported Pt-Au Catalysts," *Journal of Catalysis*, volume 212, no. 2, pp. 125 – 135, 2002

[34] Xiao, Yang, Li, Haoyang, Xiao, Guomin, Gao, Lijing, and Pan, Xiaomei, "Simulation of the Catalytic Reactive Distillation Process for Biodiesel Production via Transesterification," *International Conference on Materials for Renewable Energy and Environment ICMREE*, volume 1, pp. 196–199, 2013

[35] Liu, Wei-Wei, Feng, Yi-Si, Wang, Guang-Yu, Jiang, Wei-Wei, and Xu, Hua-Jian, "Characterization and Reactivity of γ-Al_2O_3 Supported Pd-Cu Bimetallic Nanocatalysts for the Selective Oxygenization of Cyclopentene," *Chinese Chemical Letters*, volume 27, no. 6, pp. 905 – 909, 2016

[36] Li, Haoyang, Pan, Xiaomei, Xiao, Yang, Xiao, Guomin, and Huang, Jinjin, "Simulation of Biodiesel Industrial Production via Solid Base Catalyst in a Fixed-Bed Reactor," *Journal of Southeast University English version*, volume 30, no. 3, pp. 380–386, 2014

[37] Kirsch, Harald, Tong, Yujin, and Campen, Richard Kramer, "Experimental Characterization of CCH(ads) and CCH_2(ads) During the Thermal Decomposition of Methane and Ethylene on Ru(0001)," *ChemCatChem*, volume 8, no. 4, pp. 728–735, 2016

[38] Irmawati, R., Nasriah, M.N. Noorfarizan, Taufiq-Yap, Y.H., and Hamid, S.B. Abdul, "Characterization of Bismuth Oxide Catalysts Prepared from Bismuth Trinitrate Pentahydrate: Influence of Bismuth Concentration," *Catalysis Today*, volume 93-95, pp. 701 – 709, 2004

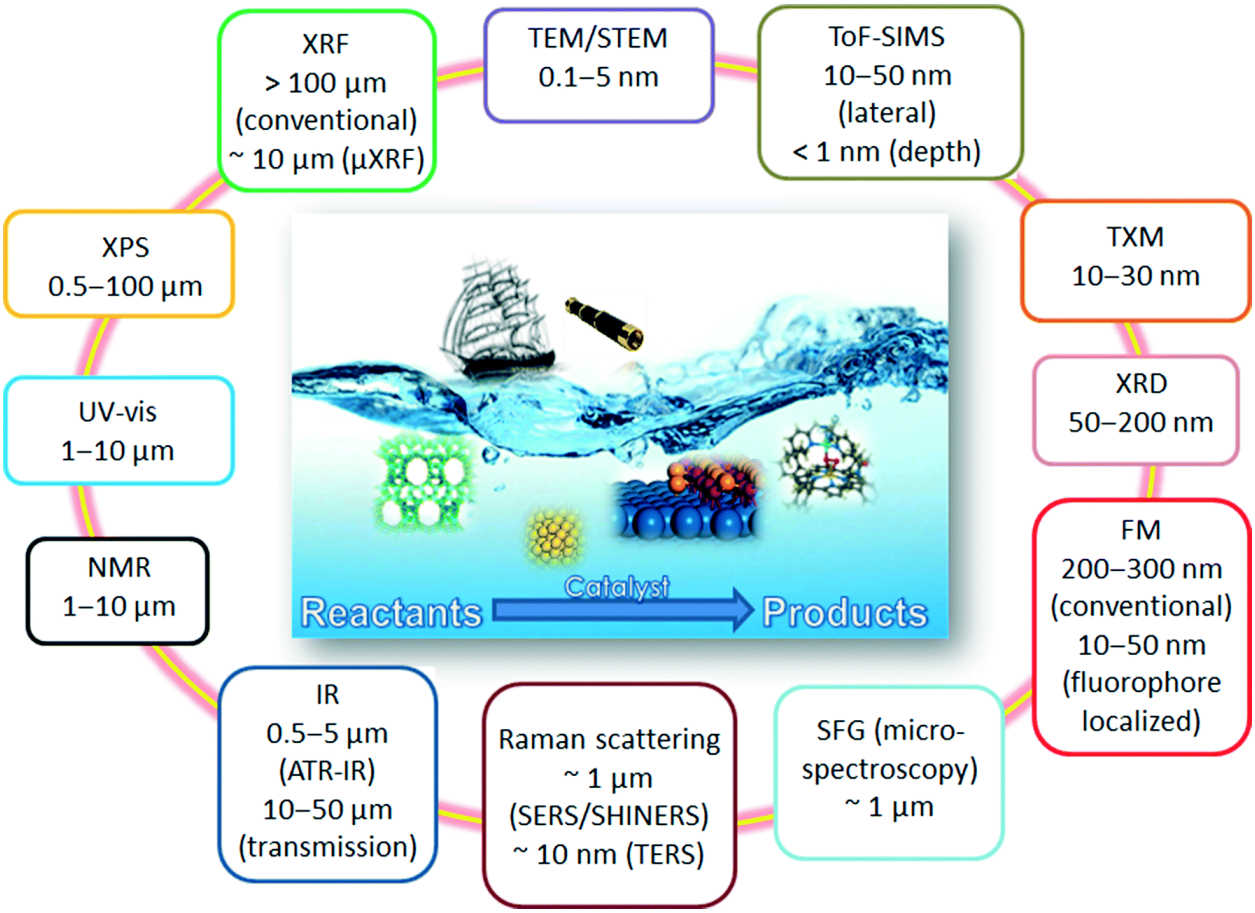

Figure 1: Various Characterization Techniques for Catalytic Glycerol Conversion [6]

Characterization of Heterogeneous Catalysts for Glycerol Catalytic Conversion

Steven Zhou and Jason Yang
X-Catalysis Group
Email: info@x-catalysis.com
Website: x-catalysis.com
Journal of X-Catalysis Group, **2017**, 1 (12), pp 31-38

Catalog: ***Catalyst Characterization***
