UNIVERSITI PUTRA MALAYSIA

SULFONATED POLYMERIC ZINC OXIDE-BASED NANOCATALYSTS FOR METHYL ESTER PRODUCTION

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By

SOROUSH SOLTANI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

Special dedicated to my dear mother for her emotional support and endless pure love.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

SULFONATED POLYMERIC ZINC OXIDE-BASED NANOCATALYSTS FOR METHYL ESTER PRODUCTION

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December 2016

Chairman : Umer Rashid, PhD
Institute : Advanced Technology

The increasing production growth and economic developments have increased not only the consumption of energy but also increased the level of pollutants. It is assumed that fossil fuels would be eliminated in years to come, which alerted an urgent need to switch to the renewable energy sources (RESs). In this research work, high free fatty acid feedstock, palm fatty acid distillate (PFAD), has been explored as non-edible feedstock for biodiesel production using efficient mesoporous zinc oxide (ZnO) based nanocatalysts.

The main purpose was to develop the mesoporous ZnO based catalysts to enhance the conversion rate of biodiesel production for PFAD. An efficient mesoporous ZnO based nanocatalysts were hydrothermally fabricated, using the polyethylen glycol (PEG) as a surfactant and D-glucose as a template. The effects of different zinc nitrate concentration and different calcination temperature were determined on the structural and textural properties. Surface functionalization is a beneficial approach which improves the adsorption capacity and surface activity of the parent materials. One route is the doping of the metal nanoparticles as support into pre-fabricated materials. In this project, ZnO has been functionalized with Al and Cu in order to improve its textural properties. Zinc aluminate ($ZnAl_2O_4$) and zinc-cupper (CuO-ZnO) mixed metal oxides possess superior advantages such as high surface area and high thermal stability. Post-sulfonation treatment is another approach which was done in order to modify the hydrophobicity via attaching of $-SO_3H$ groups on the active sites. Furthermore, the effect of sulfonation conditions on catalytic activity was also examined. It was observed that sulfonation under severe conditions led to the reduction of the textural properties.

The palm fatty acid distillate (PFAD) was chosen as feedstock for biodiesel production, containing high FFA (around 80-90%). In order to improve the esterification process for PFAD production, a comparison study was also carried out

between two efficient autoclave and microwave heating systems over synthesized mesoporous ZnO based nanocatalysts.

The influences of esterification reaction conditions (methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time) towards the catalytic performance of the synthesized nanocatalysts were also investigated to optimize the higher biodiesel yield. It was found that the functionalized mesoporous ZnO based SO_3H-ZnO, SO_3H-$ZnAl_2O_4$, SO_3H-CuO-ZnO nanocatalysts had high catalytic activity for esterifying PFAD, giving FAME yield of 91.20%, 94.65%, and 95.76%, respectively. The recyclability of the synthesized catalysts was further evaluated. According to the recyclability results, the mesoporous ZnO based nanocatalysts were able to remain active for at least eight consecutive runs without using further treatment.

Furthermore, the physico-chemical characteristics of the biodiesel produced from PFAD were tested with compliance to EN14214 and ASTM D6751 standards. The key fuel properties of the produced PFAD biodiesel were all within range of the mentioned standards.

As a conclusion, from all the results, it was found that the synthesized sulfonated mesoporous ZnO based nanocatalysts had great potential to catalyze high FFA feedstock (PFAD) for biodiesel production with high recyclability. The excellent activity and recyclability of the catalyst may be assigned to the combination of unique textural properties and polymeric attachment of the $-SO_3H$ functional group to the surface of the catalyst. The esterification reaction under solvo-thermal methods resulted in high biodiesel yield in shorter reaction rate, especially using microwave heating system.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

SULFONATE POLIMER ZINC OKSIDA NANOCATALYSTS BERASASKAN UNTUK METIL ESTER PENGELUARAN

Oleh

SOROUSH SOLTANI

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Pertumbuhan pengeluaran yang semakin meningkat dan perkembangan ekonomi telah meningkat bukan sahaja penggunaan tenaga tetapi juga meningkatkan tahap pencemaran. Adalah diandaikan bahawa bahan api fosil akan dihapuskan pada tahun-tahun akan datang, yang memberi amaran keperluan yang mendesak untuk beralih kepada sumber tenaga boleh baharu (RESs). Dalam kajian ini, asid lemak bebas suapan tinggi, Asid lemak sawit sulingan (PFAD), telah diterokai sebagai suapan bukan makanan untuk pengeluaran biodiesel menggunakan pemangkin nano berasaskan mesoporous zink oksida (ZnO) berkesan.

Objektif utama kajian ini adalah untuk membangunkan pemangkin berasaskan mesoporous zink oksida untuk meningkatkan kadar penukaran pengeluaran biodiesel untuk PFAD. pemangkin nano berasaskan mesoporous ZnO berkesan direka secara hidroterma, menggunakan polietilena glikol (PEG) sebagai surfaktan dan D-glukosa sebagai ejen pembentukan liang (templat). Kesan kepekatan zinc nitrat yang berbeza dan suhu pengkalsinan yang berbeza ditentukan pada sifat-sifat struktur dan tekstur. Pemfungsian permukaan adalah satu pendekatan berfaedah yang meningkatkan kapasiti penjerapan dan aktiviti permukaan bahan induk. Satu laluan adalah pemendapan nano zarah logam sebagai penyokong ke dalam bahan-bahan pra-fabrikasi. Dalam kajian ini, ZnO telah difungsikan dengan Al dan Cu dalam usaha untuk memperbaiki sifat teksturnya. Zink aluminat ($ZnAl_2O_4$) dan zink-tembaga (CuO-ZnO) oksida logam campuran memiliki kelebihan yang lebih baik seperti kawasan permukaan tinggi dan kestabilan haba tinggi. Rawatan pasca sulfonasi merupakan kaedah lain yang telah dilakukan bagi mengubah suai kehidrofobikan melalui melekatkan kumpulan $-SO_3H$ pada tapak aktif. Tambahan pula, kesan kondisi sulfonasi terhadap aktiviti pemangkin telah dikaji. Diperhatikan bahawa sulfonasi di bawah keadaan yang tidak baik membawa kepada pengurangan sifat tekstur.

Asid lemak sawit sulingan (PFAD) telah dipilih sebagai suapan bagi pengeluaran biodiesel, mengandungi FFA tinggi (sekitar 80-90%). Dalam usaha untuk meningkatkan proses pengesteran bagi pengeluaran PFAD, satu kajian perbandingan

telah dijalankan antara dua sistem pemanasan autoklaf dan gelombang mikro cekap ke atas pemangkin nano berasaskan mesoporous ZnO disintesis.

Pengaruh keadaan tindak balas pengesteran (nisbah molar metanol kepada minyak, kepekatan pemangkin, tindak balas suhu dan tindak balas masa) ke atas prestasi pemangkin nano disintesis juga telah disiasat untuk mengoptimumkan hasil biodiesel lebih tinggi. Ia telah mendapati bahawa pemangkin mesoporous ZnO berasaskan SO_3H-ZnO, SO_3H-$ZnAl_2O_4$, SO_3H-CuO-ZnO mempunyai aktiviti pemangkin tinggi untuk pengesteran PFAD, memberikan hasil FAME iaitu 91.20%, 94.65%, dan 95.76% masing-masing. Kebolehan kitar semula pemangkin disintesis telah dinilai selanjutnya. Menurut hasil kebolehan kitar semula, pemangkin nano berasaskan mesoporous ZnO dapat kekal aktif sekurang-kurangnya lapan kali berturut-turut tanpa menggunakan rawatan lanjut.

Tambahan pula, ciri-ciri fizikokimia biodiesel dihasilkan daripada PFAD telah diuji dengan pematuhan EN14214 dan piawaian ASTM D6751. Sifat-sifat bahan api utama yang dihasilkan biodiesel PFAD semuanya adalah dalam julat piawaian yang dinyatakan.

Kesimpulan, dari kesemua keputusan yang diperlukan, didapati bahawa pemangkin nano berasaskan mesoporous sulfonasi ZnO disintesis mempunyai potensi tinggi untuk menjadi pemangkin suapan FFA tinggi (PFAD) bagi pengeluaran biodiesel dengan kitar semula yang tinggi. Aktiviti dan kebolehan kitar semula pemangkin yang sangat baik mungkin disebabkan kepada gabungan ciri-ciri tekstur yang unik dan pelekatan polimer kumpulan kefungsian SO_3H dengan permukaan pemangkin. Tindak balas pengesteran di bawah kaedah solvothermal menyebabkan hasil biodiesel tinggi dalam kadar tindak balas yang lebih pendek, terutama sekali apabila menggunakan sistem pemanasan gelombang mikro.

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I certify that a Thesis Examination Committee has met on 30 December 2016 to conduct the final examination of Soroush Soltani on his thesis entitled "Sulfonated Polymeric Zinc Oxide-Based Nanocatalysts for Methyl Ester Production" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

AOCS	American oil chemists society
ASTM	American society for testing and materials
AV	Acid value
BET	Brunauer-Emmett-Teller
BDDT	Brunauer, Deming, Deming, and Teller
CP	Cloud point
D_P	Pore diameter
DTA	Differential thermal analysis
DW	Distilled water
EN	European standard
EtOH	Ethanol
Eq	Equation
FA	Fatty acid
FAME	Fatty acid methyl ester
FE-SEM	Field emission scanning electron microscopy
FFA	Free fatty acid
FID	Flam ionization detector
FP	Flash point
FT-IR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
GC	Gas chromatography
GHG	Greenhouse gas
GHz	Giga hertz
HMO	Household microwave oven

HPHT	High pressure high temperature
HCl	hydrochloric acid
IUPAC	International union of pure and applied chemistry
JCPDS	Joint committee on powder diffraction standard
kHz	Kilo hertz
KV	Kinematic viscosity
M	Molar weight
ME	Methyl ester
MeOH	Methanol
MHz	Mega hertz
MO_x	Metal Oxide
MPWM	Microwave-plus width modulation
MW	Microwave
N_2	Nitrogen
NH_3	Ammonia
NO_x	Nitrogen dioxide
OM	Ordered mesoporous
OMC	Ordered mesoporous carbon
OMM	Ordered mesoporous material
OMS	Ordered mesoporous silica
PFAD	Palm fatty acid distillate
PP	Pour point
RES	Renewable energy source
S_{BET}	Specific surface area
SDA	Structure direction agent

SFA	Saturated fatty acid
SG	Specific gravity
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TG	Triglyceride
TGA	Thermogravimetric analysis
V	Volume
V_P	Pore volume
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Green technology and alternative fuels

Human existence fundamentally depends on the energy sources. Currently, the fossil fuel reserves are depleting at a rapid rate as a result of both worldwide population growth and the global economy growth. This issue should be urgently tackled to eliminate the shortage of the energy sources in the future. Another challenge is to reduce the risk to the public health by decreasing the level of greenhouse gases (GHGs) emission. It is noteworthy that the global energy consumption should be green. This scenario is sadly not possible with mineral fuels that are the most dominant source of the globe's energy.

1.2 Biodiesel

The renewable energy sources (RESs), such as solar cell, wind turbines, geothermal power and biofuel have attracted scientist's attention which are less harmful to the human life. Among all RESs, biodiesel could be the best substitute to replace the fossil fuels in the near future. Biodiesel is a sulfur free liquid fuel which generated using a verity of feedstocks. It is considered as a non-toxic and environmental friendly source of energy which can substantially reduce the disease possibility due to eliminating of the carbon dioxide (CO_2) footprint by 78% (Cantrell et al., 2005).

Biodiesel can be derived from animal fats and vegetable oils via transesterification and esterification reactions. Typically, esterification is a chemical reaction by which a FFA molecule reacts with an alcohol to produce a methyl ester plus a water molecule. The reaction is directly taking place between the alcohol and the FFAs. The following equation (Figure 1-1) represents the general chemical reaction for all industrial esterification reaction with methanol:

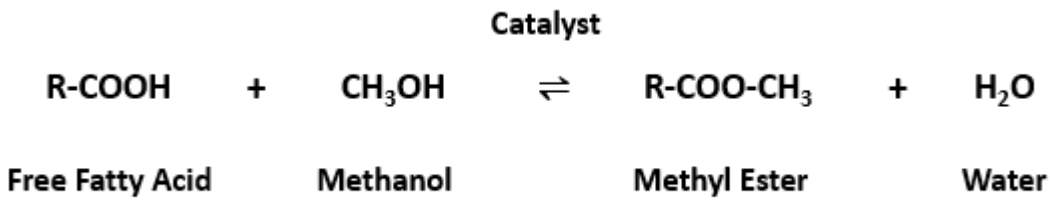

Figure 1.1 : General Esterification Process

1.3 Approaches to reduce the cost of biodiesel production

High cost is the main barrier to commercialize the production of biodiesel. It is assessed the cost of biodiesel production above 1.5 times more expensive than mineral fuels production. There are three important approaches to reduce the cost of biodiesel production: (i) selecting an appropriate cheap feedstock, (ii) employing a fast solvothermal technique and (iii) selecting a suitable catalyst.

1.3.1 Selecting an appropriate feedstock

Choosing a right feedstock plays a prominent part to achieve the high yield with lower cost; because 60-80% of the cost of biodiesel production counts from the price of the feedstocks (Gui et al., 2008; Singh and Singh, 2010). Currently, above 95% of biodiesel production are being derived from edible vegetable oils (Gui et al., 2008). Furthermore, increasing the demand on vegetable oils, subsequently increases the cost of both biodiesel and edible oil markets (Kansedo et al., 2009).

One approach to reduce the cost of production is to use non-edible oils (Canakci, 2007; Murugesan et al., 2009). Non-edible oils are classified into two groups: waste plant oils (WPOs) and waste cooking oils (WCOs). Being unfit for human consumption is the most important aspect of non-edible oils that ridiculously reduces the price of these feedstocks. In the current research, a high FFA content of non-edible byproduct from refinery of palm oil known as palm fatty acid distillate (PFAD) was chosen as feedstock for the production of fatty acid methyl ester (FAME) which is known as biodiesel (Top, 2010; Hosseini et al., 2015). In our investigation, we found that the using of PFAD can simultaneously maximize the FAME yield productivity and minimize the manufacturing cost.

1.3.2 Employing a fast solvo-thermal technique

Typically, biodiesel operates with the conventional heating systems which consume a huge amount of power and time. The major problem to conventional heating is that the heat energy can only transmit to the surface of the materials. In contrast, using a fast solvo-thermal method such as microwave equipment, conveys the heat power directly to the center of the reactants. Recently, the microwave-assisted method has been attracted vast interest in biodiesel synthesis because of its desirable properties such as shorter synthesis time, energy transferring (instead of heat transferring), selectivity in the heating of different materials, and lower manufacturing cost (Hernando et al., 2007; Azcan and Danisman, 2007; Groisman and Gedanken, 2008; Chen et al., 2012). Autoclave-assisted reactor method is another type of solvo-thermal method which provides high yield under high pressure and high temperature (HPHT) condition at a short reaction time (Byrappa, 2013). The HPHT condition inside the autoclave reactor results in cleavage between hydrogen atoms on the surface of the catalyst. The separated hydrogen atoms bond with FFAs, follows with catalyzing into methyl ester (ME) (Gao et al., 2015). Autoclave-assisted method is considered as one of the most eco-friendly method due to a sealed system condition (Yoshimura and Byrappa, 2008). To the best of our knowledge, using solvo-thermal method can highly

enhance the biodiesel productivity by enhancing the production yield in a shorter reaction rate with a cheaper production cost.

1.3.3 Selecting a proper catalyst

Another approach to speed up the process of biodiesel production is applying an appropriate catalyst in order to enhance the conversion at a shorter reaction time by increasing the number of active sites (Fukuda et al., 2001; Dmytryshyn et al., 2004; Vicente et al., 2004). An appropriate catalyst requires high considerations for biodiesel production, which consists of a large number of saturated fatty acids (SFAs) and long carbon-chains.

Generally, catalysts are categorized into three major groups; homogeneous catalyst, heterogeneous catalyst and biocatalyst. Conventionally, homogeneous base and acid catalysts are using for biodiesel production. Although, the hygroscopic nature, water and soap formation, oil losses and difficulty in separation are some undesired drawbacks of the homogenous catalysts during catalyzing reaction. Thereby, research efforts have been switched onto heterogeneous catalysts (Granados et al., 2007; Xie and Li, 2006). A number of heterogeneous solid acid catalysts have been used to catalyze the transesterification of triglycerides (TGs) and esterification of FFAs. However, the synthesized catalysts have their individual drawbacks such as complicated preparation steps, less activity and stability, less surface area and less porosity which decline the performance of synthesized heterogeneous catalysts (Jiang et al., 2008).

In this regard, mesoporous catalyst is considered as a perfect candidate to enhance the catalytic activity of biodiesel production due to unique textural properties such as high surface area and uniform and flexible pores diameter which lead to absorb long chain of FFAs (Kao et al., 2005; Kim and Park, 2007; Liu et al., 2008). Thereby, combination of higher surface area and higher porosity facilitates mass transfer or multiple scattering of the reactants through the porous framework (Yu, 2003; Zhang et al., 2013).

1.3.3.1 Surface modification

Surface functionalization is an efficient approach which improves the adsorption capacity and increases the surface activity of the parent materials. It is believed that doping a proper support element is an efficient route which leads to the breaking of the formed phase and increases the surface area of the materials (Carmo et al., 2009; Zhao et al., 2011a).

Post-sulfonation treatment is another important approach which modify the hydrophobicity of the as-prepared samples via attaching of the SO_3H to the active sites. Through catalytic reaction, hydrophobic surface plays a prominent part which firstly, increases the adsorption of long chain of FFAs and secondly, inhibits the

existence of molecule of water near the active sites (Liu et al., 2008; Mumtaz et al., 2013; Anand et al., 2013; Drelinkiewicz et al., 2014; Fraile et al., 2015). Therefore, post-sulfonation of the polymeric mesoporous catalyst is expected to provide a strong attachment of the SO_3H functional group to the active sites which significantly prohibits the leaching of sulfonic acid groups through esterification reaction (Shu et al., 2009; Wang et al., 2012; Istadi et al., 2015; Fraile et al., 2015).

In this study, a number of sulfonated mesoporous mixed metal oxides catalysts were fabricated using surfactant assisted method. The main objective was to enhance the surface area of the parent materials as high as possible in order to provide a better opportunity for the SO_3H species to be entrapped into the pores channels of the parent materials. Then, the performance and reusability of each catalyst was investigated via esterification of PFAD in presence of methanol under different reaction condition and different type of reactors.

1.4 Problem statement

The energy crisis has become the main concern for the human beings. This concern is strongly associated to the availability of natural sources of power (*i.e.*, coal, natural gases and fossil fuels) which are depleting at rapid rates. However, the world's most energy needs are met mainly by petrochemical sources; the depletion of these sources has warned human communities to discover alternative sources of energy. The increasing trend on the number of researches on biodiesel production might be a true evidence that biodiesel would be the best substitute for petroleum-based diesel. Biodiesel is a sulfur free liquid fuel, which can enhance the world's energy security. Biodiesel is generated from various feedstocks which has comparable physical and chemical characteristics to petroleum.

However, biodiesel carries a high cost in industry scale due to the expensive edible feedstocks. The use of non-edible waste material helps in reducing the cost of biodiesel production. In the current research, PFAD oil was used as starting material, which was believed to have a significant potential to reduce the cost of production and maximize the FAME yield productivity. Indirectly, the waste management from palm oil factory could be improved.

In the process of biodiesel production, a catalyst plays a prominent part to enhance the efficiency of the conversion. Recently, classical homogeneous catalysts lost their place in inorganic synthesis due to some drawbacks including the hygroscopic nature, water and soap formation, oil losses and difficulty in separation. In this work, heterogeneous catalyst was used instead of homogeneous catalyst in order to avoid these obstacles. The functionalized mesoporous mixed metal oxide catalysts were fabricated in this research, possessed unique textural properties such high surface area and uniform pore diameters. The high catalytic activity and excellent recyclability of the synthesized catalysts were attributed to the structural and textural characteristics of mesostructured catalysts.

The extended reaction time by current conventional heating systems reduces the efficiency of the process of biodiesel production. Furthermore, a large amount of heat energy is required to heat up the reaction mixture. In this work, autoclave and microwave-assisted methods were used as solvo-thermal method in order to heat up the reaction mixture. It is known that using solvo-thermal method can highly enhance the yield of production in a shorter reaction rate. In this regard, a comparison study was carried out between two different heating systems in order to find out the efficient heating reactors.

1.5 Objective

The main aim of this study is to examine the effect of surface functionalization on structural, textural, morphological, physico-chemical, and thermal characteristics of the prepared mesoporous catalysts, and further examine the catalytic activity and stability of the optimized catalysts through esterification of PFAD via fast solvo-thermal methods. The achieved results from this research work can be used to improve the new general mechanism on parallel evaluation of mesostructure and various properties of advanced materials in further studies.

Here, in this research work, the work-step objectives are elaborated in four distinctive parts as follows:

1. To synthesize and functionalize the polymeric mesoporous ZnO based material via (i) one-situ metal modification and (ii) post-acid treatment for mesoporous acidic catalyst development.

2. To investigate the structural, textural, morphological, physico-chemical, and thermal properties of the polymeric ZnO based nanocatalysts.

3. To evaluate the catalytic activity of different reaction conditions through esterification of PFAD via polymeric ZnO based nanocatalysts using autoclave and microwave system and recyclability of the synthesized catalysts.

4. To determine some key fuel qualities of the produced PFAD methyl ester using polymeric ZnO based nanocatalysts and comparsion with EN14214 and ASTM D6751 standards.

1.6 Scope of the research

The scope of this research was to fabricate a polymeric mesoporous nanomaterials and then functionalize it with proper metal oxides in order to enhance the textural properties. Furthermore, the post-sulfonation treatment was applied in order to improve the acidity of active sites and catalytic activity, simultaneously. Moreover, the physico-chemical, structural, textural, morphological, and thermal characteristics of the synthesized mesoporous catalysts were investigated. The catalytic activity of the synthesized polymeric mesoporous solid acid nanocatalysts have been assessed through esterification of the PFAD. A comparison study was carried out between two

different heating systems to find out the efficient heating reactors. The key fuel properties of the optimized PFAD methyl ester was further assessed with compliance to EN14214 and ASTM D6751 standards.

1.7 Thesis outline

This chapter briefly describes the general introduction of the current scenario on conventional energy and biodiesel, fundamental properties of the mesoporous nanocatalyst, surface functionalization process, and the problem statement as well as the research objectives. In chapter two, it reports the overview of previous literatures about the preformed synthesis methodology, surface optimization and the progress of the biodiesel production over functionalized mesoporous catalysts. Chapter three presents the methodology of the catalysts and biodiesel preparation and the equipment that were used to characterize the occurred changes in the products; such as structural, textural, morphological, physico-chemical, and thermal properties under various conditions. Chapter four is about the obtained results from the current research work and discussion. The summery of the concluded results is presented in chapter five which followed by feature research suggested recommendations. Finally, the references, appendix and the list of publications are attached, accordingly.

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