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The effects of microwaves on the catalyst preparation and the oxidation of *o*-xylene over a V_2O_5/SiO_2 system

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Abstract

With microwave irradiation, phthalic anhydride was obtained with a high yield of 67 mol% at ca. 563 K by the oxidation of *o*-xylene with air over V_2O_5/SiO_2 system. It is found that dispersion of V_2O_5 on SiO_2 is more homogeneous when the catalyst is prepared by microwave irradiating method. In the microwave catalytic process the optimum reactor bed temperature of the title reaction decreases to 563 K (653 K in the conventional process). The effects of the microwave electromagnetic field on the catalysts are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Microwave; *o*-Xylene; Oxidation; V_2O_5/SiO_2

1. Introduction

Phthalic anhydride (PAN) is one of the most important products of modern large scale organic synthesis. Today more than 80% of phthalic anhydride is obtained from *o*-xylene due to lower cost, availability, and ease of transportation than those for naphthalene. During investigations of the oxidation of *o*-xylene, it was apparent that a silica-gel-supported catalyst had very poor yield for PAN compared to V_2O_5/TiO_2 [1]. On the other hand, in recent decade there have been a great number of articles concerning microwave irradiation as an alternative form to the direct supply of thermal energy [2]. One of the areas where microwave irradiation appears to have a beneficial effect is heterogeneous catalysis, in which microwave dielectric heating seems to be a process well-suited for activating solid catalysts [3–7]. The origin of the microwave coupling dielectric heating effect lies in the capacity of an electric field to polarize charges in a material. This effect is enhanced when the irradiated material has a strong dipolar character. This is particularly the case with those catalysts where the support is an oxide with numerous polar OH groups. Moreover, when polar molecules are present on the surface such as V_2O_5, stronger coupling effect with microwave energy will be made [2,3]. The other reasons for the interest in a microwave process over conventional heating methods include the potential for

1. significant reduction in the costs due to energy savings and shorter processing time,
2. improved product distribution, and
3. improved or unique micro-structures and properties of the catalysts prepared with the microwave irradiating method.

In our work, when the oxidation of *o*-xylene was carried out over V_2O_5/SiO_2 catalyst with the microwave irradiation, 67 mol% of yield and 94 mol% of

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selectivity to PAN were obtained under mild conditions. The probable reason for the influences of the microwave energy on the catalyst preparation and the oxidation of *o*-xylene are discussed.

2. Experimental

The microwave oven used for the catalytic reaction is a commercial oven operating at 2450 MHz with variable power levels (80–750 W). The catalytic tests were carried out in a flow fixed-bed quartz reactor system, its schematic diagram is shown in Fig. 1. The reactor of 18 mm ID was loaded in the microwave oven and the catalyst bed was kept at the center of the oven. A 2 mm ID quartz capillary was located in the reactor as the outlet to accelerate the flow of the reaction products out of the catalyst bed to suppress deep oxidation of products to CO_x. The temperature of the reaction bed was measured using a thermometer (273–773 K) inserted into the catalyst bed, and could be continuously regulated by controlling the microwave power levels (We found mercury in the thermometer, enclosed by glass tube and the catalyst, is shielded well from the microwave electromagnetic field. Mercury and microwaves do not interact with each other.) The temperature measurement method was not able to detect the non-homogeneous bulk temperature distribution. The volume of the catalyst was 2 ml (particle size: 0.45–0.9 mm). The ratio of the mixed reactant stream of evaporated *o*-xylene and air was 1:99 (volume). The velocity of air was 5 cm^3/s. The total space velocity of feed gas was 7200 h^{-1}. The reaction products were collected in an ice–salt condenser (ice+H_2O+NaCl) and acetone continuously. In the conventional process, all the reaction conditions were the same except the use of a classical heating oven.

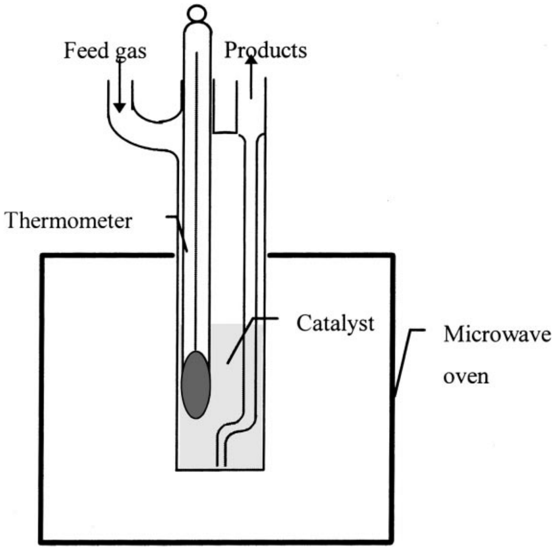

Fig. 1. Schematic diagram of the reaction apparatus.

The catalysts V_2O_5/SiO_2 were prepared by wet impregnation method under microwave irradiating method and conventional thermal method, respectively. Support SiO_2 (amorphous) was commercial and sieved to sizes 0.45–0.9 mm. Microwave preparation method: SiO_2 was impregnated with NH_4VO_3 aqueous solution at a proportion of 8 wt% V_2O_5, followed by irradiating at the microwave power level of 150 W for 5 min, and at the microwave power level of 600 W for 5 min, respectively. Conventional preparation method: SiO_2 was impregnated with NH_4VO_3 aqueous solution at the proportion of 8 wt% V_2O_5, followed by drying at 383 K for 2 h and calcining at 670 K for 4 h. In such way, under microwave irradiating, 8 wt% V_2O_5/SiO_2 (sample A) was prepared in only 10 min; in the conventional case the preparation was finished after 8 h (sample B). The differences between sample A and sample B in SEM morphology were recorded by JEM-1200EX/S (EDAX9100). The segregation of V_2O_5 particles on the surface of SiO_2 in sample A and sample B was analyzed by XRD on a D-MAX-RB diffractometer with Cu K_α radiation.

3. Results and discussion

SEM morphology of sample A and sample B, depicted in Fig. 2, indicates that V_2O_5 particles in sample A have uniform sizes, but sample B presented a segregation of V_2O_5 particles on the surface of SiO_2. The XRD patterns are not able to detect the presence of V_2O_5 crystallites in sample A, but in sample B a weak pattern of V_2O_5 crystallites phase existed at $2\theta=20.21^\circ$ (d=0.439 nm), which was the result of the exaggerated grain growth of V_2O_5 particles. It confirmed that V_2O_5, on the surface of sample A, was dispersed more homogeneously than that on sample B surface. For the same molecules, microwave heating

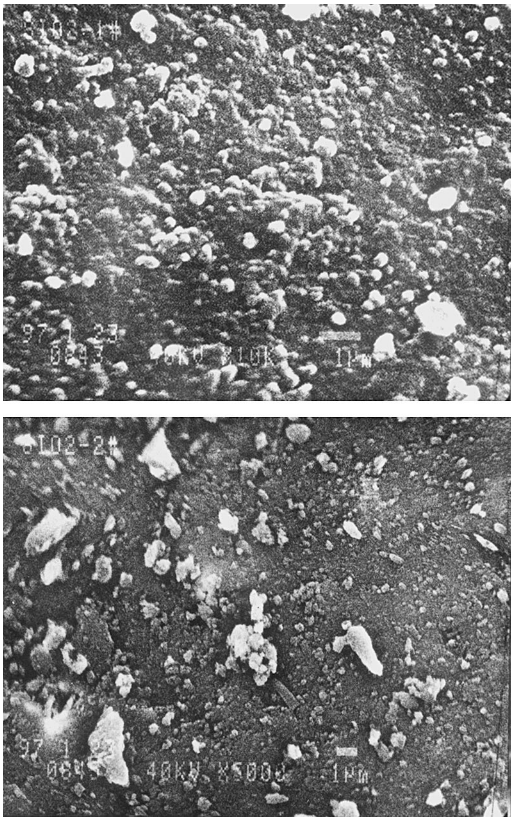

Fig. 2. SEM morphology of sample A and sample B.

process is a isothermal one due to the absence of the heat conduction. So the extent of non-isothermal processes such as segregation of V_2O_5 particles to grains is minimized. Since calcining time is reduced, the possibility of exaggerated grain growth may be reduced too. By minimizing particle segregation and decreasing grain size, the dispersion of active phase V_2O_5 on SiO_2 surface becomes highly uniform. It points out that under microwave irradiation, a homogeneous dispersion of V_2O_5 on the support would probably result in the rich exposition of V=O groups to the surface of SiO_2, leading to more catalytic active sites and higher catalytic activities to the title reaction.

Table 1
Comparison of the conventional heating process and the microwave activation process for the catalytic oxidation of *o*-xylene to PAN over a V_2O_5/SiO_2 system

	Conventional heating		Microwave activation	
	Sample A	Sample B	Sample A	Sample B
Yield (mol%)	28	15	67	51
Conversion (mol%)	30	18	71	53
Temperature (K)	653	653	563	563

The results of the oxidation of *o*-xylene over sample A and sample B in the microwave process or conventional heating process are given in Table 1. It shows that at 563 K the yield of PAN, under microwave irradiating, is higher than that in the conventional case; no matter which catalyst is used. But, in the conventional heating process, sample A, which was prepared under microwave irradiation, showed better catalytic performance than sample B, due to highly dispersed V_2O_5, and by consequence, to more catalytic active sites exposed onto SiO_2 surface. At a relatively low temperature 563 K, in the microwave activation process, the high yield of PAN indicates that the conversion rate of the catalytic reaction increases dramatically. It is clear that the energy of the microwave photon (10^{-5} eV) is too low, compared to one of a chemical bond, and no breaking of such bonds can be induced by absorption of the microwave photon [8]. According to the higher yield, at 563 K, under microwave irradiation than under classical heating, we have to invoke the influence of hot-spot effect [9]. It is noted that the origin of the microwave coupling dielectric heating effect lies in the capacity of an electric field to polarize charges in a material. The mobile electric dipoles and the distinctive charges oscillate rotationally and transitionally, respectively. This coherent movement of electric species inside the material induces heat from a part of the energy required by the material polarization. The microwave dielectric heating effect is more significant when the irradiated material has a strong dipolar character [2,3,13,14]. This is particularly true for the case of the catalysts using SiO_2 with numerous polar OH groups as support and V_2O_5 polar molecules as active phase. For the much stronger polarity of V=O groups than that of OH and Ti–O ones, the microwave heating effect on V_2O_5 is more effective than that on SiO_2 (under microwave irradiation at the power level of 1 kW, V_2O_5 can be heated to a temperature of 974 K in 9 min, whereas, SiO_2 to a temperature of 393 K in 30 min [2]), and V_2O_5 became super-heating molecules (>563 K, even close to 653 K) which are generated by intensive localized coupling of microwave energy [2]. Furthermore, microwaves can pass through these super-heating molecules to lattice oxygen defects on the catalyst surface, resulting in low valence oxides (active species for catalytic oxidation) to stimulate the reaction. In the microwave process, because of the absence of the heat conduction, V_2O_5 molecules serve dual purposes as the catalyst as well as the "microwave energy converter" [12], i.e., the energy absorbed by V_2O_5 is transformed from a rapidly oscillating electric field into thermal energy in a "in situ" mode, instead of a conduction one. So, more polar groups of vanadyl oxygen of V_2O_5 are activated into catalytic active sites, leading to better catalytic activities. Since only the catalyst surface is heated to high temperature, there is a very large temperature gradient between the surface, the bulk of the gas phase and the SiO_2 support, creating an efficient reactant circulation. The total combustion will tend to be minimized by lower temperature of the gas phase. For the microwave oven used is working with the on–off cycle between each microwave pulse, the weak coupling dielectric SiO_2 can release the heat from the hot surface (covered with V_2O_5 molecules) and the heat from the oxidation reaction, keeping the reaction bed at a relatively low temperature.

In order to confirm the existence of super-heated molecules induced by microwave energy, the reaction was carried out under different temperatures in the conventional and microwave process, respectively. The results are shown in Fig. 3. With the enhancement of the temperatures in the reaction bed, obviously the conversion of *o*-xylene increased in both processes, although it was much lower in the conventional case. However, in the microwave process, the selectivity of PAN greatly decreased when the temperature was higher than 563 K, due to the deeper oxidation of *o*-xylene to CO_x. It is suggested that, when the reactor temperature is higher than 563 K, the temperature of V_2O_5 super-heating molecules is too high (>653 K, which is the optimum temperature for the selectivity and yield of PAN in the conventional process) for *o*-xylene oxidation to form PAN but CO_x. This means that the temperature of the catalytic active phase V_2O_5 is not identical with, but much higher than that of the bulk support SiO_2 or reaction bed. In the conventional process, the temperatures of the reaction bed, support SiO_2 and active phase V_2O_5 are identical. The higher the temperature, the higher the catalytic activities up to 653 K. These results confirmed that the super-heating V_2O_5 molecules in the microwave process take place.

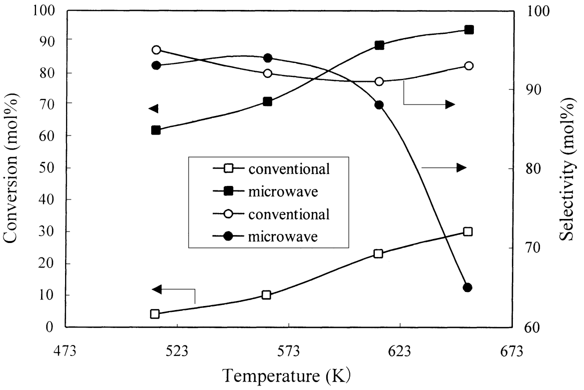

Fig. 3. Conversion of *o*-xylene and selectivity of PAN via the temperatures in the conventional heating process and the microwave process (over sample A).

It is considered that the microwave heating effect can be located on the catalyst dielectric component with effective microwave coupling ability, such as V_2O_5, leading to the different temperature distribution for active phase V_2O_5 (high) and support SiO_2 (low), favoring the selectivity to PAN.

A great amount of work has also suggested that, when dielectric heating effects of microwave energy are applied, the enhanced mass transport properties [10,11] and the localized discharge are the special phenomena that universally occur with solid oxide catalytic system [2,9,12]. These phenomena induce the following consequences:

1. An efficient reactant circulation can be realized, inhibiting the formation of CO_x by shortening the absorption time of PAN on the catalyst surface.
2. The lattice oxygen in the effective microwave coupling dielectric V_2O_5, becomes more mobile, inducing V_2O_5 into low valence oxides.
3. The charge transition between V_2O_5 and SiO_2 can decline the reduction potential of V_2O_5 and oxidation potential for deep oxidation of PAN, favoring the initiation of the reaction and the selectivity to PAN.

These suggestions need further proof.

Considering the overall results, we conclude that the microwave process has the following advantages for the oxidation of *o*-xylene over V_2O_5/SiO_2:

(1) In microwave preparation process, the dispersion of V_2O_5 on the surface of SiO_2 is more homogeneous. The extent of non-isothermal processes such as segregation of particles to grains, which often happens in a conventional process, is minimized by using the microwave preparation method. Since calcining time is reduced, the possibility of exaggerated grain growth may be reduced too. By minimizing particle segregation and decreasing grain size, the dispersion of active phase V_2O_5 on SiO_2 surface becomes highly uniform, which can make more catalytic active sites V=O groups exposed on the catalyst surface.

(2) In the microwave process, the catalytic reaction rate of *o*-xylene oxidation to PAN increases remarkably under relatively lower temperature (yield: 67 mol% at ca. 563 K). The results can be due to the super-heating of V_2O_5 molecules, the enhanced mass transport properties of the reactants and the products, and the localized discharge phenomenon induced by the microwave energy.

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