

# **Chapter 4. Synthesis of mesoporous tungsten oxide/ $\gamma$ -alumina and surfactant-capped tungsten oxide nanoparticles and their catalytic activities in oxidative cleavage of oleic acid**

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*International Journal of Chemical Reactor Engineering*, 2016; 14(4), 899-907

*Special Issue in honor of Dr. Serge Kaliaguine*

## Résumé

Les acides gras insaturés peuvent être convertis en acides mono- et dicarboxyliques, qui sont des matériaux de valeur utile, par réaction de clivage oxydatif en présence d'un système catalyseur / oxydant hautement efficace. Dans ce travail, deux types de catalyseurs hétérogènes avancés ont été développés; (i) oxyde de tungstène mésoporeux / oxyde de  $\gamma$ -alumine à haute surface spécifique et (ii) nanoparticules d'oxyde de tungstène coiffées de tensioactif. Diverses techniques, y compris les isothermes d'adsorption / désorption de  $N_2$ , XRD, SEM, EDS, TGA et test catalytique ont été utilisées pour contrôler les propriétés physico-chimiques et catalytiques de ces matériaux. Les résultats de caractérisation ont révélé que ces types de matériaux (i) présentent une surface spécifique élevée et une distribution granulométrique étroite, et que le tensioactif utilisé pourrait couvrir assez quantitativement la surface de ces types de matériaux(ii).

Les activités catalytiques de ces matériaux dans le clivage oxydatif de l'acide oléique avec  $H_2O_2$  en tant qu'oxydant ont été étudiées. La GC-MS a été utilisée pour déterminer les quantités produites des produits désirés, les acides azélaïques et pélargoniques. Les résultats des essais catalytiques ont montré une conversion de plus de 90% pour ce type de catalyseur (ii) en une réaction de 5 h à 120 ° C avec des rendements de production acceptables pour les acides azélaïques et pélargoniques. L'activité significativement plus élevée de ce catalyseur par rapport à ce genre (i) provient des propriétés de surface intéressantes des nanoparticules d'oxydes de tungstène qui les rendent capables d'exploiter les bonnes caractéristiques des catalyseurs homogènes et hétérogènes.

## Abstract

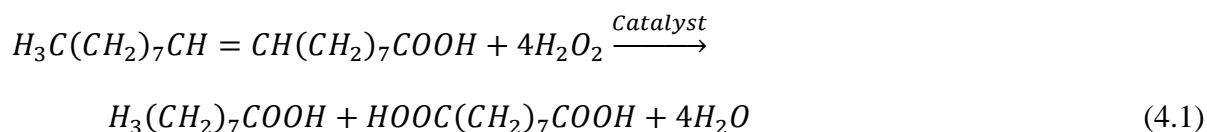
Unsaturated fatty acids can be converted into mono and dicarboxylic acids, which are applicably valuable materials, through oxidative cleavage reaction in the presence of a highly efficient catalyst/oxidant system. In this work, two types of advanced heterogeneous catalysts have been developed; (i) high surface area mesoporous tungsten oxide/ $\gamma$ -alumina mixed metal oxide, and (ii) surfactant-capped tungsten oxide nanoparticles. Various techniques including  $N_2$  adsorption/desorption isotherms, XRD, SEM, EDS, TGA and catalytic test were used to monitor the physicochemical and catalytic properties of these materials. The characterization results revealed that type (i) materials exhibit high surface area and narrow particle size distribution, and the used surfactant could quantitatively enough cap the surface of type (ii) materials. The catalytic activities of these materials in the oxidative cleavage of oleic acid with  $H_2O_2$  as oxidant were investigated. GC-MS was used to determine the produced amounts of the desired products, azelaic and pelargonic acids. The catalytic test results showed more than 90% conversion for type (ii) catalyst in 5 h reaction at  $120\text{ }^\circ\text{C}$  with acceptable production yields for azelaic and pelargonic acids. The significantly higher activity of this catalyst compared to type (i) arises from the interesting surface properties of tungsten oxides nanoparticles, which make them able to exploit the good features of homogeneous and heterogeneous catalysts.

## 4.1 Introduction

Oils and fats of vegetable and animal origin have rapidly attracted a growing interest as renewable materials for feedstock in oleochemical industries [12,6,8,13]. This attention arises from not only environmental reasons, but also economic ones. Unsaturated fatty acids, as the constituents of lipids, could undergo different reactions to produce a variety of products, even more than petrochemistry products [7]. Oxidation of unsaturated fatty acids possesses an industrially great importance, since it results in the production of mono and dicarboxylic acids which are applicably valuable materials. This oxidation reaction, which is called oxidative cleavage due to the cleavage of carbon-carbon double bond(s) during the reaction, can be done in the presence of a highly efficient catalyst/oxidant system. Currently, azelaic acid (C9, dicarboxylic acid) is produced in large-scale via ozonolysis of oleic acid. Pelargonic acid (C9, monocarboxylic acid) is obtained as a co-product but also a valuable chemical [1]. These types of saturated acids that have short and odd hydrocarbon chains are rare in natural resources [2]. On the other hand, they are very attractive initial materials for the development of numerous bio-based products [4,3]. For instance, azelaic acid converts into different esters for the preparation of polymers (Nylon 6:9), plasticizers, adhesives, solvents, biodegradable lubricants, corrosion inhibitors, and anti-acneic agent for cosmetics [2,3]. Pelargonic acid is an intermediate in the production of lubricants, plasticizers, perfumes, herbicides, fungicides, resins [5,3].

Although the ozonolysis of oleic acid has shown high conversion and selectivity [25,2,1,3], hazardous problems associated with the use of ozone have always been a challenge [8]. Using benign oxidants such as hydrogen peroxide in the oxidation reaction (Equation 4.1), however, makes it necessary to employ a highly efficient catalytic system. In our recent review paper, all the catalytic systems reported in literature for this purpose have been thoroughly investigated[91]. Transition metals such as osmium, cobalt, molybdenum, chrome, gold, manganese, iron, ruthenium, and tungsten have been used as catalytic active sites, with more emphasis on Ru and particularly W. In spite of the excellent conversion and selectivity shown by homogeneous catalysts [64,60,59,2,65,63,61,62,58,57,54,56,55,53,3], their large-scale applications have been always restricted due to the lack of catalyst recovery. Curiously, use of heterogeneous catalysts with recycling ability has been scarcely reported [75,48,45], which would arise from their lower

conversion compared to homogeneous catalysts. This is mainly because of low catalyst/reactant contact from either low active site availability or pore diffusion limitations. Mesoporous materials have shown potential applications as either catalysts or supports for liquid-phase reactions of oils and fats [333,37]. Using mesoporous MCM-41 and microporous zeolites as catalyst support in the oxidative cleavage of oleic acid, Dapurkar et al. demonstrated the advantages of mesoporous catalysts compared to microporous ones [75]. Another way to improve the performance of heterogeneous catalysts is employing advanced nanocatalysts. The available results for nanocatalysts, although very rare, confirm that they could increase the activity of solid catalysts in oxidative cleavage of oleic acid [87,1]. Surface properties of metals oxides nanoparticles provide a great promise in their further modifications, which will make them favorable for use as catalysts in the biphasic oxidation reactions of unsaturated fatty acids.



In this work, we report a facile synthesis method for incorporating tungsten oxide into mesostructured  $\gamma$ -alumina with high surface area. In order to investigate the effect of  $WO_3$  on the porosity of the mixed metal oxide, samples with different loadings of tungsten oxide were compared to pure alumina and pure  $WO_3$ . Then, the catalytic activities of  $WO_3/\gamma\text{-Al}_2O_3$  samples in the oxidative cleavage of oleic acid were investigated. Furthermore, capping the surface of tungsten oxide nanoparticles with a surfactant, as a strategy for enhancement of catalytic performance, was developed, and the results were compared to those of the mesostructured catalysts.

## 4.2 Experimental

### 4.2.1 Materials and reagents

Aluminium isopropoxide ( $Al(O\text{-}i\text{-}Pr)_3$ ,  $\geq 98\%$ ), oleic acid (90%), tert-butanol ( $\geq 99\%$ ), and boron trifluoride ( $BF_3$ -methanol, 10% w/w) were purchased from Sigma Aldrich Co. Ammonium tungsten oxide hydrate  $(NH_4)_6W_{12}O_{39}\cdot xH_2O$  and D-(+)-Glucose (anhydrous, 99%) were provided by Alfa Aesar Co. Hydrogen peroxide (aqueous solution, 30 %) was purchased from Fisher Scientific Co.

## 4.2.2 Synthesis

*Mesoporous tungsten oxide/ $\gamma$ -alumina mixed metal oxide.* Tungsten oxide/ $\gamma$ -alumina were synthesized using a facile hydrothermal method followed by calcination. In a typical synthesis, 2.1 g (10.28 mmol) of Al(O-*i*-Pr)<sub>3</sub> and 1.8 g glucose were dissolved into 30 ml water/propanol (50/50 volume ratio). Then, nitric acid (10 wt %) was added dropwise to the solution to adjust the pH at around 5. Subsequently, a certain amount of ammonium tungsten oxide hydrate (0.13, 0.65, and 1.3 g for the samples II, III, and IV, respectively and 1.3 g for sample V) was added to the solution under high stirring. The prepared mixture was, then, transferred to a stainless steel autoclave and thermally treated at 200 °C for 24 h. After naturally cooling down, the obtained powders were separated using centrifuge at 5000 rpm and washed several times with water and ethanol. In the final step, the as-prepared dry products were annealed in a furnace at 600 °C for 3 h in air.

*Surfactant-capped tungsten oxide nanoparticles.* 0.70 g of ammonium tungsten oxide hydrate was dissolved into 15 ml water/ethanol (50/50 volume ratio), followed by adding 0.21 g oleic acid as surfactant, and the prepared solution was then transferred to the stainless steel autoclave for thermal treatment at 200 °C for 24 h. Finally, separation with centrifuge at 5000 rpm and washing several times with water and ethanol were carried out. The prepared samples and synthesis conditions are shown in Table 4.1.

**Table 4.1.** Synthesis conditions and prepared samples.

Sample	Thermal treatment		Calcination temperature (°C)	WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio	Surfactant/W molar ratio
	Temperature (°C)	Time (h)			
Mesoporous tungsten oxide/ $\gamma$ -alumina mixed metal oxide					
I	200	24	600	0	-
II	200	24	600	1/10	-
III	200	24	600	5/10	-
IV	200	24	600	10/10	-
V	200	24	600	-	-
Surfactant-capped tungsten oxide nanoparticles					
VI	200	24	-	-	0.26

### 4.2.3 Characterization

N<sub>2</sub> adsorption-desorption isotherms were determined at the temperature of liquid nitrogen with a Quantachrome Autosorb-1 system. The BET surface areas were calculated in the range of 0.05-0.3 P/P<sub>0</sub>. Before the measurements, the samples were outgassed under vacuum for 6 h at 150 °C. The total pore volume (V<sub>pore</sub>) was calculated from the amount of nitrogen adsorbed at P/P<sub>0</sub> = 0.95. Powder X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker SMART APEXII X-ray diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda=1.5418$  Å). Scanning electron microscopy (SEM) images were taken on a JEOL 6360 instrument at an accelerating voltage of 3 kV. Thermogravimetric analysis (TGA) was performed with a TGA Q500 V20.13 Build 39 thermogravimetric analyzer from room temperature to 800 °C with a heating rate of 5 °C min<sup>-1</sup> under an air flow of 50 mL min<sup>-1</sup>.

### 4.2.4 Oxidative cleavage reaction of oleic acid

Typically, a 50-mL, round-bottom flask was used to conduct the reactions under a batchwise constant temperature and constant pressure mode. This reactor was equipped with a condenser, a magnetic stirrer and an oil bath. The reaction feed included 2 g oleic acid, 6 mL H<sub>2</sub>O<sub>2</sub> (30% concentration), and 15 mL tert-butanol as solvent. After adding a constant amount of the synthesized catalyst (0.9 g) to the reaction media, the flask was put in the oil bath which was previously heated and maintained at the constant temperature of 120 °C. During the reaction, the reactor content was agitated continuously with the magnetic stirrer. After 5 h reaction, the catalyst particles were separated using centrifuge at 6000 rpm.

*Quantitative analysis of the reaction products:* Gas chromatography-mass spectrometry (GC-MS) was used for the separation and quantification of methyl esters of fatty acids. The GC-MS system included a Hewlett-Packard HP 5890 series GC system and MSD Hewlett-Packard model 5970. The GC system was equipped with Zebron ZB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25 mm). Helium was used as a carrier gas with the flow rate of 30 mL/min. A split ratio of 15:1 was fixed. The front inlet temperature was 280 °C. The oven temperature program consisted of maintaining at 50 °C for 2 min, then a ramp rate of 10 °C/min to 160 °C following by a hold-up time of 1 min, and further increase with the rate of 5°C/min to 290 °C. Direct injection was

employed with 0.1  $\mu\text{L}$  injection amount for each run. HP Chemstation software was used to analyze data.

Fatty acids are difficult to analyze with GC, because these highly polar compounds tend to form hydrogen bonds with the stationary phase in GC columns, leading to adsorption issues. Reducing their polarity make them more amenable for analysis. Esterification of fatty acids to fatty acid methyl esters is the most common method for preparation of fatty acids prior to GC analysis. Methyl esters offer excellent stability, and provide quick and quantitative samples for analysis. Therefore, All samples were converted to their respective methyl esters before analysis by Metcalfe et al. derivatization procedure [334,335] using boron trifluoride solution in methanol.

In order to present the results more clearly, the terms conversion (mole %) and yields (mole %) are defined as follows:

$$\text{Conversion} = \frac{\text{Total amount of oleic acid consumed}}{\text{Initial amount of oleic acid}} \times 100 \quad (4.2)$$

$$\text{Yield}_{(A)} = \frac{\text{Amount of chemical A produced}}{\text{Total amount of oleic acid consumed}} \times 100 \quad (4.3)$$

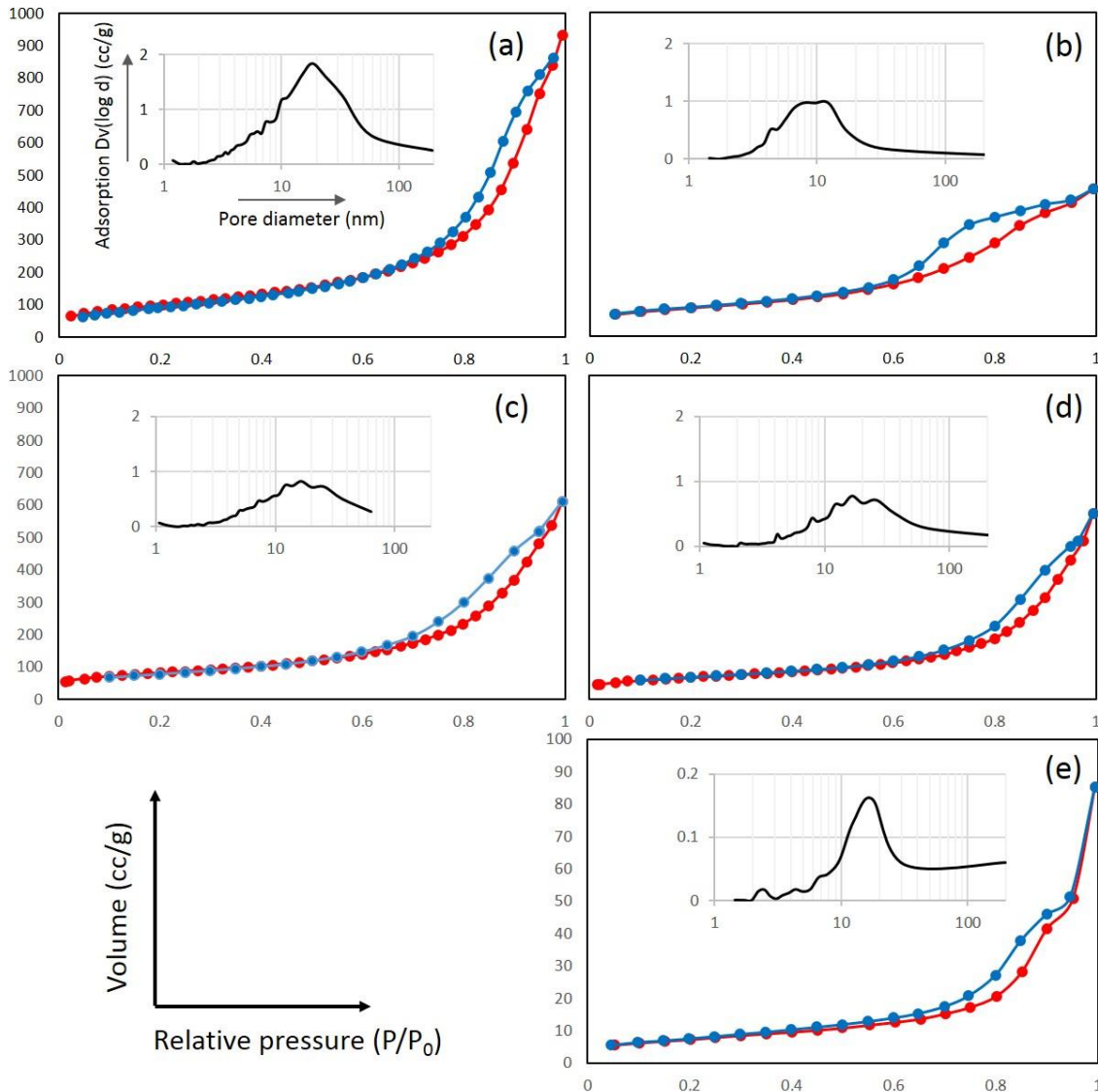
## 4.3 Results and discussions

### 4.3.1 Synthesized samples characterization

$\text{N}_2$ -adsorption/desorption isotherms confirmed the formation of mesoporous structures for the samples I-V (Figure 4.1). All of these samples possessed type IV isotherm (based on IUPAC definition) which is characteristic of mesoporous materials. In fact, the presence of glucose in the synthesis media is critical for the formation of the mesoporous structure. It has been shown that in the synthesis of alumina, no uniform pores can be obtained when glucose is not used [336]. The role of glucose would be as a template that interacts with the metals species via hydrogen bonding. The high amount of functional hydroxyl group in the structure of glucose provides an appropriate charge on its surface in the synthesis precursor, which will make adsorption of the metals cations



easier. Such interactions could play an important role in directing the structure to mesophase formation during the gelation [337].



**Figure 4.1.**  $N_2$ -adsorption/desorption isotherms and pore size distributions of (a) sample I, (b) sample II, (c) sample III, (d) sample IV, and (e) sample V.

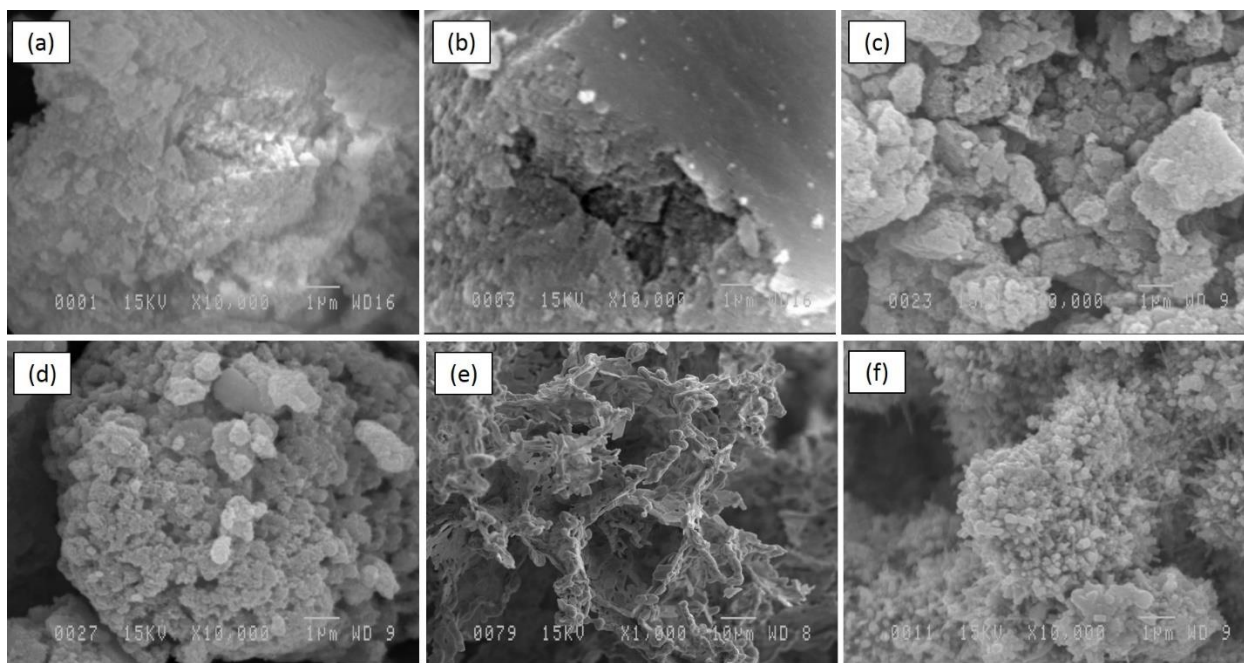
A high BET surface area ( $361 \text{ m}^2/\text{g}$ ) and a narrow pore size distribution were obtained for pure  $\gamma$ -alumina (sample I, Table 4.2). Increase in tungsten oxide content decreased the surface area; as Table 4.2 shows. Prepared samples with  $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$  molar ratio of 1/10, 5/10, and 10/10 had

surface area of 308, 251, and 204 m<sup>2</sup>/g, respectively. It should be highlighted that these high surface areas were obtained even after the calcination at 600 °C. This means that the synthesized mesoporous tungsten oxide/ $\gamma$ -alumina mixed metal oxides had very high thermal stability which can arise from thick pore wall. Adding WO<sub>3</sub>, also, reduced the average pore size due to the difference in dimensionality of molecules of tungsten and aluminium oxides. Sample IV, however, did not comply with this trend. It would be because of a disorder in the mesostructure of alumina that happened at high content of WO<sub>3</sub>. Curiously, there was a significant decrease in the surface area of pure tungsten oxide (sample V) compared to previous samples. The main reason is that the hollow structure, which could be obtained by using glucose as template, collapses during the calcination at high temperatures in the absence of alumina because of less thermal stability. This collapse in the hollow structure for sample V is obvious in its SEM image (Figure 4.2 e). Comparing the SEM images of the samples I-IV in Figure 4.2 reveals a slight change in the morphology of the samples, from uniform morphology to two-phase morphology. Also, it is clear in Figure 4.2 f that the presence of oleic acid as surfactant in the synthesis of sample VI strongly affected its morphology.

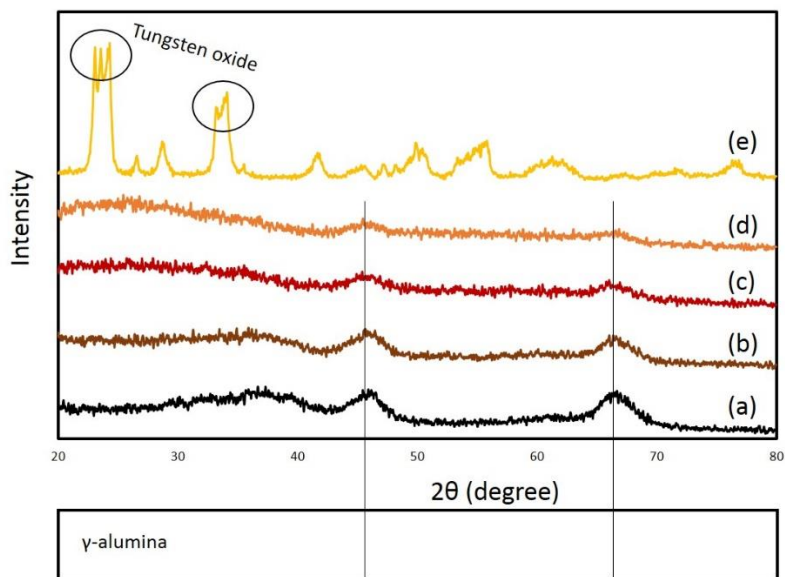
Powder X-ray diffraction (XRD) patterns of the samples I-V are presented in Figure 4.3. Pure metal oxide samples, samples I and V indicated the crystalline structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and tungsten oxide, respectively. Incorporating tungsten oxide into the structure of alumina, however, decreased the intensity of the characteristic peaks of  $\gamma$ -alumina. This shows that crystalline structure of mesoporous alumina can be affected by incorporating another metal oxide. On the other hand, by increasing WO<sub>3</sub> content, one of the main peaks of tungsten oxide ( $2\theta \approx 24^\circ$ ) was emerged in sample IV pattern. Energy-dispersive X-ray spectroscopy (EDS) results of the samples I-IV, as shown in Figure 4.4, demonstrate the increase of tungsten oxide content in the mesostructure of  $\gamma$ -alumina.

**Table 4.2.** N<sub>2</sub>-adsorption/desorption isotherms results.

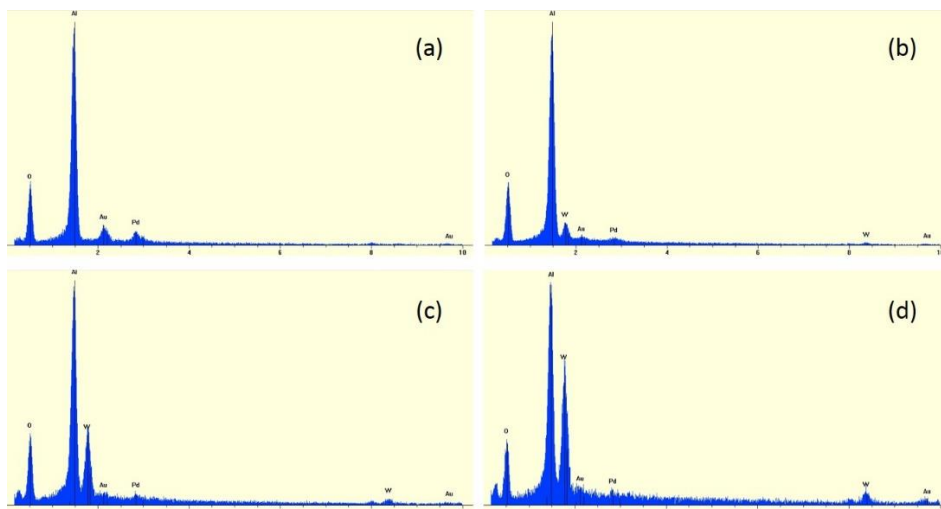
Sample	WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
I	0	361	1.30	14.5
II	1/10	308	0.64	8.3
III	5/10	251	0.68	5.5
IV	10/10	204	0.62	12.2
V	-	26	0.08	11.9



**Figure 4.2.** SEM images of (a) sample I, (b) sample II, (c) sample III, (d) sample IV, (e) sample V, and (f) sample VI.

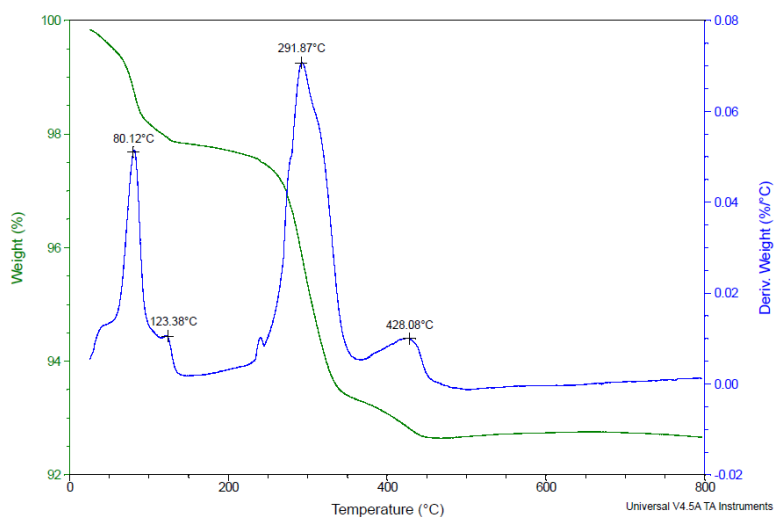


**Figure 4.3.** XRD patterns of (a) sample I, (b) sample II, (c) sample III, (d) sample IV, and (e) sample V.



**Figure 4.4.** EDS spectrums of (a) sample I, (b) sample II, (c) sample III, and (d) sample IV.

In order to investigate the presence of surfactant on the surface of tungsten oxide nanoparticles thermogravimetric analysis (TGA) of the sample VI is shown in Figure 4.5. The amount of surfactant oleic acid on the surface of  $\text{WO}_3$  nanoparticles was approximated about 5.25 wt%.



**Figure 4.5.** Thermogravimetric behavior of sample VI.

### 4.3.2 Catalytic study

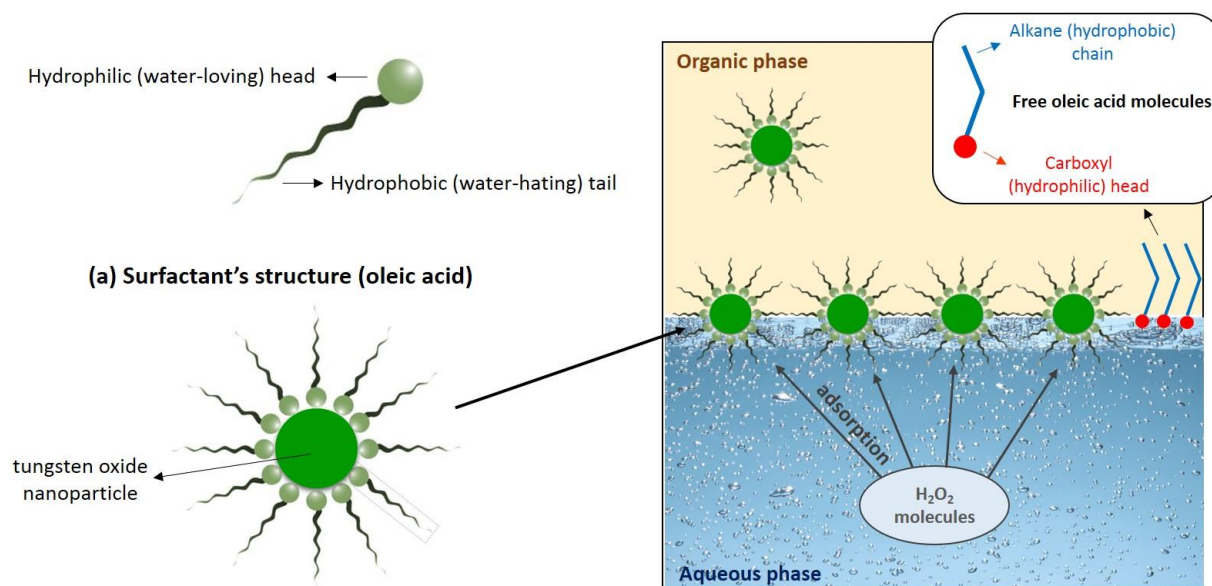
Sample II, III, and IV (mesoporous tungsten oxide/ $\gamma$ -alumina) and sample VI (surfactant-capped tungsten oxide nanoparticles) were employed as catalysts in the oxidative cleavage of oleic acid to investigate the effect of  $\text{WO}_3$  loadings on the catalytic activity, on one hand, and compare the activities of the two types of advanced heterogeneous catalysts, on the other hand. The catalytic tests results are summarized in Table 4.3.

**Table 4.3.** Catalytic test results.

Sample	Conversion (%)	Yield (azelaic acid) (%)	Yield (pelargonic acid) (%)
II	78	20	7
III	72	28	9
IV	60	32	15
VI	95	58	24

After 5 h reaction, sample II could convert 78% of initial oleic acid. The yields of production of the desired products, i.g., azelaic and pelargonic acids, however, were quite low. Increasing  $\text{WO}_3$  loading in samples III and IV although made higher yields, slightly decreased the conversion. Among all the porous structures, mesoporous catalysts seem to be more convenient for oxidative cleavage of oleic acid, because of the higher dimensionality of the interaction between the components and the catalyst surface. Microporous materials, which are widely used as heterogeneous catalysts in the refining and petrochemical industry mainly due to their high surface area, are not useful for the oils and fats reactions because of the relatively large molecular size of oleochemicals; molecules of oleic acid (molecular size about 2 nm [72]) cannot easily enter the pores of microporous catalysts (pore size less than 2 nm [71]), so all the surface area is not accessible. On the other hand, the catalytic activity of macroporous materials is poor as the result of their relatively low surface area. Average pore size of 8.3, 5.5, and 12.2 nm in samples II, III, and IV, respectively, and relatively high surface areas resulted in the acceptable reaction conversion. A downward trend in the reaction conversion from sample II (with higher surface area) to sample IV (with lower surface area) is because of the decrease in contact area between the reactants and catalysts. The obtained higher yields for samples III and IV arise from the presence of more tungsten oxide as active sites in the catalyst structure.

The surfactant-capped nanoparticles catalyst (sample VI) showed excellent activity; 95% conversion for oleic acid and 58% and 24% production yields for azelaic and pelargonic acids, respectively, were obtained. Generally capping the surface of nanoparticles with surfactant could be an efficient strategy to increase their catalytic performance. In particular, in the liquid medium of oxidation of oleic acid reaction, using a proper surfactant could result in better dispersion due to the fact that surfactants can oppose van der Waals forces. In this way, the aggregation of particles will be prevented and, consequently, catalytic activity of the catalyst will not decrease during the reaction [90]. Scheme 4.1 illustrates the performance of surfactant-capped tungsten oxide nanoparticles as catalysts in the oxidative cleavage of oleic acid with hydrogen peroxide in a molecular view[91]. The surfactant capped on the surface of tungsten oxide nanoparticles is oleic acid. Having both hydrophilic head and hydrophobic chain, surfactant molecules reinforce the stability of emulsion in the biphasic reaction which consists of aqueous phase ( $H_2O_2$  solution) and organic phase (oleic acid). Moreover, free molecules of oleic acid, which can be located at the interface due to having hydrophilic and hydrophobic parts, also contribute to the emulsion stability. Since the reaction occurs mostly at the interface, high concentration of the heterogeneous catalyst at the interface is preferred which is highly likely possible with the aid of surfactant. This is the result of two counter effects; while hydrophilic surface of tungsten oxide immerses them into the aqueous phase, hydrophobic chain of surfactant drags the catalyst toward the organic phase.



(b) **Surfactant-capped nanoparticle:** molecules of surfactant oleic acid attach to the surface of tungsten oxide nanoparticles from hydrophilic head.

(c) **Performance in the reaction (under high stirring):** H<sub>2</sub>O<sub>2</sub> molecules are adsorbed on the surface of nanoparticles which are accumulated at the interface.

**Scheme 4.1.** Schematic illustration for surfactant-capped tungsten oxide nanoparticles as efficient nanocatalyst. (a) Surfactant (oleic acid) molecule, (b) hydrophobic surface of surfactant-capped nanoparticles and (c) Performance in the biphasic oxidative cleavage of oleic acid. Presence of surfactant (i) contribute to the stability of emulsion and (ii) prevents aggregation of the catalyst particles [91].

The presence of the surfactant-capped catalysts at the interface makes adsorption of H<sub>2</sub>O<sub>2</sub> molecules from aqueous phase easier. Then, a kind of peroxy-metal complex can be formed at the surface of tungsten oxide particles. On the other hand, the hydrophobic chain of the surfactant attracts the oleic acid molecules, as the main reactant, from organic phase, and then the reaction takes place on the surface of tungsten oxide particles. The peroxy-metal complex is believed to be efficiently responsible for oxidizing of olefins [45]. As soon as one molecule of H<sub>2</sub>O<sub>2</sub> becomes consumed to produce peroxy species, another molecule of hydrogen peroxide will be adsorbed on the surface, and therefore the reaction will be continued. Actually, the role of phase transfer agent in the homogenous systems, to which the high reaction efficiency was ascribed [64,2,65,63,62,3], can be played by the surfactant in this heterogeneous catalytic system. Capping the tungsten oxide nanoparticles with oleic acid, a catalytic system was developed in this work that has the best properties of both homogeneous and heterogeneous systems.

## 4.4 Conclusion

In order to overcome the common disadvantages of heterogeneous catalysts in the oxidation reactions of unsaturated fatty acids, two types of advanced heterogeneous catalysts were developed in this work. To increase the contact area and time between the reactants, high surface area tungsten oxide/ $\gamma$ -alumina mixed metal oxides with different loadings of  $\text{WO}_3$  were successfully synthesized. The mesoporous structure of these catalysts provided a higher dimensionality between the components and the catalyst surface which resulted in an acceptable conversion. Also, to increase the dispersion of the solid catalyst particles in the biphasic oxidative cleavage reaction of oleic acid, surfactant-capped tungsten oxide nanoparticles were synthesized. The catalytic test results demonstrated that capping the surface of tungsten oxide nanoparticles with oleic acid as surfactant could considerably increase the catalytic activity of the solid catalyst. In fact, the unique properties of nanoparticles would propose them as the frontier of homogeneous and heterogeneous catalysts that can exploit the high activity of homogeneous catalyst. However, an obstacle remaining in the application of nanocatalysts is their recovery from the liquid solution after catalytic reactions. To overcome this limitation, the nanomaterials assembled with a super-paramagnetic material such as  $\text{Fe}_3\text{O}_4$  nanoparticles should be studied.

## Acknowledgment

This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC) through the INNOV-UC and Discovery grants. The authors wish to thank the industrial partners (Oleotek and SiliCycle Inc.) for stimulating discussions and comments.