Title: Microwave Applications in Heating and Drying of Biological Materials

G.S.V. Raghavan and V. Orsat

Department of Agricultural and Biosystems Engineering Macdonald Campus, McGill University, Ste-Anne de Bellevue, Quebec, Canada, H9X 3V9

# ABSTRACT

combining two or more heat and mass transfer processes. Attention is being given to heat-sensitive investigated include dielectric heating with microwaves and radio frequencies, and hybrid systems commercial partners, successful commercial applications. At present, leading technologies being uniformity of heating, at improving product quality, and at developing, with the assistance of aim at reducing the energy consumption, at shortening the process duration, at improving the study of conventional and non-conventional drying/thermal processing techniques aims at the requires both heat and mass transfer where the addition of heat sustains the evaporative process. Heating and drying are among the most important steps in preparing food and agricultural products biological materials since they require improved processes to attain desirable quality improvement of both heat and mass transfer. Through experimentation and modelling, these studies Heating and drying are by far the most energy intensive phases of the food transformation chain. The for processing, handling and preservation. While heating only involves a transfer of energy, drying

### MICROWAVE-ASSISTED PROCESSES IN ANALYTICAL CHEMISTRY

### Irina Kubrakova

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin str., 19, Moscow 117975, GSP-1, Russia

The actual problem of chemistry today is a search of methods of influence on chemical reactions. A solution of this problem is especially important for analytical chemistry, in part, for the promotion of processes and operations preceded a measurement of analytical signal.

One of the ways to speed up physical and chemical interactions in homogeneous and heterogeneous systems is the use of microwaves. Investigations of chemical reactions under microwave heating are carried out in Russia since 1988. To summarize the results obtained, an approach including a comparison of some parameters of the reactions under thermal and microwave heating (time; recovery or yield; composition and structure of reaction products; activation energy), was used. Within the framework of this approach a number of reactions (hydrolysis of organic and inorganic compounds, complexation of metal ions with organic reagents in solutions and in a sorbent phase, oxidation of organic substances by mineral acids) was studied, and a predominant role of kinetic factors was demonstrated.

To expand the analytical applications of microwaves, a mathematical model of kinetics of chemical reaction in a closed vessel heated by microwaves, was developed. On this base the dynamic method is proposed for the determination of activation energy (Ea) for oxidation of organic substances by nitric acid, when Ea can be calculated from experimental exponential function of pressure vs reciprocal temperature. Data obtained, being in a good agreement with the literature, confirm the possibility to apply the microwave systems for the receiving of quantitative characteristics of the reactions and modeling of slow interactions.

A labilization of substitutionally inert metal compounds in a microwave field under their complexation with N-,S-,O-containing organic reagents is grounded on the example of noble metals ions. The dramatic acceleration of all constituent processes, including hydrolysis, metal ion reduction and complex formation itself, as well as the increase of complex recovery has been demonstrated. The structure of complexes formed was shown to be similar for thermal and microwave heating. Sorption processes carried out in static conditions and in a flow were also studied. A contribution of athermal effects to the results obtained is discussed.

Another field of application of microwaves in analytical chemistry is the synthesis of macroheterocyclic compounds and polymers, important for analytical purposes. Microwave procedures were shown to be extremely effective in these cases due to short time, high yields and possibility to regulate the composition of products.

Microwave-assisted sample preparation in a present work is considered as a stage, summarizing various physical and chemical interactions. It is a good basis for the further expansion of possibilities of determination methods in the analysis of both inorganic and organic matrices. Reduction of pretreatment time, simplicity of combination with instrumental techniques, possibility of automation, and a variety of analytical operations and processes accelerated by microwaves, promote a creation of modern analytical schemes for the determination of traces.

Such schemes, based on microwave pretreatment (including decomposition of samples and

sorption extraction of trace elements) are considered. The procedures have been developed for the analysis of biological and environmental samples (including speciation), geological samples, containing noble metals, and technological materials, including high purity substances. Results obtained, as well as main principles, features and advantages of microwave-assisted sample preparation coupled with atomic spectroscopy, in part, ETAAS and ICP-AES, are discussed.

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### ON THE DEVELOPMENT OF MICROWAVE CHEMISTRY

### Qinhan Jin

Changchun Research and Development Center for Analytical Instruments Department of Chemistry, Jilin University, Changchun 130023, P. R. China

Microwave chemistry has been growing up as a very active and promising area of research and application. A monograph *Microwave Chemistry* with 15 chapters was published last year in China, which summarized the progresses in the field made till two or three years ago<sup>[1]</sup>. Recently, some new advances have appeared. In this report, several important examples will be given:

- (1) Studies on non-thermal microwave effect with contradictory conclusions<sup>[2-4]</sup>;
- (2) The synthesis of a blue laser material (GaN) with the assistance of microwave radiation<sup>[5]</sup>;
- (3) The simulation of photosynthesis of organic compounds from carbon dioxide and water by using microwave induced catalytic reactions<sup>[6]</sup>;
- (4) The commerciallization of microwave plasma torch (MPT) spectrometer<sup>[7]</sup>;
- (5) The development of microwave thermospray nebulizer<sup>[8]</sup>.

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PREPARATION OF HIGH CONTENT SURFACTANT-FREE NARROWLY DISTRIBUTED MACROMOLECULE NANOPARTICLE LATEX BY MICROWAVE IRRADIATION.

Zhang Wenmin<sup>2</sup> Wu Chi <sup>1,3</sup> Ngai To <sup>1</sup> Lou Chianwa<sup>1</sup>

1. Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong; 2. Department of Chemistry, Anhui Normal University, Wuhu, Anhui 241000; 3. The Open Laboratory of Bond Selection Chemistry, Department of Chemical Physics, The University of Science and Technology of China, Hefei, Anhui 230026)

Abstract Emulsifier-free emulsion polymerization of styrene in acetone-water medium was carried out using microwave irradiation. Below acetone content of 50 %, narrowly distributed nanoparticles stabled in water were obtained. The average particle hydrodynamic radius  $\langle Rh \rangle$  decreased from 278 to 35.4 nm with an increase in acetone content in the range 0-50 %. When the initiator amount is kept a constant, the  $\langle Rh \rangle$  value is increased proportional to the monomer concentration, in the range from 1.2 to 7.0 %. When the monomer concentration is kept a costant and the initiator concentration is decreased (from 0.27 to 0.027 %) the  $\langle Rh \rangle$  value is decreased from 25 to 22 nm and then increased. On the bases of the initiator, potassium persulfate (KPS), acts as a source of surface charge and ionic strength has both the stabilizing and coagulating effects in the polymerization process, we successfully found a simple formula to describe the relationship between the particle size  $\langle R_B \rangle$  and mass ratio ( $m_{monomer}$  /  $m_{initiator}$ ). Adding a few

amount of methyl methacrylate (MMA) monomer, the size the copolymer particles remarkably decreased from 35.4 to 16.0 nm. It was shown that the increased stability of the resulted dispersion is due to the increase of surface hydrophilicity of latex particles. The stability and uniformity of the final latex did not change any more before and after the vacuum distillation of the acetone from the dispersions. Consequently, we can get a high concentration latexes very conveniently by simply distill out the acetone from the latex solution. The reaction rate was accelerated obviously by microwave irradiation and final particle size was smaller than that prepared by conventional method.

Keywords: Emulsifier-free emulsion polymerization, Polystyrene, Methyl methacrylate, Microwave irradiation

<sup>\*</sup> The project is supported by SNFC

# MICROWAVE ASSISTED CHEMICAL REACTION ON POLYMERS DEACETYLATION OF CHTIN

Dok-Chan Kim, Young-Shin Park, Sam-Hui Lee, and Joo-Hee Hong Department of Chemical Engineering, University of Seoul, Seoul 130-743, Korea

### Introduction -

Chemical reactions on polymers has emerged as one of the most active fields in polymer science because of its ability to produce specialty polymers with desirable chemical and physical properties through modification of readily available polymers.

Chitin, poly-N-acetyl-D-glucosamine, having cellulose-like rigid structure is one of the most abundant natural polymers and considered having high potential as a specialty polymeric material in various fields such as biomedical, biotechnological, and industrial applications. However, intractability of chtin such as poor solubility, reactivity, and processability has limited its utilization as a polymeric material. Chemical modifications of chitin are thus becoming increasingly important for developing advanced materials. Chitin may be deacetylated to an acid-soluble derivative, chitosan by treatment with concentrated aqueous NaOH solutions. Such a process usually requires very long-time treatments. A few reports have been published on this process by use of microwaves, aiming to decrease the long processing times [1,2,3,4]

The aim of this study was to show the effects of pulsed microwave power and liquid media on deacetylation of chitin. The chitin was treated in various media - water, alcohol or dimethyl sulfoxide(DMSO) - with different concentrations of aqueous NaOH solution at atmospheric pressure by pulsed microwave irradiation.

### Experimental

As microwave applicator was utilized a multimode cavity of a domestic oven (magnetron output, 650W) equipped with an on-off microprocessor controller for pulsed irradiation (pulse time interval, 2 seconds). Water, alcohol(methyl, ethyl, t-butyl alcohol and ethylene glycol) and dimethyl sulfoxide(DMSO) were used as media. Commercial crab shell chitin and chitosan(75~85% deacetylation) was used. Chitin(Sigma) was intimately mixed with organic liquid-NaOH(aq) solution. Mass ratio of chitin to liquid was 1 to 10. The mixture was packed in a round in a round-bottomed flask fitted with a reflux condenser. Degree of deacetylation was determined by I.R. spectroscopy and colloid titration method. Intrinsic viscosity was measured by Ubbelohde viscometer.

### Results and Discussion

The experimental results were presented in Table 1 and Fig. 1. In DMSO or water deacetylation was relatively fast whereas in alcohol slow. It is generally known as chitin chains consist of amorphous micellar regions and crystalline regions. Therefore resistance to deacetylation is primarily due to inactivity in the crystalline regions of the micelles. This may be caused inaccessibility of reactive sites to the deacetylation catalyst or by stabilization through hydrogen bonding. [4] It is thus considered that DMSO or water is conductive to cause sufficient swelling to permit high degree of deacetylation.

From the observed results in Table 2, degree of deacetylation through this investigation is higher to those of reported number. This reveals that pulsed microwave power could accelerate the reaction more than continuous microwave power.

### Conclusion

A pulsed microwave(pulse time interval, 2seconds) was used for deacetylation of chitin to produce chitosan in media - water, alcohol, and DMSO - with aqueous NaOH solutions and found that the pulsed microwave power was effective in this heterogeneous reaction. As reaction media DMSO and water were useful.

### Acknowledgement

Support from University of Seoul is gratefully acknowledged.

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Table 1. Degrees of deacetylation by pulsed microwave irradiation.

| Media                                     |    | Water | •  | Me | ОН | Et | ЭН | t-Bı | ıOH | l  | Et-<br>col |    | DM | ISO |    |
|---|----|-------|----|----|----|----|----|------|-----|----|------------|----|----|-----|----|
| **NaOH<br>(wt%)<br>Reaction<br>time (min) | 20 | 30    | 50 | 20 | 30 | 20 | 30 | 20   | 30  | 20 | 30         | 05 | 10 | 20  | 30 |
| 4   | 56 | 72    | 76 | 26 | 41 | 50 | 54 | 57   | 63  | 33 | 47         | 34 | 44 | 42  | 50 |
| 8   | 60 | 76    | 77 | 28 | 49 | 57 | 58 | 60   | 67  | 47 | 63         | 47 | 62 | 72  | 86 |
| 15  | 63 | 79    | 81 | 28 | 50 | 59 | 59 | 60   | 67  | 52 | 68         | 67 | 74 | 77  | 92 |
| 20  | 63 | 88    | 88 | 29 | 55 | 61 | 63 | 61   | 68  | 63 | 71         | 71 | 78 | 82  | 92 |
| 25  | 64 | 90    | 90 | 29 | 56 | 63 | 64 | 66   | 68  | 64 | 72         | 75 | 81 | 83  | 93 |

<sup>\*</sup>Et-glycol= ethylene glycol.

Table. 2. Results of microwave deacetylation of chitin in aqueous NaOH solutions.

| Raw chitin             | Reaction time (power, temp)     | (power, temp) NaOH |  | Viscosity         | Reference           |
|------------------------|---------------------------------|--------------------|--|-------------------|---------------------|
| Chitin<br>(Crab shell) | 25min<br>(650W,pulse,<br>120°C) | 30%                | 90%                                    | 388ml/g           | This investigatio n |
| Chitin<br>(Squid pen)  | 22min                           | 30%                | 87.2%                                  | 659ml/g           | Goycoolea<br>et.al  |
| Chitin                 | (700W)                          | 45%                | >80%                                   | 3.80-9.00<br>Pa•s | Yan<br>et.al        |
| Chitin                 | 7min                            | •                  | 75%                                    | -                 | Guo                 |
| Chitin<br>(Crab shell) | (390W,<br>150°C)                | 50%                | Complete<br>soluble 2% HAc<br>solution | 1.1x10³cP         | Peniston<br>et.al   |

<sup>\*\*</sup> for example, 20%={(2g NaOH)/(6g Organic liq.+2g Water+2g NaOH)}x100

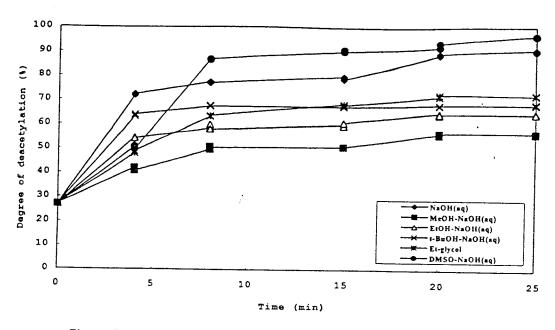


Fig. 1. Degree of deacetylation of chitin in media with 30% NaOH(aq).

## APPLICATION OF DIELECTRIC PROPERTIES IN MICROWAVE-ASSISTED MAILLARD-REACTION BEFORE REACHING BOILING

Xiangjun Liao\*1, G. S. V. Raghavan1, A. V. Yaylayan2

- 1 Dept. of Agricultural & Biosystems Engineering, Macdonald Campus, McGill University, 21,111 lakeshore road, Ste-Anne-de-Bellevue, Quebec, Canada H9X3V9, E-mail: xliao@po-box.mcgill.ca, Phone: (514) 398-7641 Fax: (514) 398-8387
- 2 Dept. of Food Science and Agricultural Chemistry, Macdonald Campus, McGill University, 21,111 lakeshore road, Ste-Anne-de-Bellevue, Quebec, Canada H9X3V9

Maillard Reaction is one of typical chemical reactions in the food processing. In recent years, the Maillard Reaction has far reaching implications in the production of flavors and aromas, nutrition, toxicology, technology in food processing. Glucose is an important reduced sugar in food product [1, 2]. In addition, the use of microwave irradiation in food engineering and organic chemistry will be promising due to the fact that the use of microwave irradiation has some advantages over the traditional heating methods such as the fast heating rate, time-saving and good quality product and selectivity [3]. Here, the Maillard reaction of the glucose with lysine before it reaches boiling is investigated under microwave irradiation. The relationships between the yields, reaction rate and the factors that affect microwave heating such as dielectric properties (dielectric constant and dielectric loss factor), penetration depth are presented. The higher concentration of the reactants, the higher reaction rate is observed. In view of dielectric properties, there is not much change in the dielectric constant, but there is some important change in the dielectric loss factor during the reaction. Further, the parameters such as temperature, the composition of the initial reaction mixture, the addition of the other dielectric materials that have influences on the dielectric properties will be discussed. This information is helpful to better understand the effect of microwave irradiation in chemical reactions and give some insight on the chemical reactions at various power levels. The results from the different heating methods (microwave heating and conventional heating) are compared at molecular level.

Acknowledgment: We thank CIDA (Canadian International Development Agency) for their financial support.

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Synthesis of Complexes Metal Ion and Schiff Bases ligands in Solid-State under Microwave Irradiation

Meng Ji-ben\* Wang Yong-mei Zhou Wu-xing Jin jin Deportment of Chemistry, Nankai University, Tianjing 300071

Abstact: In recent years, there has been considerable interest in the chemistry of metal chelates<sup>1</sup> <sup>2,3</sup> but these take some hours or several days and have lower yields in general condition. In the present paper we report that a series of new complexes (scheme 1) of bivalent ions of Co,Cu and Ni with Schiff bases SB<sub>1</sub>,SB<sub>2</sub> and SB<sub>3</sub> derived from 4-nitroanilin, 1,4-benezendiamine, ethenediamine and 2-hydroxy-1-benzaldehyde have been synthesized in solid-state under microwave irradiation and characterized by IR(table1). We have succeeded in developing a convenient and rapid method, which is taken only several minutes in solid-state on microwave irradiation and have yields higher than those previously reported.

Scheme 1: reaction of metal and Schiff bases

OH
$$CH=N \longrightarrow NO_2 + M^{2+} \longrightarrow M(SB_1)_2$$

$$SB_1 \qquad HO$$

$$CH=N \longrightarrow N=CH \longrightarrow + M^{2+} \longrightarrow M(SB_2)$$

$$SB_2 \qquad M = Cu$$

$$OH \qquad HO$$

$$CH=N-CH_2CH_2-N=CH \longrightarrow + M^{2+} \longrightarrow M(SB_3)$$

$$SB_3 \qquad M = Co,Ni,Cu$$

We introduce microwave irradiation to promote the reaction of metal and Schiff bases. The reactions are simple and were accelerated. The results are shown in Table 1

Table 1: Results of the reaction

| ligands | Metal ion        | Mi    | crowave   | Yield % | Description         |  |  |
|---------|------------------|-------|-----------|---------|---------------------|--|--|
|         |                  | Power | Time(min) |         | 2 coorpaint         |  |  |
| SB1     | Co <sup>2+</sup> | 240W  | 25        | 53      | Red powder          |  |  |
| SB1     | Cu <sup>2+</sup> | 138W  | 15        | 45      | Red-brown powder    |  |  |
| SB2     | Cu <sup>2+</sup> | 138W  | 15        | 55      | Blake-brown powder  |  |  |
| SB3     | Co <sup>2+</sup> | 138W  | 5         | 37      | Yellow-green powder |  |  |
| SB3     | Ni <sup>2+</sup> | 138W  | 20        | 68      | Orange powder       |  |  |
| SB3     | Cu <sup>2+</sup> | 138W  | 5         | 54      | Purple Powder       |  |  |

The main points of the infrared bands of the ligands and the complexes are given below: the free ligands exhibit a band at  $1600 \text{cm}^{-1}$  due to azomethine group v (N=CH) which shifts towards lower frequency ( $\triangle$  v =20-30 cm<sup>-1</sup>)in the spectra of the complexes. (table 2)

Table 2 The Infrared Spectra data of the Complexes

| Ligands         | Metal ion        |  |                                  |
|-----------------|------------------|--|----------------------------------|
| 2.64103         | IVICIAI IOII     | IR –Ligands (cm <sup>-1</sup> )  | IR-Complexes (cm <sup>-1</sup> ) |
| SB <sub>1</sub> | Co <sup>2+</sup> | 3450,1620,1600,1570,1520,1490,1460,<br>1380,1340,1280,1180,1120,1040,920,<br>860,740,690.                    | 1570,1518.1460,<br>1430, 1345.   |
| SB <sub>1</sub> | Cu <sup>2+</sup> | As Same (1570,1180)  | 1540, 1200                       |
| SB <sub>2</sub> | Cu <sup>2+</sup> | 3400,1610, <u>1570</u> ,1490,1420,1370,1320,<br>1280,1200, <u>1180,1160,1140,1120</u> ,1030,<br>970,860,750. | 1550,1240,1180,<br>1160,1140.    |
| SB₃             | Co <sup>2+</sup> | 3450,2900,1640,1620,1580,1500,1460,<br>1420,1380,1320,1290,1250,1200,1150,<br>1040,1020,980,860,780.         | 1600,1560,1060,<br>1040,900,800. |
| SB <sub>3</sub> | Ni <sup>2+</sup> | As same (1580,1020,860)  | 1560,1100,900.                   |
| SB <sub>3</sub> | Cu <sup>2+</sup> | As same (1620,1380,1040,1020,860)  | 1600,1350,1060,1040,<br>900      |

Experimental: general procedure under microwave irradiation: A mixture of Schiff (SB<sub>1</sub> 2mmole; SB<sub>2</sub>、SB<sub>3</sub> 1mmole) and metal salts [Co(Ac)<sub>2</sub> • 4H<sub>2</sub>O; NiCl<sub>2</sub> • 6H2O; CuCl<sub>2</sub> • 2H<sub>2</sub>O] was ground with an agate mortar and pestle and was placed in a beaker .The beaker was irradiated in the microwave oven with a power of 240-138W for several minutes. The mixture was thoroughly washed with ethanol or benzene and the product was obtained.

We synthesis six coordinate compounds of Schiff bases and metal ions with irradiation to promote. The method rapid and yield purer products because of a shorter residence time at the high temperature.

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孟继本 教授 王永梅 教授

### Synthesis of poly sodium acrylate-bentonite water superabsorbent by microwave technique

Pu Minli #Han Jiaxiang #Zhang Chunxiang Lin Tianming Li Jing (College of Material Science & Engineering, Tianjin University, Tianjin, 300072) (#Institute of Elemento-organic Chemistry, Nankai University, Tianjin, 300071)

Superabsorbents are crosslinked networks of hydrophilic polymers with a high capacity for water uptake and have a variety of valuable applications such as disposable diapers, soil for agriculture and horticulture, water blocking tapes, medicine and so on. In this article, superabsorbent polymers based on sodium acrylate (SA) and bentonite are prepared by microwave technique. The time of reaction is reduced from 4-6h to 2-4min, compared with solution polymerization or inverse suspension polymerization. With the addition of bentonite, the cost can be reduced and the thermal stability of polymers can be improved.

The rate of polymerization can be improved with the increase in the energy of irradiation. (see in table 1) For the same energy of irradiation (P=150w), when the time of irradiation is less than 120s, the polymerization can not proceed completely and the absorption is very low. When the time of irradiation is between 150s and 210s, the polymerization can proceed normally and the water-absorption capacity is high. When the time of irradiation is more than 240s, fiercely polymerization occurs and the water-absorption capacity decreases. The effect of the concentrateion of crosslinker on water-absorption capacity is shown in Fig.1. The water-absorption capacity decreases with the increase in the amount of bentonite (see in Fig.2). The effect of the concentration of initiator and the monomer neutralization on the water-absorption capacity has also been investigated. Besides, the morphology of absorbent gels is shown in Fig.3. It appears that the particles of bentonite well disperse in the molecular networks of poly(sodium acrylate).

TGA curve of two kinds of water absorbents is shown in Fig.4. It shows that the thermal stability of poly (sodium acrylate)-bentonite is improved.

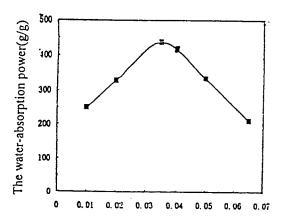
### Acknowledgment:

We thank Dr. Jocelyn Pare of Environmental Technology Centre, Environment Canada for giving Soxwave 100 unit (Prolabo Co.) and Canadian International Development Agency for the support to this work.

Table 1 The effect of the time of irradiation on the state of the system of reaction and water absorption

| Time of Irradiation(s) | State of Reactive System | Water Absorption (g/g) |  |  |
|------------------------|--------------------------|------------------------|--|--|
| 60                     | not sticky               | (8)                    |  |  |
| 90                     | sticky                   | 50                     |  |  |
| 120                    | sticky                   | 140                    |  |  |
| 150                    | gel state                | · 490                  |  |  |
| 180                    | gel state                | 540                    |  |  |
| 210                    | gel state                | 510                    |  |  |
| 240                    | fiercely polymerization  | 180                    |  |  |

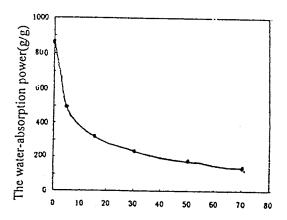
bentonite/monomer (wt%): 5%, atmosphere: N2, the energy of irradiation: 150w



The concentration of crosslinker (wt%)
Fig.1 The effect of the concentration of
crosslinker on water-absorption capacity
Bentonite/monomer(wt%):5%



Fig.3 Micrography of absorbent gels (x 200)



The concentration of bentonite (wt%) Fig.2 The effect of the concentration of bentonite on water-absorption capacity

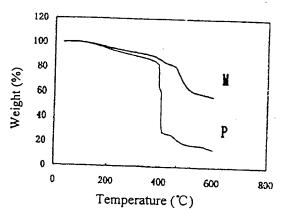


Fig.4 TGA curve of two kinds of water absorbents

P: poly(sodium acrylate)

M: composite (acrylate/bentonite=100:30)
Rate of heat-up:10 °C/min, atmosphere: N2

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# SYSTEMATICAL STUDIES ON LIGHT HYDROCARBON ROMATIZATION: MICROWAVE HEATING AND AROMATIZATION OVER ZnNi/HZSM-5 CATALYST"

Zhang Jinsheng Sun Zhaolin Gao Changlu Cheng Zhilin

Department of Applied Chemistry, Fushun Petroleum Institute, Fushun Liaoning, 113001, P. R. China

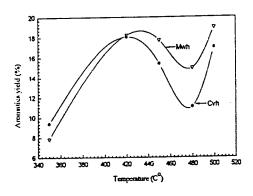
Aromatization of light hydrocarbons over metal-modified ZSM-5 zeolites is a process of practical importance <sup>[1]</sup>. The active species of this catalyst involve numerous polar -OH groups and the oxides strongly and selectively absorb microwave energy. Thus, our lab has attempted to apply microwave technology to this catalytic reaction.

This project was financially supported by the National Natural Science Foundation of China (No. 2976008)

<sup>\*</sup>Corresponding author: Zhang Jinsheng. Tel: (0413) 6650342; Email: zjs@fra.fspu.edn.cn

For the purpose of comparison, the experimental catalyst prepared by our lab is of low activity. Aromatization reactions, by microwave heating (Mwh) and conventional heating (Cvh) methods, have been undertaken using n-hexane or mixed  $C_4$  as sources under the conditions of WHSV=1h<sup>-1</sup> and different temperatures.

Fig.1 gives the comparison of aromatics yield for the two different heating methods using n-hexane as source at different temperatures. From 350°C to 420°C, aromatics yield of conventional aromatization (CA) is a little higher than that of microwave aromatization (MA). The difference of aromatics yields decreases as the temperature increases. At above 420°C, aromatics yield of MA is obviously higher than that of CA. Aromatics yield of MA are higher by 4% compared with that of CA at 480°C. The main reason is that n-hexane is cracked into small molecular hydrocarbons and aromatization is difficult at between 420°C and 480°C. Apparently, microwave "hot spot" effect makes small molecular hydrocarbons into aromatics more easily than Cvh does. At above 480°C, both aromatics yields increase again.



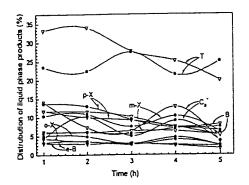


Fig. 1 Comparison between Mwh and Cvh liquid using n-hexane as source at different temperatures °C

Fig. 2 Relationship between distributions of phase products and reaction time at 450

• stands for Cvh,  $\nabla$  stands for Mwh.

Table 1 shows the comparison of the selectivity for the two heating methods at 450  $^{\circ}$ C. Benzene and toluene yields of Mwh increase 4% and 5%, respectively, compared with those of Cvh, but meta-xylene yield decreases 2.8%. The  $C_6^{\circ}$  and  $C_9^{\circ}$  contents further prove that Mwh can easily turn light Hydrocarbons into aromatics.

Tab. 1 Comparison of the selectivity between Mwh and Cvh using n-hexane as source (reaction time: 5h)

| source (reactio     | n time. Ju   | )       |                      |                    |           |           |         |
|---------------------|--------------|---------|----------------------|--------------------|-----------|-----------|---------|
| Temperatur<br>e (℃) | Technol      | 0       | Distri<br>products ( | butions of<br>(w%) | the gas a | ınd liqui | d phase |
|                     | gy           | B<br>C. | T<br>C₀⁺             | e-B                | m-X       | p-X       | o-X     |
| 450                 | Mwh<br>3.120 | 30.000  | 10.200<br>9.145      | 29.165             | 2.894     | 6.220     | 9.101   |
|                     | Cvh<br>4.019 | 36.935  | 6.170<br>6.435       | 24.006             | 3.218     | 9.046     | 10.153  |

B = benzene, T = toluene, e-B = ethylbenzene, m-X = meta-xylene, p-X = para-xylene, o-X = ortho-xylene.

The relationship between distributions of liquid phase products and reaction time is showed in Fig.2. With increasing time, the toluene yield of Mwh decreases from 34% to 20%, while that of Cvh fluctuates between 21.5% and 27.4%. Benzene and ortho-xylene yields of both methods change little and the para-xylene yield of Cvh decreases gradually.

Tab. 2 Comparison between microwave aromatization and the conventional one using mixed C<sub>4</sub> as source

| Technol | Reactio<br>n            | BTX<br>yield | produ     | Distribution of gas and liquid pheroducts (w %) |          |          |           |      |                  |                  |  |
|---------|-------------------------|--------------|-----------|---|----------|----------|-----------|------|------------------|------------------|--|
| ogy     | temperat<br>ure<br>(°C) | (W<br>%)     | В         | T   | e-B      | m-<br>X  | p-X       | o-X  | C <sub>9</sub> ⁺ | C <sub>6</sub> · |  |
| Mwh     | 400                     | 29.5<br>1    | 16.7<br>7 | 34.3  | 2.4      | 8.0      | 18.8      | 6.89 | 6.42             | 6.1              |  |
| Cvh     | 400                     | 12.4<br>3    | 8.45      | 16.8<br>3                                       | 3.2<br>4 | 7.5<br>9 | 12.6<br>9 | 5.80 | 17.7<br>4        | 27.<br>26        |  |

BTX = benzene + toluene + xylene.

In term of the characteristic of Mwh, our lab has been undertaking investigations on mixed  $C_4$  aromatization. Table 2 gives the comparison of aromatization results between Mwh and Cvh using mixed  $C_4$  as the source at 400 °C. The BTX yield of MA increases 17.08% and aromatics selectivity is higher than that of Cvh. Since the active species of the catalyst are heated selectively under microwave irradiation, oligomerization, cyclization, dehydrogenation can, using mixed  $C_4$ , olefinrich, as source, occur more easily than under Cvh at lower temperatures.

In general, microwave irradiation technology applied to aromatization, especially using light hydrocarbons as source, is a promising method and has important theoretical value.

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### KNOEVENAGEL CONDENSATION UNDER MICROWAVE IRRADIATION

### Mahmood Tajbakhsh

Department of Chemistary, University of Mazandaran, Babolsar, Iran

Knoevenagel condensation of carbonyl compounds on compounds containing an active methylene group is one of the most important preparation method of substituted alkenes. Reactions are gerenally catalyzed using bases or Lewis acids[1]. Recently use of inorganic solid supports as catalysts, resulting in higher selectivity, milder conditions and easier work up has rapidly increased and has been reported as a useful condition for Knoevenagel reaction. Microwave heating in organic synthesis is now widely used. Its application in the case of inorganic solidsupported reactions has been greatly examined [2]. It is well known that carbonyl condensation with active methylene compounds may be catalyzed both by base and by acid. However it has been claimed that the acid-catalyzed reaction leads to lower yields and does not appear efficient amongst conventional methods [3]. When benzaldehyde and malonitrile were adsorbed on montmorillonite K-10 and submitted to microwafe irradiation for the appropriate time and power the desired olefin was obtained in excellent yields. Consequently a systematic study of this reaction to establish the generality of the method has been undertaken with various aldehydes and active methylene compounds utilizing montmorillonite K-10 under microwave irradiation in solventless system. Aliphatic aldehydes did not give any good results but aromatic aldehydes bearing a variety of functional group namely P-bromobenzaldehyde and P-nitrobenzaldehyd are reacted with methylene compounds such as malonitrile and ethylcyanoaccetate in the presence of montmorillonite K-10 under microwave irradiation in solvent free conditions, these reactions lead to completion in 45-85% yield. In conclusion, this methodology, which associates dry heterogeneous media with microwave irradiation, appears easy, fast and clean to perform the Knoevenagel reaction. Furthermore, by development of a continuous microwave reaction for organic synthesis [4,5] this work may have more industrial application where the absence of solvent and low cost of the method may lead to environmental and cost advantages.

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OXIDATION OF ALCOHOLS AND DIRECT OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL AND TETRAHYDROPYRNAYL ETHERS USING ZEOFEN UNDER MICROWAVE IRRADIATION WITHOUT SOLVENT

### M.M.Heravi

Department of Chemistry, School of Sciences, Azzahra, University, Vanak Tehran, Iran

Zeofen(short for zeolit HZSM5,ferric nitrate) has been prepared and used for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds under microwave irradiation in solvent-free condition. Oxidative deprotection of structurally different trimethysilyl and tetrahydropyrnyl ethers to the corresponding carbonyl compounds has been achieved in the presence of aforementioned reagent. Under microwave irradiation and in solvent-free condition this reagent has been used successfully for oxidative deoximation and desemicarbonization.