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Microwave Electromagnetic Field Effects on Reforming Catalysts

I. Higher Selectivity in 2-Methylpentane Isomerization on Alumina-Supported Pt Catalysts

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The effects of microwave irradiation of an alumina-supported 0.2 wt.% platinum catalyst are studied. In the case of the isomerization of hexanes, the selectivity in isomers is increased (by a factor 1.3 to 2) when the thermal treatment of the catalyst and/or the reaction are performed under the electromagnetic field. The isomer selectivity remains high even when such catalysts are subsequently tested under classical heating conditions. These permanent and profitable effects of the microwaves could be interpreted in terms of modifications of the geometric and/or electronic properties of the platinum particles. It is pointed out that the microwave irradiation could be a new and promising way for activating catalysts. © 1994 Academic Press, Inc.

INTRODUCTION

Early attempts were made to find alternative or complementary procedures to conventional conductive heating for introducing energy into chemical reactions. More recently, with the progress of technique, several papers have described the application of new activation methods in different branches of chemistry and more especially in the field of heterogeneous catalysis (1–3). In this way, the *in situ* mode of electromagnetic energy conversion has received strong attention. The effects of magnetic and electrostatic fields as well as the influences of acoustic waves on the catalytic reactivity or on the physical properties of catalysts have been investigated (4–6).

Among these different techniques, microwave dielectric heating seems to be a well-suited process for activating solid catalysts (7, 8). The microwave dielectric heating effect uses the ability of some materials to convert electromagnetic energy into heat. The origin of this specific heating lies in the capacity of an electric field to polarize charges in a material and the inability of this polarization to follow alternative changes of an electric field when the field is varying with high frequency. The mobile electric dipoles and the distinctive charges oscillate rotationally and translationally, respectively, and the movement inside the material tends to a stable equilibrium after a constant time which is the relaxation time. This phenomenon is called "dielectric relaxation." The coherent movement of electric species inside the material induces heat from a part of the energy required by the material polarization.

In the microwave range of frequencies, the associated wavelengths (from millimeter to meter) are in the same range of size as that of typical catalytic materials. On a macroscopic scale, owing to its size, a catalytic material will be a good microwave energy "receptor." So, in this range of frequencies, the electric energy alteration is the most important. This phenomenon is more emphasized when the irradiated material has a strong dipolar character. This is particularly the case with those catalysts where the support is an oxide, more or less hydrated, and contains numerous polar OH groups. Moreover, when polar adsorbed molecules are present on the surface, such as water which has a large frequency range of absorption by relaxation, this increases the dielectric losses of the material and hence the microwave energy absorption.

Microwave dielectric heating is characterized by important interference phenomena, due to the reflection of the waves at the interfaces of the materials. Hence metallic particles deposited on a support may locally induce an increase of the electric field. Moreover, if the metallic particles have a size much lower than the effective penetration depth ∂ of the waves in the metal (for platinum, $\partial \approx 3.2$ μm at 2450 MHz), the dielectric losses are even favored by conduction inside the metal. Finally, the heat produced by microwave irradiation always increases, in a very rapid manner, in the heart of the materials which absorb the electromagnetic field, especially if the material is a good thermal insulator.

It therefore seems that, in heterogeneous catalysis, mi-

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crowave dielectric heating should be considered in principle as a real alternative to the direct supply of thermal energy in classical heating. Thiébaut and co-workers (9–11) are among the few to describe in practical terms the use of microwave irradiation for the activation of catalytic reactions or for the preparation of catalysts.

The aim of this paper is to show the profitable influence of a microwave field on the activity of a reforming catalyst and more particularly on the selectivity in 2-methylpentane isomerization on a 0.2 wt.% Pt/Al_2O_3 catalyst. We shall also distinguish the microwave field influence during the preparation step of the catalytic material from that occurring during the catalytic reaction.

METHODS

Apparatus

The *in situ* thermal treatment of the catalysts and the catalytic reactions are performed in a plug-flow and airtight system working under isothermal and isobaric conditions (see detailed description in Garin and Gault (12)). The system works under constant hydrogen flow and a series of hydrocarbon injections are performed.

We can control kinetic parameters such as:

—the gas flow, with a Brooks flowmeter,

—the hydrocarbon flow, with thermal conductivity detectors,

—the hydrogen pressure, by the use of manometers,

—the hydrocarbon pressures, by the use of a saturator which fixes a constant partial pressure of the reactant, at a given temperature of the cooling trap.

We checked that no mass or heat diffusion limitations occur. The measurement and regulation of the reactor temperature depends on the kind of thermal power supply employed.

Gas Handling

The purity of synthetic air is higher than 99.95%. For hydrogen the purity is higher than 99.995%, the gas being purified by passing through two traps containing silicagel and 13X Zeolite cooled by liquid nitrogen. Air is purified by using Carbo-ice at 195 K. Gases flow through a Supelco OMI-1 filter in order to complete the purification. The hydrocarbon is Fluka puriss grade.

Heating Procedures

The catalytic bed can be heated either by a "classical thermal" heating (noted as CT), i.e., by using a classical electric oven, or by microwave irradiation (noted as MW) by using a magnetron and a waveguide.

(*a*) *Classical heating* (*CT*). The reactor is placed in a tubular electric oven. The catalyst bed is located in an area of high convection. The temperature inside the oven is regulated by the use of two thermocouples located at the same level as the catalyst bed, on the external face of the reactor. These thermocouples are linked to a Minicor thermal regulator which controls temperature with an accuracy of ±1 K and to a galvanometer which allows direct readout of the temperature with an accuracy of ±0.5 K.

(*b*) *Microwave irradiation* (*MW*). The microwave setup and the method of temperature measurement have been previously described in detail elsewhere (13). The microwave supply is a Microton generator. The range of power of this magnetron is 20 to 200 W; the emitted frequency of the electromagnetic field is 2450 MHz. The waveguide is a rectangular metallic channel which allows the transmission of the microwave field from the magnetron to the microwave cavity. The silica reactor is placed in this single mode resonant cavity, perpendicular to the broad wall of the waveguide and parallel to the direction of the electric field. The single mode resonant heater allows the catalyst bed to be placed at the position of high electric field strength. By varying the position of the plunger, the cavity can be made to resonate at the working frequency. Use of a resonant cavity increases the effective cavity power, allowing the microwave irradiation of relatively low-loss materials such as the catalyst studied in this work.

The temperature of the sample is continuously regulated by controlling the resonance frequency of the cavity and the emitted power of the generator. The mean temperature of the catalyst bed is measured by the use of thermocouples which are fastened perpendicularly to the reactor and the direction of the electric field. The very small size of the thermocouples (0.2 mm) and their chosen location allow us to minimize interference with the microwave field. The reactor is lagged, so that the difference of temperature into the bulk of the catalyst and the heat losses to the cavity are attenuated.

The temperature measurement method does not completely cancel the interference of the electromagnetic field with the metallic thermocouples or the effect of nonhomogeneous bulk temperature. Nevertheless, one can determine the temperature with reasonable accuracy in spite of the limitations inherent in the experimental setup. With the useful power for heating the sample varying generally between 100 and 150 W, one can estimate that the absolute error on the measurement of the catalyst mean temperature is about 5 to 8 K and that the relative determination of temperature is accurate to close to 2 K.

Preparation of the Catalysts

The alumina support (γ-Al_2O_3 purchased from Woelm AG, specific area 164 m^2/g; mean pore size 34 Å; no metal detected by X-ray fluorescence) is impregnated by a large excess of hexachloroplatinic acid solution, the pH of which is kept lower than 2. The cationic adsorption occurs completely as an interaction with the support. The excess of water is eliminated by slow and well-controlled evaporation. The resulting powder is dried under air for 24 h at 373 K. the platinum loading is 0.2 wt.%.

Characterization of the Catalysts

Besides hydrogen chemisorption, which provides an estimate of the metal cluster mean diameter, particle size distributions are obtained by electron microscopy using the replica technique. The microscope is a Philips EM 300G instrument whose resolution is around 5 Å and the magnification is from 2,800 to 500,000 times.

Thermal Treatment of the Catalysts

Two types of catalyst result from different thermal treatments of the same initial 0.2 wt% Pt/Al_2O_3 material: the first is the classically treated catalyst (CTcat), which is considered as the reference catalyst and which is reduced as usual, under hydrogen, in an ordinary oven, while the second is the microwave catalyst (MWcat) which is reduced under hydrogen by the use of an electromagnetic field.

The following general nomenclature is used from now on. The catalysts are designated as $[A_{\mathrm{cal.T}}/B_{\mathrm{red.T}}/C_{\mathrm{reac.T}}]$ where A is the calcination step (either CT or MW) and cal.T is the calcination temperature, B is the reduction step (either CT or MW) and red.T is the reduction temperature, and C is the reaction step under CT or MW performed at the temperature reac.T. C_V means that the temperature of reaction is varying for the different catalytic tests.

Experimental conditions for these two thermal treatments are as follows:

—the gas flow is 60 cm^3/min.

—the catalyst weight is 100 mg. Under microwave irradiation, this amount is diluted in 600 mg of pure Woelm alumina in such a way to obtain a reasonable volume to be able to measure the temperature with enough accuracy. We have made blank experiments to check (i) the nonreactivity of the alumina in the skeletal rearrangement of the hydrocarbons and (ii) that this dilution does not modify either the selectivity or the reactivity.

—the reduction times are 30 and 120 min under microwaves and under classical heating, respectively, up to 623 K.

—the heating rate, in the case of CTcat, is 5 K/min.

—the time for increasing the temperature up to 623 K is less than 2 min in the case of MWcat.

We can note that, in the case of the catalysts used in the present work, the calcination step is not performed, so the value of $A_{\mathrm{cal.T}}$ is omitted.

Catalytic Experiments

The catalytic tests (2-methylpentane isomerization) either under classical heating or under microwave irradiation are performed in such a way that the total conversion of the reactant is between 4 and 10%. As the reaction temperatures are modified from 523 to 613 K, the hydrogen flow will be varied from 20 to 140 cm^3/min to obtain low total conversions. The total pressure is equal to 101 kPa and the hydrocarbon pressure is kept constant at 0.6 kPa by the use of a cooling trap. The reactant (2 to 100 μl) is introduced as a pulse for each experiment. The reaction products are analyzed by using gas chromatography (Varian GC 3300) with fused-silica capillary columns (S.G.E. BP-1).

The isomerization of 2-methylpentane (2MP) on all the catalysts studied in this work can be defined as a "metallic-type reaction"; that is to say, the isomers formed are 3-methylpentane (3MP), *n*-hexane (*n*C6), and methylcyclopentane (MCP). No branched hydrocarbons such as 2-2-dimethylbutane and 2-3-dimethylbutane are formed and the production of cyclohexane and benzene can be neglected.

Hence the selectivity ($S_{\%}$) in isomers represents the percentage of isomer products (α_i; sum of the mol fraction X of each isomer product) divided by the total conversion of the reactant (α_t).

$$S_{\%} = 100 \cdot (\alpha_i/\alpha_t) = 100 \cdot (X_{3\mathrm{MP}} + X_{n\mathrm{C6}} + X_{\mathrm{MCP}})/(1 - X_{2\mathrm{MP}}),$$

where $X_{2\mathrm{MP}}$ is the mol fraction of the nonconverted reactant

The dehydrocyclization into methylcyclopentane is included in the isomer selectivity.

During the catalytic conversion of 2-methylpentane, in addition to the isomer formation, some cracking reactions occur. At low conversion, cracking is limited to only one carbon–carbon (C–C) bond rupture. The products formed are methane and pentanes (iso- and *n*-) in equimolar amount, and ethane and butanes (iso- and *n*-) in equimolar amount and propane. We have to point out that *n*-butane is formed in a very small amount, which indicates that no repetitive processes occur because this alkane cannot be obtained from 2-methylpentane with only one carbon–carbon bond rupture.

RESULTS

The two 0.2 wt.% Pt/Al_2O_3 catalysts used are denoted as CTcat [-/CT$_{623}$/-] and MWcat [-/MW$_{623}$/-]; their mean metallic particle sizes measured by TEM are around 1 and 2.1 nm, respectively, and the accessibilities of platinum for hydrogen are 1.6 and 0.3, respectively. For the two catalysts, the distributions of particle sizes are very homogeneous.

We must note that the thermal treatment conditions of the CTcat have been optimized in order to reach the best isomer selectivity (41% at 533 K, Ref. (14)). Whatever the treatment, calcination and/or reduction, at temperature varying from 523 to 773 K, we could not modify the very high Pt dispersion of this catalyst (14). At higher temperatures, metallic particles were sintered.

Three types of experiments have been performed in order to point out the influence of the microwave electromagnetic field on the catalytic selectivity in isomers.

Process I

We have compared the selectivity in isomers for the catalyst CTcat [$-CT_{623}/CT_{533}$] (experiment 1) and for the catalyst MWcat [$-/MW_{623}/MW_{533}$] (experiment 2), at the same temperature of reaction (533 K) and under the same experimental conditions, as defined above, except in the nature of the heating process during the reaction. Results are presented in the first two columns in Table 1 and in Fig. 1.

As the nature of the products formed during experiments 1 and 2 is similar, the comparison of the selectivities is significant. The selectivity in isomers for the MWcat is twice as great as for the reference CTcat. Therefore, an influence of the microwave irradiation on the isomer selectivity of a 0.2 wt.% Pt/Al_2O_3 catalyst is indicated. This effect, for MWcat, can be considered as a global one because it results from a thermal treatment (reduction step) plus a catalytic reaction, both of which are performed under microwave irradiation.

Process II

In order to distinguish the direct effects of the microwave treatment from those of catalytic reaction under microwave irradiation, we have placed the MWcat used in experiment 2 in a classical thermal heating oven (MWcat′ [$-/MW_{623}/CT_{533}$]—experiment 3).

TABLE 1

Isomer Selectivity on 0.2 wt.% Pt/Al_2O_3 Catalysts (Processes I and II)

	Catalysts		
	CTcat [$-/CT_{623}/CT_{533}$]	MWcat [$-/MW_{623}/MW_{533}$]	MWcat′ [$-/MW_{623}/CT_{533}$]
Process	I	I	II
Experiment	1	2	3
Selectivity (%)	41	79	81

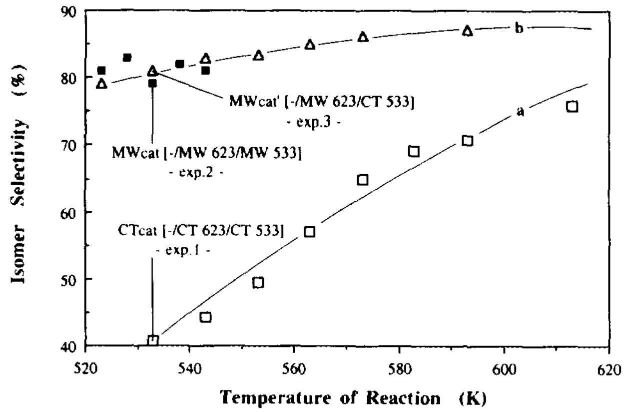

FIG. 1. Isomer selectivity on 0.2 wt.% Pt/Al_2O_3 catalysts. (a) CTcat [$-/CT_{623}/CT_V$]; (b) MWcat [$-/MW_{623}/MW_V$] and MWcat′ [$-/MW_{623}/CT_V$].

The isomer selectivity does not change (Table 1, third column and Fig. 1). Hence the nature of thermal heating during the catalytic reaction has no direct influence on the isomer selectivity for a catalyst previously treated under microwave irradiation.

The results obtained in processes I and II are reinforced by the study of the selectivity in isomers versus the temperature of reaction for these three catalysts CTcat, MWcat, and MWcat′ (Fig. 1). Whatever the temperature of the catalytic reaction, in a range of 80 K between 533 and 613 K, the "microwave-type" catalysts present a higher selectivity than the reference catalyst. In both cases, the selectivity increases with the temperature of reaction. The catalysts MWcat and MWcat′ present the same isomerisation behavior versus the temperature. Thus we have found that the isomerization power of a 0.2 wt.% Pt/Al_2O_3 catalyst, reduced under microwave irradiation at high temperature in hydrogen, is modified in a permanent way. The isomer selectivity in this case is increased whatever the temperature of reaction and the nature of heating for the catalytic reaction.

Process III

In order to highlight the microwave irradiation effect during the catalytic reaction on a classically treated catalyst, we have placed the CTcat from experiment 1 in the microwave reactor (CTcat′ [$-/CT_{623}/MW_{533}$]—experiment 4). Results are presented in Table 2 and Fig. 2. A strong increase of the selectivity in isomers up to 80% is again observed.

The CTcat′ has been subsequently placed in a classically heated reactor (CTcat″ [$-/CT_{623} + MW_{533}/CT_{533}$]—experiment 5). The selectivity decreases in comparison with experiment 4, although staying higher than the initial value we obtained with CTcat (experiment 1).

Hence we have shown that microwave irradiation of a classically treated catalyst, only limited to the catalytic

TABLE 2

Isomer Selectivity on 0.2 wt.% Pt/Al_2O_3 Catalysts (Process III)

	Catalysts		
	CTcat [-/CT_{623}/CT_{533}]	CTcat′ [-/CT_{623}/MW_{533}]	CTcat″ [-/CT_{623} + MW_{533}/CT_{533}]
Process	I	III	III
Experiment	1	4	5
Selectivity (%)	41	79	48

reaction, is enough to obtain a selectivity as high as the one obtained with a microwave-treated catalyst. We can see that we have modified the isomerization power of such a catalyst in a permanent way, but at a lower level than the previous experiment.

These results are confirmed when we study the isomer selectivity versus the temperature of reaction for the three catalysts CTcat, MWcat (or MWcat′), and CTcat″ (Fig. 2). Whatever the temperature of reaction (α_t being always in the range 5 to 10%), the irradiated CTcat″ catalyst presents higher selectivity than the reference CTcat but less than the MWcat. However, note that CTcat″ has been irradiated to a lesser extent than MWcat (temperature and time of irradiation).

DISCUSSION

In this paper, we have not mentioned the catalytic activity because all the experiments were performed so as not to exceed a total conversion of 10%; we shall therefore discuss selectivity only.

Among all the questions induced by these results, we would like to restrict the discussion, in this article, to the question, What are the reasons why cracking reactions are lowered in the isomerization process which takes place on the microwave irradiated catalysts?

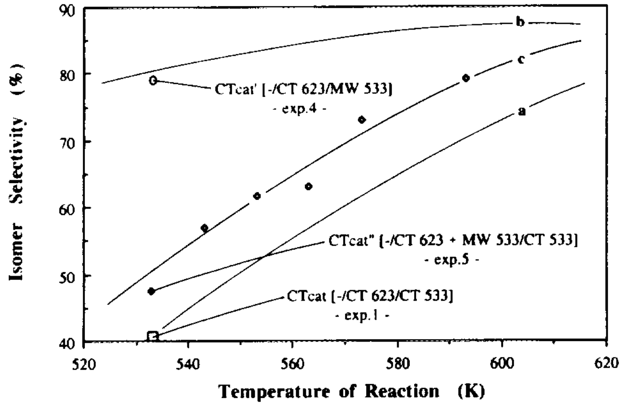

FIG. 2. Isomer selectivity on 0.2 wt.% Pt/Al_2O_3 catalysts. (a) CTcat [-/CT_{623}/CT_V]; (b) MWcat [-/MW_{623}/MW_V] and MWcat′ [-/MW_{623}/CT_V]; (c) CTcat″ [-/CT_{623} + MW_{533}/CT_V]. (Curves a and b are already presented in Fig. 1; hence in this figure experimental points are omitted and only the shape of the curves is shown.)

First of all, an isomerization reaction consists of a carbon–carbon bond rupture followed by a carbon–carbon bond recombination in the adsorbed phase. Thus the rate for the C–C bond rupture and recombination have to be altered to make a change in the selectivity. We may ask what the microwave irradiation is able to modify, reorganize, and/or transform.

We have noted that a permanent effect on the catalytic reactivity appears after microwave irradiation; hence it seems reasonable to link the gain in isomer selectivity to a specificity of the metallic structure of the irradiated catalyst. In other words, the microwave irradiation may induce a surface (re)construction which is characterized by the suppression of the catalytic sites responsible for the cracking and/or by the creation of sites where C–C bond recombination occurs at a higher rate than the desorption of the two entities formed after the C–C bond rupture.

From previous results obtained in our laboratory with experiments performed on platinum stepped surfaces, we were able to attribute the 1-2 alkyl shift named "bond shift mechanism" to the presence of a small ensemble of five atoms having (311) or (110) orientation named "B5 sites" (15, 16, 17). From kinetic measurements, we have pointed out that bond shift and cracking have the same apparent activation energy (12, 15, 16). Thus we could conclude that B5 sites are also responsible for cracking reactions; then, does the microwave field inhibit the formation of B5 sites while the mean metallic particle size of the MWcat is optimum to their production (18)?

However, we cannot relate the high isomerization power of the "microwave-type" catalysts only to the increasing size of the platinum particles. In fact, recent results (14, 11, 19) have indicated that all the catalysts treated under microwaves (whatever the experimental conditions) always present higher isomer selectivities than the optimized reference "CTcat," the mean size of these irradiated catalysts varying from less than 1 to 8.2 nm. We can propose that the microwave electromagnetic field not only modifies the size of the platinum particles and their distribution but maybe also their shape and consequently the nature of the active sites.

Besides this structural effect, we can also invoke some electronic effect connected with the charge on the platinum. It has been shown that the presence of oxidized platinum can modify the reactivity of a catalyst. Botman and Ponec (20, 21) observed that, under their experimental conditions, a small amount of platinum may exist as Pt-ions and they found a correlation between the amount of Pt^{n+} and the catalytic reactivity. If the amount of these unreduced species is lowered due to a higher reduction power of hydrogen under microwaves, new catalytic behavior may arise. Thus a specific reduction power could suppress, for example, the unreduced parts of the catalyst located at the metal–support interface of the metallic crystallites, responsible for cracking reactions. In other respects, a higher reduced state of the catalyst under microwaves could also be attributed to an easier desorption of water (22), which encapsulates metallic ions efficient in degradation reactions. If the metal–support interface is more reduced and if the water around the crystallites is removed the microwaves may then modify the metal–support interaction and consequently the catalytic selectivity. On the other hand, it is known that small particles may have surface atoms slightly positively charged (23, 24). Following the pioneering work of Barron *et al.* (25), Anderson and Shimoyama (26) have shown that the rate of hydrogenolysis per unit of platinum area is high on small particles and decreases with increasing crystallite size. Since the irradiated catalysts with such small particles exhibit the same isomer selectivity as those with larger particles, it seems that the microwave field has a direct effect on the electronic state of the platinum particles. The irradiated particles could be less positively charged and so their isomer selectivity will be increased.

All these speculative points have to be confirmed. Experiments are in progress to invalidate or to strengthen the hypotheses raised in this discussion. New work will supplement results described in this paper. Some experiments have already shown further aspects of using microwave irradiation to be especially attractive; these include the high sensitivity of platinum catalysts (whatever their metallic loading) to thermal treatment conditions and an increase of catalytic activity (turnover frequency).

Results concerning the physical and chemical characterization of irradiated catalysts as well as results of reaction mechanism studies using ^{13}C isotopic labelling will be presented in a subsequent article.

CONCLUSIONS

Thermal treatment under microwave irradiation modifies in a permanent and profitable way the isomerization power of 0.2 wt.% Pt/Al_2O_3 catalysts. The isomer selectivity in 2-methylpentane isomerization can increase from 40 to 80%, according to experimental conditions.

Microwave irradiation promises to be a new and original way to treat supported metallic catalysts and particularly reforming catalysts. It permits an increase in catalytic performance and creates catalysts with a different structure and reactivity (27).

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