Partial oxidation of isobutene to methacrolein on Bi-W / Fe-Co-Mo-K catalysts

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The partial oxidation of isobutene to methacrolein and methacrylic acid was studied on oxidic catalysts containing mainly a mixture of bismuth tungstate and iron-cobalt-potassium molybdate. Catalyst shaping was done by extrusion. The kinetic measurements were performed by monitoring the gas-phase composition along the length of a fixed bed of catalyst. The reactor was treated as an isothermal plug-flow system. The network of parallel and consecutive reactions taking place in this system can be described by a simplified scheme. It is possible to predict the gas-phase composition prevailing in the reactor using five different kinetic parameters. In the temperature range $380 < \vartheta < 420°C$ grain selectivities as high as 85% combined with yields of methacrolein and methacrylic acid about 72% at 92% conversion were obtained.

Keywords: Partial oxidation; isobutene; methacrolein; reaction network; multiphase oxidic catalyst

1. Introduction

Selectivity is the most important quantity in a reacting system, if different sets of stoichiometrically independent products are generated from the starting material, but will be meaningful only if it refers to a defined control volume, e.g. a fixed bed reactor in stationary state [1]. In that case the overall integral selectivity is a function of conversion of reactants and depends on reactor configuration and flow rate. In order to specify the catalytic properties of the active component of the catalyst independently of the above mentioned reactor characteristics and of catalyst shape, intrinsic parameters, e.g. the intrinsic selectivity, have to be considered. The intrinsic selectivity can be determined from experimentally accessible quantities and represents the upper limit attainable in the reactor [2]. The knowledge of the relevant intrinsic parameters allows the prediction of the gas-phase composition in the reacting system by use of a mathematical model relating the flow patterns in

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the reactor to a network of stoichiometrically independent reactions. Partial oxidations of hydrocarbons are typical examples of such multicomponent reaction network and in the following we shall look in more detail to the selective oxidation of isobutene.

In that case multicomponent molybdate catalysts are the most efficient catalysts for the selective oxidation of isobutene [3–7]. These catalysts contain two or more phases. In order to answer the question why real catalysts should contain several phases a large number of catalyst systems composed of two separately prepared oxides have been studied [8–13]. Dramatic synergy effects were obtained. One of the oxides (donor) adsorbs gas-phase oxygen and produces mobile oxygen species which spill over onto the other oxide (acceptor) where selective oxidation takes place [8–11]. These investigations were done on model catalysts containing only two defined phases, whereas real industrial catalysts contain generally more than two phases. In the following we shall report upon catalyst preparation and kinetic measurements in the study of isobutene oxidation on catalysts containing mainly a mixture of several phases consisting of bismuth tungstate and iron-cobalt-potassium molybdate [14].

2. Experimental

2.1. CATALYST PREPARATION

The Bi-W/Fe-Co-Mo-K catalysts ($BiW_2Fe_{0.35}Co_6Mo_{12}K_{0.5}SiO_x$) were prepared via a precipitation synthesis method [14].

To obtain the bismuth tungstate catalyst bismuth nitrate was added to an aqueous solution of ammonium tungstate while stirring. The sample was concentrated by evaporation at 80°C, dried overnight at 120°C and calcined in air at 750°C for 2 h.

The necessary amounts of aqueous solutions of ammonium molybdate, cobaltous nitrate, potassium nitrate and the bismuth tungstate powder were mixed while stirring. Then ferric nitrate dissolved in water was added carefully. The dispersion was concentrated by evaporation at 80°C and dried overnight at 120°C. The residue was ground and calcined at 450°C for 2 h in air.

For shaping the obtained sample mixed with ammonium alginate and a silica binder was plasticized and extruded. After drying overnight in air at room temperature the hollow cylindrical catalysts ($\phi_i = 2$ mm, $\phi_o = 4$ mm) were calcined at 450°C for 2 h in air.

2.2. KINETIC MEASUREMENTS

Kinetic measurements were performed by monitoring the gas-phase composition along the length of a fixed bed of catalyst 1500 mm in length and 15 mm in diameter. The reactor was made of stainless steel, consisting of six segments with individual temperature control within each segment and additional temperature measurement at the end of each segment (fig. 1). Heated capillaries were located at the inlet, outlet and between each segment, leading to a multiposition valve which fed gas samples to the analysis section, consisting of nondispersive IR-spectrometers for CO, CO_2 and isobutene and a gas chromatograph with FID for separation and determination of organic compounds. The feed of isobutene, nitrogen and air was prepared by use of mass flow controllers. Automatic continuous operation of the unit was possible as all functions were controlled and recorded by computer. The reactor was treated as an isothermal plug-flow system.

The partial oxidation was investigated in the temperature range $380 < \vartheta < 420^\circ\mathrm{C}$ at 1.3 bar total pressure. The mole fraction of isobutene in feed was varied from 0.03 to 0.05 and the mole fraction of oxygen in feed from 0.1 to 0.2. The volumetric flow rate ranged from 15 to 80 cm^3/s (0°C, 1.013 bar).

3. Results and discussion

Fig. 2a illustrates how the composition expressed as C-fraction contained in isobutene and in the products methacrolein, methacrylic acid and "combustion products" varies with the residence time defined as the ratio of catalyst mass to volumetric flow rate at temperature and pressure prevailing in the reactor. CO_2,

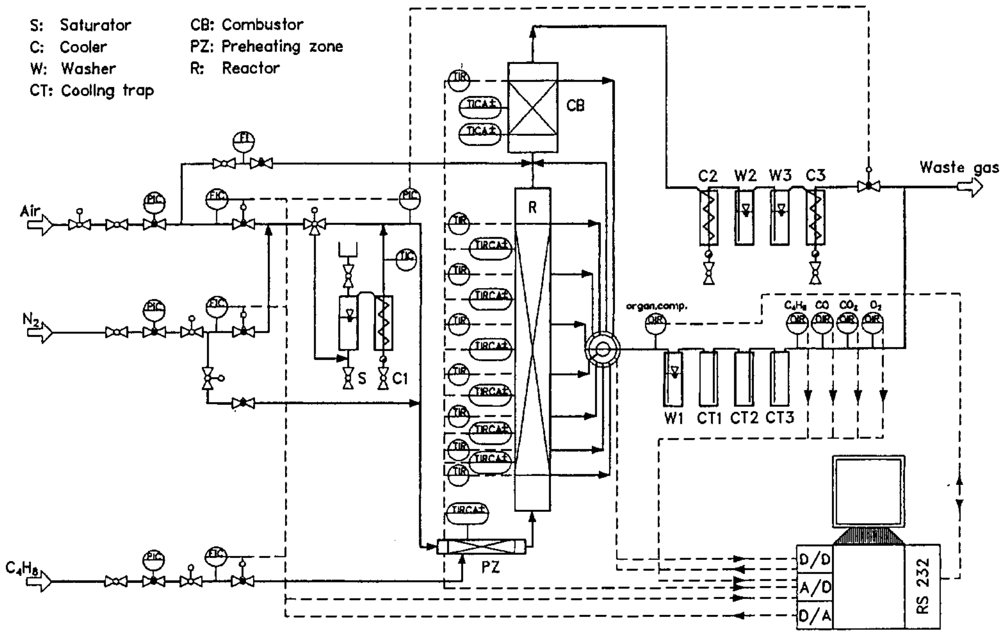

Fig. 1. Apparatus for catalytic oxidation of isobutene.

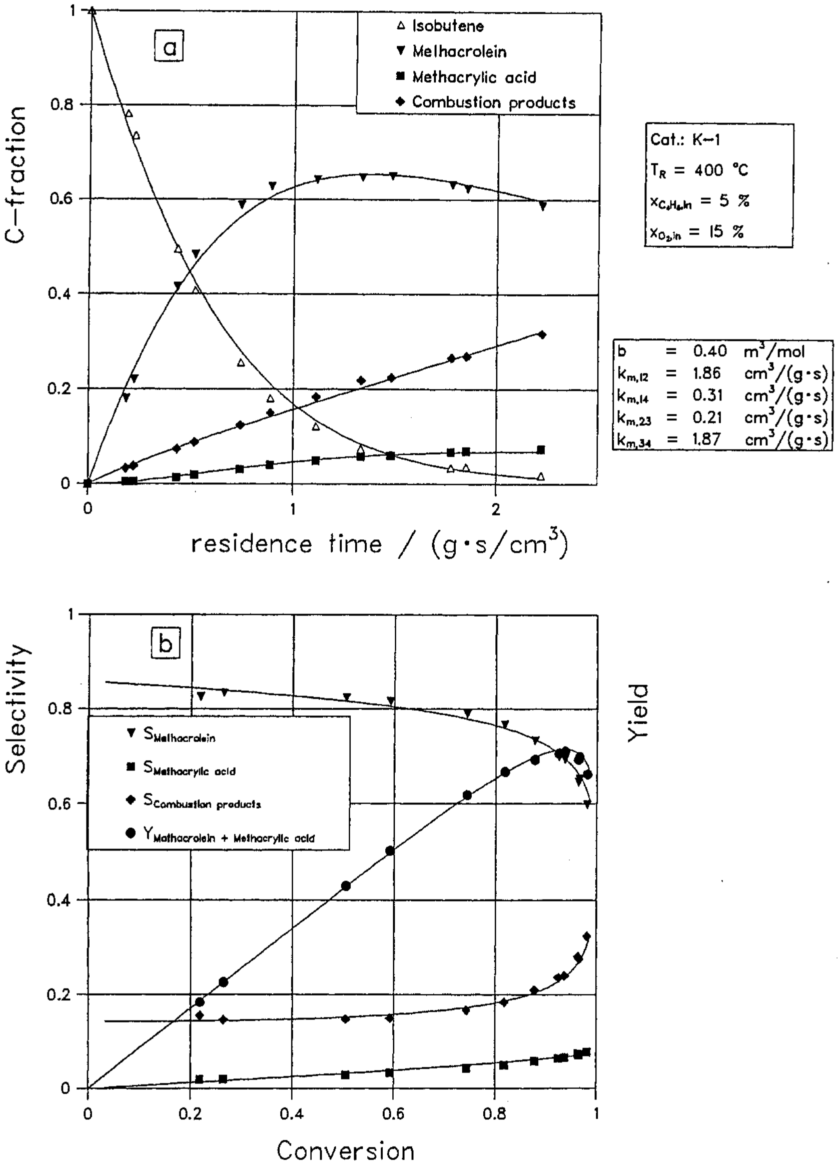

Fig. 2. Product distribution in selective isobutene oxidation. Symbols: experimental data; lines: calculated after curve fitting by use of the rate constants given above.

CO and the organic compounds acetic aldehyde, acetone, acrolein and acetic acid generated in small amounts can be lumped into one pseudo-species ("combustion products").

The distribution of the different products can be characterized by a dimensionless selectivity,

$$S_i = \frac{c_i}{c_{C_4H_8,\mathrm{in}} - c_{C_4H_8}} .$$

The reactor selectivity S_i is a function of conversion of isobutene as shown in fig. 2b. The yield Y of product is equal to the C-fraction.

It is clearly evident from fig. 2 that parallel and consecutive reactions are occurring simultaneously in this system. The finite values of selectivity of methacrolein and combustion products at low conversion indicate their generation in parallel reactions from isobutene. The yield of methacrolein as function of residence time shows a maximum. This points out that methacrolein will be converted in a consecutive reaction probably to methacrylic acid. The value of the selectivity of methacrylic acid at low conversion seems to be zero. Methacrylic acid is obviously not directly generated from isobutene. At high conversion the values of the selectivities of partially oxidized products tend to zero, whereas the selectivity of the combustion products reaches unity.

The kinetic behaviour of the selective oxidation of isobutene can therefore be described by a simplified scheme (fig. 3). The rate of the individual reactions in this system can be represented by the rate equations

$$r_{12} = \frac{k_{m,12} c_{C_4H_8}}{1 + b c_{C_4H_8}}, \quad r_{14} = \frac{k_{m,14} c_{C_4H_8}}{1 + b c_{C_4H_8}},$$

$$r_{23} = k_{m,23} c_{C_4H_6O}, \quad r_{34} = k_{m,34} c_{C_4H_6O_2},$$

where r_{ij} is in $\mathrm{mol\,g^{-1}\,s^{-1}}$. In order to obtain the coefficients $k_{m,ij}$ and b a set of four simultaneous differential equations is solved numerically by use of the Runge–Kutta method combined with the Nelder and Mead Simplex method. The quality of adjustment is judged by the Likelyhood function.

In addition to the experimental points the curves as represented by the mathematical model are shown in fig. 2. Obviously the partial oxidation of isobutene on bismuth tungstate/iron-cobalt-potassium molybdate catalyst is described very well by the model shown above.

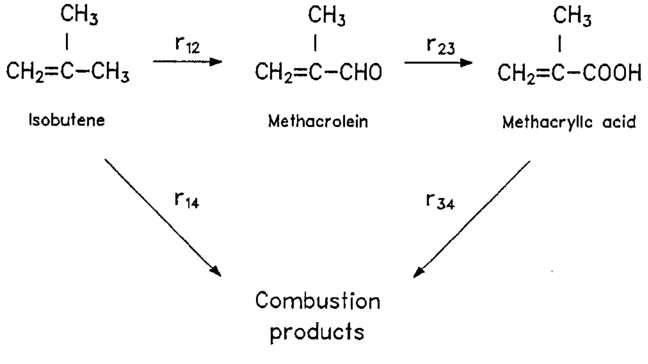

Fig. 3. Reaction network.

4. Conclusions

Grain selectivities as high as 85% have been obtained in the partial oxidation of isobutene on multiphase oxidic catalysts. The selectivities lead to yields of methacrolein and methacrylic acid up to 72% at 92% conversion in the temperature range $380 < \vartheta < 420°C$ compared to values of about 35% maximum reported for model catalysts [10]. Those values are high enough to motivate further investigations in view of practical applications.

Furthermore the excellent description of the experimental data by use of a rather simple reaction network will enable us to quantify the influence of catalyst composition and shape by determining the evolution of the different rate coefficients of the sequence. Similar reaction networks had been proposed in the partial oxidation of propene [15] or *o*-xylene [16] on oxidic catalysts, but to our knowledge not in the case of the model catalysts referred to at the beginning.

Finally, the proposed network offers the possibility to look for improvements in reactor design and operation, e.g. the use of a structured catalyst bed. Thus the simulation of an adequate temperature profile along the tubular reactor promised the increase of the expected yields up to three points and had been verified experimentally.

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