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Effects of microwave radiation on one-step oxidation of benzene to phenol with nitrous oxide over Fe-ZSM-5 catalyst

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Abstract

Direct oxidation of benzene to phenol over Fe-ZSM-5 catalyst was chosen as a model reaction to characterize the influence of microwave irradiation on ad-/desorption processes during heterogeneously catalyzed reactions. The direct oxidation of benzene was investigated under different reaction conditions (temperature, residence time, reactant-concentrations) and microwave power in a specially designed reactor. The results obtained by additional microwave radiation were compared to those obtained by conventional heating under similar reaction conditions. In addition, ex situ TG-MS analyses were also conducted to study the sorption behaviour. Extensive investigations were carried out to determine adsorption–desorption effects (benzene, phenol and a mixture of both) and the coking behaviour under microwave conditions. Microwave induces a trend towards increased phenol selectivity and relative deactivation during the reaction. However, there was no conclusive improvement in the performance was obtained by means of microwave heating.

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1. Introduction

The concept of using microwave as an energy source for chemical reactions involving solid catalysts has been investigated intensively in recent years [1,2]. These studies show that in some cases the reaction rates are enhanced while in others the product selectivity changes when microwave radiation is used instead of conventional heating. Whether this is due to faster and selective dielectric heating provided by microwave or due to any specific microwave effect (e.g.: specific bond activation), is a matter of debate [3–7].

An advantage of microwave heating compared to other heating methods is that any substance with high dielectric loss factor (ability of the substance to absorb the electromagnetic energy) can couple easily with microwave radiation and gets heated. But substances with low dielectric losses remain nearly unheated under microwave radiation. This effect can also be used to influence desorption processes on adsorbents. If an adsorbent (catalyst) has a low dielectric loss factor and is loaded with two species, namely, non-polar and polar, the latter can be selectively desorbed by microwave radiation [8].

In this work direct oxidation of benzene to phenol on Fe-ZSM-5 catalyst with N_2O as an oxidant is used as a model reaction to determine the influence of microwave irradiation on catalytic reactions. The choice of the model reaction is not only due to the economic and scientific importance of the reaction but also due to the fact that this reaction has been investigated extensively in the past 20 years [9,10]. The biggest problem of this reaction is the short life time of the catalyst due to coking and by-product formation. Recently, it has been reported that the strong phenol adsorption on the catalyst is supposed to be the reason for the coking process [11]. A solution to that problem is rather modifying the catalyst or optimizing the process. A third possibility, on which this work is based, is to selectively desorb phenol by microwave radiation. Most importantly, unlike phenol, the reactants (benzene and nitrous oxide) and the catalyst have low dielectric loss factors. Hence microwave should selectively heat phenol and thus facilitate selective desorption. This effect (selective desorption) should reduce coke formation which in turn will increase phenol selectivity and the catalyst lifespan. A schematic representation of selective desorption of phenol is illustrated in Fig. 1. In this work we report about our investigation on the principle of selective desorption by microwave in heterogeneous catalysis. Therefore, the conventional and the microwave assisted process are compared under identical conditions.

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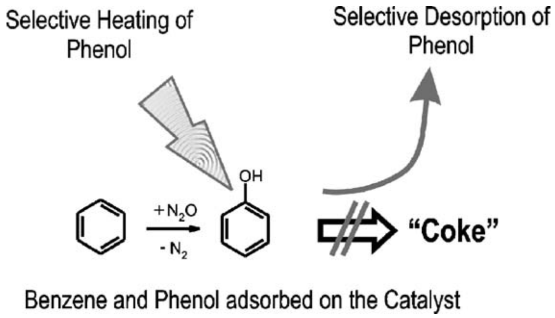

Fig. 1. Reaction scheme describing the idea of microwave selective desorption of phenol.

2. Experimental

2.1. Experimental setup

The laboratory scale experimental setup consists of a packed bed quartz glass reactor and a multimode microwave oven (Ethos 1600; MWS). The setup allows combined dielectric and conventional heating with an exact temperature control (IR-Pyrometer) and minimal temperature gradients within the catalyst bed. A detailed description of the experimental setup is given elsewhere [12].

Benzene was dosed with a HPLC pump (K-120; Knauer) and evaporated with N_2 as carrier gas. Nitrous oxide and nitrogen were dosed with mass flow controllers. An online gas chromatograph (VARIAN 3600) was used for the analysis of reactants and products. The GC was equipped with FID and TCD detectors and fused silica column of type HP-5 from the manufacturer Hewlett Packard (length 25 m; Ø 0.53 mm). Methane was used as the internal standard for the product analysis (GC) and measurements were taken for every 8 min over a period of 2 h. The benzene conversion was calculated from the molar ratio of converted amount of benzene to its initial amount. The yield of phenol was calculated from the obtained molar amount of phenol. The selectivity of phenol is defined as the molar ratio of the phenol obtained relative to benzene conversion. Modified residence time (τ_{mod}) was calculated as the ratio of weight of the catalyst to the molar flow rate of the reactant gas mixture. The catalyst was regenerated to enable its continuous usage after each reaction. Complete regeneration was achieved by heating the catalyst to 530 °C using an oxygen/nitrogen mixture for one hour in order to restore the initial activity. The temperature was then decreased to the desired reaction temperature under a flow of nitrogen (200 $\mathrm{ml_N}$/min) for 1 h. Prior to each reaction, by-pass measurements were taken to determine the reactant concentration in the feed gas. Influence of various parameters such as temperature (300–400 °C), residence times (90 and 120 g min/mol) and microwave power settings (100 W and 200 W) were investigated.

2.2. Catalyst preparation

Fe-form of zeolite ZSM-5 ($SiO_2/Al_2O_3 = 92$) was used as catalyst throughout this work. This Fe-ZSM-5 catalyst contained 1.16 wt.% of Fe. The catalyst powder was calcined at 900 °C. The catalyst powder was pressed into pellets before being crushed and sieved to obtain a particle size of 1–1.2 mm. One gram of catalyst was diluted with 20 ml of quartz glass beads (0.8–1.0 mm particle size) and filled in the reactor. Preliminary heat up experiments showed that this catalyst and quartz mixture is transparent to microwave radiation and it will not be heated by microwave.

2.3. Catalyst characterisation

Thermogravimetry coupled with mass spectroscopy (TG-MS) was employed to identify the adsorbed species and to determine the temperature required to desorb each species from the catalyst surface. The used TG equipment was of type SDT 2960 (TA Instruments). A quadrupole mass spectroscope of type Thermostar 2000 (BALZERS) was connected to the outlet of the TG furnace.

2.4. Experimental procedure

The aim of this work was to achieve selective desorption of phenol as well as to determine the influence of microwave on benzene oxidation reaction. Systematic investigations were carried out in order to realize this aim. Firstly, the influence of microwave on N_2O decomposition was tested as it is considered to be the vital part in this reaction [9]. Secondly, the influence of microwave on the benzene oxidation reaction was investigated by comparing the experimental results obtained by using microwave radiation with the one obtained by conventional heating. Finally, TG-MS analysis of ex situ loaded samples and spent catalysts from the reactions were conducted. This was done to get an insight into the effect of microwave on adsorption/desorption properties of the reactants and the product.

It is important to know the influence of microwave on the N_2O decomposition reaction before applying microwave in the benzene oxidation reaction. N_2O decomposition experiments were carried out in the same experimental setup as the benzene oxidation experiments. N_2O was detected by an infra red N_2O analyser of the type URAS 10E (Hartmann & Braun). This detector was detached during the benzene oxidation experiments. By keeping the residence time constant, N_2O decomposition was conducted with conventional heating by varying the bed temperature (300–500 °C). Each experiment was repeated with additional 120 W of microwave power.

The investigation of one-step benzene oxidation reaction includes observing benzene conversion (X), phenol yield (Y), phenol selectivity (S), benzoquinone selectivity (S) and relative deactivation (ΔX) with time on stream (TOS). All these experiments were performed with conventional as well as with combined conventional/microwave heating. Reason for this is that a catalyst transparent for microwave radiation cannot be heated to the desired reaction temperature by microwave radiation alone. This mixed energy input is called as "microwave assisted reactions/experiments". It should be noted that during microwave assisted experiments the catalyst bed temperature

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