MICROWAVE EFFECTS IN HETEROGENEOUS CATALYSIS

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Microwave activation of catalytic reactions has been the subject of many studies, however, the mechanism of these reactions is not yet fully understood. The question is how to interpret differences in rates or in selectivities in conventionally and microwave heated reactions under the same conditions. There are the following microwave effects which do not exist in conventionally heated reactions but they can be created by microwaves and they can explain these differences.

Superheating

occurs in liquid reaction mixture where reactants are heated above their boiling point. In solids like in solid catalysts or supports superheating can be much higher than in liquid phase due to lower heat transfer. Such a localized superheating produces hot spots (vide infra), which is advantageously used by synthetic chemists, especially for reactions performed on inorganic supports under solvent free (dry media) conditions.

Selective heating

means that in a sample containing more than one component, only that component which couple with microwaves is selectively heated. Selective heating is very important in catalytic reactions, for example when catalyst is selectively heated in nonpolar media.

Hot spots

are created by a nonlinear dependence of thermal and electromagnetic properties of the catalyst being heated. There are two kinds of hot spots – *macroscopic* and *microscopic.*

- *Macroscopic* hot spots are large scale nonisothermalities, which can be detected and measured.
- *Microscopic* hot spots posses molecular dimensions and can be created in catalysts, for example by selective heating of active sites.

Microwave heating under simultaneous cooling

is the most recent discovered microwave effect which can significantly improve yields and selectivity of catalytic reactions [1-5]. It is obvious that nonisothermal conditions induced in catalyst by microwave heating lead to very different results from those obtained under conventional heating conditions. When intensive cooling is used, e.g. with liquid nitrogen, these differences are more profounded [1-3,5]. Because the temperature of the reaction mixture is lower than the temperature of the catalyst, the back, side or consecutive reactions can occur to a lesser extent, i.e. selectivity of the reaction can be significantly improved.

In our studies of microwave activation of catalytic reactions all results were explained by thermal effects. Non-thermal effects, i.e. specific effects, were excluded.

References

[1] M. Hájek, M.T. Radoiu, *Ceram. Trans*. **2001**, 111, 257-264.
[2] J. Kurfürstová, M. Hájek, *8th Int. Conf. Microwave and High Frequency Heating*, Bayreuth, Germany,3-7 September **2001**, Book of Abstracts pp. 269-270.
[3] M. Hájek, *Microwave Catalysis in Organic Synthesis* in *Microwaves in Organic synthesis*, ed. A. Loupy, Viley-VCH, Weinheim, **2002**, pp. 368 and 2nd eddition 2006, Chapter 13.
[4] C.E. Humphrey at al, *Org. Letters,* **2003,** 5, 849-852.
[5] J. Kurfürstová, M. Hájek, *Res. Chem. Intermed.,***2004**, 30, 673-681.