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Durable changes of the catalytic properties of alumina-supported platinum induced by microwave irradiation

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The isomerization of 2-methylpentane over a 0.2 wt% platinum dispersed on γ-alumina catalyst is studied when the catalyst is heated either by microwave irradiation or by a classical oven. The selectivity for isomerization is considerably increased, from 45 to 80%, when the catalyst has been previously treated by microwaves or when the catalytic reaction is performed under the electromagnetic field. The isomerization power of such an irradiated catalyst remains high even when it is subsequently tested according to classical conditions. It is consequently suggested that the microwaves induced durable and profitable modifications of the catalytic behaviour of alumina-supported platinum.

Keywords: Microwaves; electromagnetic field; supported catalysts; platinum; skeletal isomerization; hexanes; isomer selectivity.

1. Introduction

The microwave electromagnetic field constitutes an original source of energy to activate chemical reactions. This energy has been particularly used for the catalytic conversion of methane to ethylene [1] and other hydrocarbons, for inducing decomposition of organic halides over a metal-containing catalytic surface [2] and for accelerating the rates of chemical organic processes [3–5]. Experiments have been performed using either commercial microwave ovens or single mode resonating cavities. In heterogeneous catalysis most experiments were carried out with metal powders or metal wires because of their ability to initiate an electric

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discharge in an electromagnetic field such as that which exists in a microwave oven [6].

We have studied the application of microwave irradiation to the skeletal rearrangement of hydrocarbons on supported catalysts using a resonating cavity [7].

The aim of this paper is to present some preliminary results obtained on an alumina-supported platinum catalyst submitted to the microwave field and/or heated in a classical electric oven.

2. Experimental

The studied material is a 0.2 wt% platinum dispersed on a neutral γ-alumina catalyst. The support (wolem alumina) is a low-loss dielectric material in the microwave frequency domain. Nevertheless it can be heated so that catalytic reactions can take place in a microwave cavity. 0.1 g of catalyst is used, the aliquot is diluted with 0.6 g of γ-alumina when the catalyst is submitted to microwaves [7]. Under our experimental conditions, bifunctional catalysis does not occur. We checked it by using olefins which react at similar rates as alkanes and blank experiments have shown the non-reactivity of the alumina used.

The reactant used, 2-methylpentane (2MP) diluted in a hydrogen flow, $(P_{H_2} + P_{2MP})$ = atmospheric pressure, $(P_{H_2}/P_{2MP}) = 120$. The amount of reactant, equal to 5 µl, is introduced as pulse for each experiment. The total gas flow-rate is 60 ml/min. The crossing time of the reactant over the catalyst which is classically heated or irradiated by microwaves is about 2 min. A small quantity of the reaction products is withdrawn and analysed by gas chromatography (Varian GC 3300) on fused-silica capillary columns (SGE BP 1). The selectivity in isomers is defined as the percentage of isomer products divided by the total reactant conversion.

The microwave setup has been previously described in detail in ref. [8]. The sample is placed at the center of a waveguide (single mode resonating cavity), in a cylindrical tube (parallel to the electromagnetic field) which is connected to an all-glass flow system working under constant hydrogen flow and hydrocarbon pulses. The applicator is fed by a stabilized microwave generator (2.45 GHz, 20–200 W). This arrangement provides a electromagnetic field sufficiently constant and uniform to avoid too large an inhomogeneity of the temperature inside the sample. This temperature is continuously measured and regulated by controlling the resonance frequency of the cavity and the emitted power of the generator. This specific heating mode is compared to the classical one using an electric oven. Whatever the heating procedures are, the experimental parameters – gas flow rates and partial pressures, catalyst weight, thermal treatment temperature – are kept constant, in such a way to obtain directly comparable sets of experiments and the conversion is maintained below 30% to avoid any secondary process.

3. Results

The experiments are first performed on a classically treated catalyst reduced during 2 h, at 623 K under hydrogen. The 2-methylpentane transformation is carried out in a classical oven at different temperatures varying between 543 and 573 K; the isomer selectivity, on this reference catalyst, is around 45% (table 1 and fig. 1, curve a). When the 2-methylpentane isomerization is then carried out under microwave irradiation, the isomer selectivity increases up to 80% (fig. 1, curve b). When the isomerization reaction is performed again in the classical oven, the isomer selectivity decreases to around 60% but remains 25% higher, in our range of temperature, than for the reference catalyst (fig. 1, curve c). These results suggest that microwaves induce a stable and durable change in the catalytic properties of platinum.

The second time, experiments are carried out on a microwave treated catalyst at 623 K under hydrogen for 30 min (table 1 and fig. 1). The catalytic reactions are performed under classical heating for the three experiments at 543, 563 and 573 K (fig. 1, curve d) and also under microwave heating for the 533 K experiment (fig. 1, curve e). Whatever the nature of the heating is during the catalytic reaction, the selectivity is high and reaches 75%. This value is nearly the same as the high selectivity, around 80%, obtained on the classically treated catalyst on which the reaction is performed under microwave field. Whenever the microwave irradiation occurs during the catalytic reaction or during the thermal treatment, the isomer selectivity can be doubled.

On the other hand, we may observe that, for the same reaction temperature,

Table 1
Conversion and isomer selectivity on different 0.2% Pt/Al_2O_3 [a]

T	a		b		c		d		e	
	C	*S*	*C*	*S*	*C*	*S*	*C*	*S*	*C*	*S*
523	–	–	3	79	–	–	–	–	–	–
528	–	–	5	81	–	–	–	–	–	–
533	–	–	8	80	–	–	–	–	17	74
538	–	–	11	80	–	–	–	–	–	–
543	5	47	13	79	–	–	3	75	–	–
553	11	44	–	–	8	61	–	–	–	–
563	16	43	–	–	16	59	9	77	–	–
573	25	48	–	–	27	60	17	76	–	–

[a] *T*: temperature of reaction (K); *C*: reactant conversion (%); *S*: isomer selectivity (%). a: Reference catalyst which has been treated and tested by classical heating; b: catalyst which has been classically treated and tested under microwaves; c: catalyst b which has been classically tested; d: catalyst which has been treated under microwaves and classically tested; e: catalyst which has been treated and tested under microwaves.

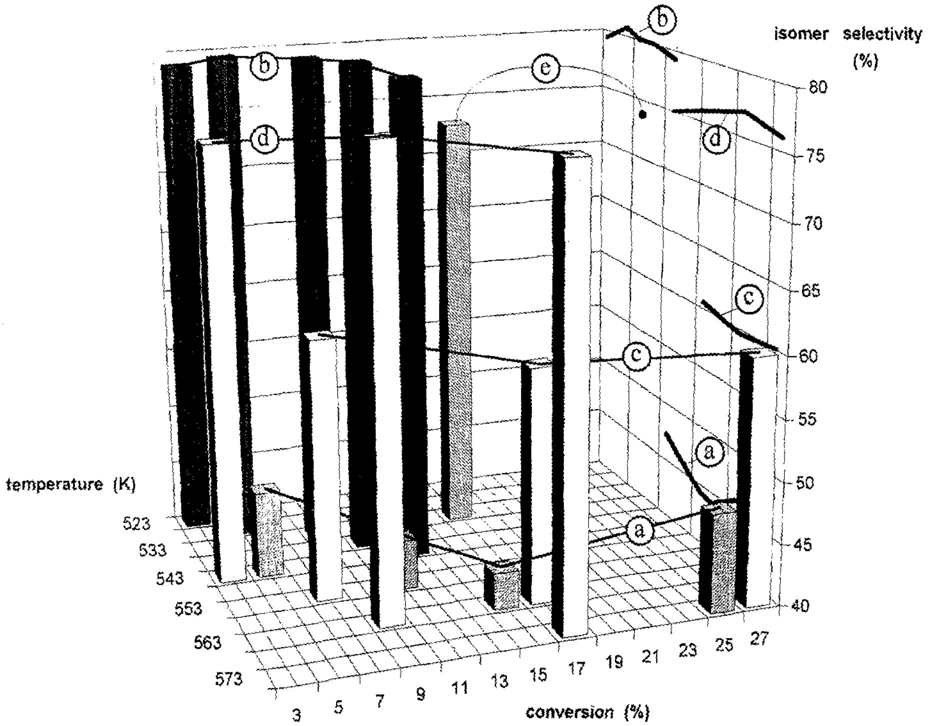

Fig. 1. Conversion and isomer selectivity on different 0.2% Pt/Al_2O_3 catalysts. (a) Reference catalyst which has been treated and tested by classical heating, (b) catalyst which has been classically treated and tested under microwaves, (c) catalyst b which has been classically tested, (d) catalyst which has been treated under microwaves and classically tested, (e) catalyst which has been treated and tested under microwaves.

there is a gain in conversion when the catalytic reaction is performed under microwaves (table 1 and fig. 1).

4. Discussion

Since the early 1980's, the high efficiency of microwave processing has been associated with hot spots in the temperature distribution, especially when a plasma is created. In the present case, no plasma occurs but the catalyst is a strongly contrasted heterogeneous material, if dielectric properties are considered. When such a composite material is irradiated under an intense electromagnetic field, the effective temperature could be greater for the platinum particles than for the alumina support which is a low-loss material and therefore greater than the estimated mean macroscopic temperature of the catalyst. This could explain why the conversion of the reactant is generally enhanced by microwave energy. Nevertheless, this simple interpretation fails to explain why the isomer selectivity of the catalyst is increased when the reaction is performed under microwaves and why it remains high, in classical heating conditions, when the catalyst has been previously irradiated. The experimental results clearly demonstrate that the catalyst has been modified in a durable way by the microwave field. The decrease of the contribution of the cracking reactions could be attributed to this structure modification. Until now, the nature of the catalytic sites responsible for the cracking reactions is not well established. They are supposed to involve either corner or edge atoms or both of them [9]. According to such an interpretation, it would seem that microwave irradiation could modify these low coordinated atoms.

Many experiments are still required to achieve a better understanding of the specific catalytic behaviour of platinum under the electromagnetic field and to correlate the properties of the catalyst with microwave processing.

5. Conclusion

Isomer selectivity of 2-methylpentane on 0.2 wt% platinum supported on alumina is increased from 45 to 80% when the catalyst is irradiated by microwave energy during the reaction and also, when the catalyst is tested in a classical way, after being submitted to microwaves. This profitable change in selectivity is durable and may be due to a drastic modification of the physical properties of the catalyst. These results open very interesting tracks in the field of heterogeneous catalysis [10].

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