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Dynamic Experimental Methods Using *in situ* Measurements of the Surface Intermediates Applied to the Fine Chemistry

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Abstract. Unsteady-state kinetics can be used for the determination of the reaction mechanism of a heterogeneous catalytic reaction, and the characteristic shape of the time evolution curves of the concentrations at the outlet of the reactor can be associated with rate-limiting steps. To complete the information, *in situ* measurements of surface intermediates can be correlated with those response curves to get a physical meaning to the determined kinetic parameters. It is shown, how such an experimental setup can be realized. That the knowledge of the reaction mechanism and the identification of the active sites on the catalyst are of great use for reaction engineering is shown with the example of the methylation of catechol, an intermediate in fine chemistry, where the catalyst has been selectively modified to increase the yield of the desired 3-methylated product from 25 to nearly 70%.

1. Introduction

The dimensioning and optimization of chemical reactors need, as a prerequisite, the knowledge of the kinetics of the various reactions that occur in the system. Since a catalytic process is very complex, due to simultaneous mass transfer, chemical reaction, and pore diffusion, a simplified formalism is used when dealing with engineering aspects. This *Hougen-Watson* formalism is a description of the observed reaction rates in terms of lumped parameters, which have no physical sense, and, therefore, do not allow extrapolations out of the domain of investigation. This means, that a lot of work has to be done to measure empirical parameters and that this work has to be repeated for every modification of the catalyst or a change of the reaction conditions.

On the other hand, fundamental studies of the kinetics from a physico-chemical point of view are usually performed under well controlled conditions that are

far away from any industrial application, such as ideal surfaces or high vacuum, and are usually ignored during process development. The work in our laboratory can be defined in this context as an interface between catalysis and reaction engineering, where the aim is to bridge the gap between those two sciences.

Historically, the starting point was to understand the dynamic behavior of catalytic reactors, which may tremendously differ from steady-state. The importance of the dynamics lies not only in start-up and shut-down procedures of reactors, but has also a great importance when dealing with reactor safety or with environmental catalysis. A good example is the automotive catalyst, where the inlet concentrations of the catalytic converter vary continuously, due to changes in the engine velocity. Kinetic measurements under dynamic conditions also give a better insight on the intrinsic kinetics than those performed under steady-state conditions and, therefore, can be used as a tool for investigations on the reaction mechanism. In this field, our group has good European (Gent, Erlangen) and worldwide (Novosibirsk, Waterloo) contacts with other research groups.

Of course, the use of unsteady-state kinetics, as a tool for reaction-mechanism

determination and for catalyst design, has to be implemented with *in situ* measurements of adsorbed surface intermediates, which is done by IR spectroscopy in our laboratory or with physico-chemical analysis of the catalyst, which is performed with the help of the Department of Material Science. It has also to be integrated with more fundamental aspects, such as molecular modeling (Geneva), as well as with practical applications in environmental catalysis (Villigen), or in fine chemistry (industries in Switzerland and Europe).

It has been pointed out that kinetic studies under dynamic conditions are much more sensitive to the reaction mechanism than the traditional catalyst screening and, if combined with *in situ* measurements of the adsorbed reaction intermediates, can lead to a physico-chemical knowledge on the reaction-elementary steps and the nature of the involved active sites. This can be used for the selective design of the catalyst by modification of the important characteristics of the active sites. This procedure is described by an example, how the experimental setup has been optimized to get all the needed information for reactor and catalyst design [1–5]. Reaction engineering and catalysis aspects are discussed, how surface measurements have been successfully applied to the modification of a γ -alumina catalyst involved in the selective methylation of catechol (= benzene-1,2-diol), an intermediate in fine chemistry. In a first step, knowledge of the reaction scheme is applied to minimize the consecutive reactions of polymethylated catechol formation [6][7], and consecutively a physico-chemical description of the active sites is used for catalyst modification by doping with Mg^{2+} , in order to modify the initial selectivities of the parallel reactions of monomethylation of catechol [8].

2. Dynamic Behavior of Catalytic Reactors

The selection and scale-up of chemical reactors are based on kinetic models that describe the behavior of the reaction rates with sufficient accuracy in between a certain range of parameters. Because of the complicated relationships in heterogeneously catalyzed reactions, due to simultaneous mass and heat transfer, adsorption, desorption, and surface reactions, so-called semi-empirical kinetic models are used. Those models are based on a simplified physical and chemical approach. The model parameters are usually estimated by fitting the mathematical relationships on

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experimental results, and, therefore, are not physical constants, they are model-dependent. The drawback of those models is that they are only valuable for interpolations in the investigated parameter range. Extrapolations at other ranges of pressure, temperature, and feed composition are not possible *a priori*. The same considerations also apply to the design of other reactors or reaction modes. Hence, the models determined with steady-state experiments are not able to describe the dynamics of heterogeneously catalyzed reactions. They cannot predict the transient behavior and the optimum regulation parameters for catalytic reactors with changing input conditions. An example is the catalytic treatment of waste gases, where the concentrations, flow rates, and temperatures are subject to extended variations.

The dynamic response of a catalytic reactor to a change of the input concentration of one or various reactants is very sensitive to the reaction mechanism. Therefore, if the reactant and product concentrations are analyzed as a function of time, the specific shape and time constants of the response curves contain information on the elementary steps of the reaction path, such as surface reaction, reactant adsorption, product desorption, regeneration of active sites, inhibition of a reaction intermediate *etc.* [9]. These feed-concentration variations can be roughly ordered into two classes: transient variations and periodic operation. The former is a sudden (generally stepwise) change in concentration, either an increase or a decrease. The transients between the initial steady-state and the steady-state after perturbation are measured and analyzed. This type of experimentation is nearly state of the art in chemical reaction engineering as well as

in biotechnology. The latter is a periodic repetition of the concentration perturbations leading to additional operation parameters, such as cycle time, cycle split, and perturbation amplitude. The periodic response is more sensitive to the reaction mechanism than the transient response, but the analysis of the data is quite more ambitious, so that this experimental technique is generally used only for the validation of kinetic models derived from transients.

However, independently of the dynamic experimental technique used, the mathematical description is often complicated and suffers from the lack of objective information on the postulated reaction mechanism. Therefore, spectroscopic methods have been applied to measure directly the adsorbed surface intermediates by *in situ* infrared spectroscopy (FT-IR). Hence, the identification of the surface species under reaction conditions give the necessary physico-chemical background for the reaction mechanisms derived from the analysis of the concentration responses during dynamic experiments.

However, it is necessary to distinguish between reaction intermediates and so-called *spectator species* sticking on the surface of the catalyst or of the support without direct implication in the reaction path. This can only be performed by comparing under identical conditions the dynamic behavior of the surface intermediate with the dynamic behavior of the gas phase. Both informations have to be consistent with respect to the amplitude of the variations as well as to their time constants. To perform this, an experimental setup has been developed in our laboratory to investigate simultaneously the sur-

face and gas-phase concentrations (*Fig. 1*). The heart of the installation is a fixed-bed reactor which is directly coupled to a diffuse reflectance (DRIFTS) cell *via* an external recycle loop [10]. The effluent from the reactor is continuously analyzed by a mass spectrometer. As only a small amount of catalyst is present in the DRIFTS cell, temperature gradients can effectively be avoided. The main reaction takes place in the fixed-bed and allows kinetic studies at high conversion. Arranged as such, the infrared cell can be regarded as a window in the reactor providing a view on the catalyst at normal reaction conditions.

Fig. 2 shows typical response curves measured in this type of setup. The model reaction for the development was the CO₂ methanation on a Ru/TiO₂ catalyst at 110°. Infrared identified surface species are carbon monoxide and formates. The carbon-dioxide concentration is periodically switched between 0 and 10% (v/v) in a constant hydrogen concentration of 40% (v/v). The model description takes into account the formate dissociation to adsorbed CO as it is proposed by *Marwood et al.* [2] as well as the existence of an inert CO reservoir on the surface of the catalyst [12]. The description of the data is good and, as previously mentioned, allows a good validation of a reaction mechanism derived from transient experiments.

3. Yield Optimization by Catalytic Reaction Engineering

A reaction mechanism, as complicated as it may be, can be expressed as a block of parallel and consecutive reactions, where the desired product is generally not placed at the end of a reaction route, but lies somewhere in that block, for example it may react further to produce waste. The reaction conditions must, therefore, be optimized by means of chemical reaction engineering to achieve the best yield, for example the best ration between product produced and reactant consumed. This may be shown on the example of the catalytic gas-phase methylation of catechol, an intermediate in the production of fine chemicals. The alkylation agent is MeOH and the aim is the selective production of 3-methylcatechol. Catalytic methylation of catechol leads to many different products which can be classified into two groups: the polymethylated and the monomethylated products. The former are produced by consecutive reactions of the monomethylated compounds. The three monomethylated species are 3-methylcatechol, 4-methylcatechol, and guaiacol (2-

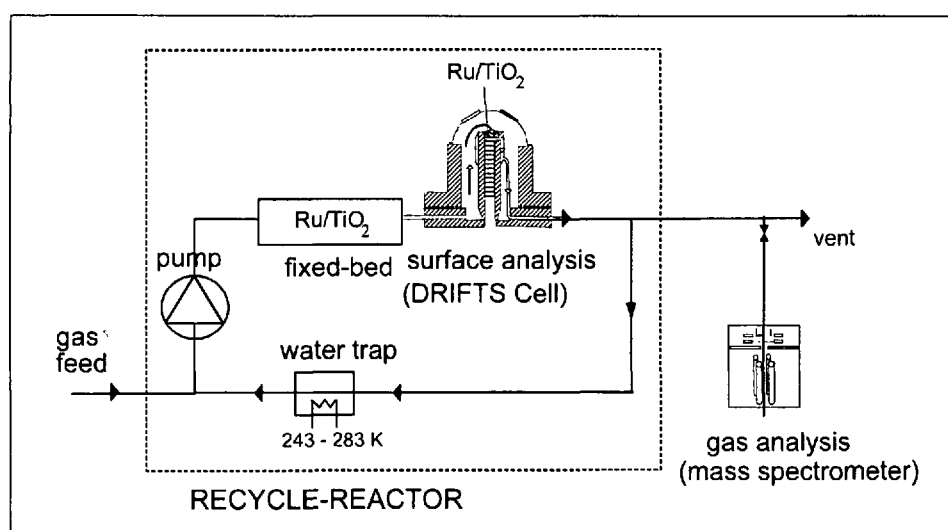


Fig. 1. DRIFTS-recycle reactor experimental setup for unsteady-state kinetic investigations with simultaneous in-situ surface intermediates measurements

methoxyphenol). γ -Alumina was found to be an effective catalyst for the gas-phase methylation of catechol with MeOH [6]. The process can be schematically presented as in the *Scheme*.

Direct methylation to 3-methylcatechol and 4-methylcatechol as well guaiacol formation are parallel pathways. The reverse reaction of guaiacol leads to the initial products catechol and MeOH. The rearrangement of guaiacol in the sequential reaction yields 3-methylcatechol. To avoid the formation of polymethylated products the conversion has to be kept low, since they are produced in a consecutive step. On the other hand, the conversion has to be increased to favor the guaiacol rearrangement. A good compromise has been found by using a conversion of less than 0.3 and a temperature range of 260–310°. At low conversion (<0.05) the rate of rearrangement was negligible and guaiacol was the main product, but the production of polymethylated heavy compounds, which may precipitate and plug the reactor are avoided. The C-alkylation is mainly 3-selective (*Fig. 3*) and a low yield of undesired 4-methylcatechol is measured.

4. Selectivity Optimization by Catalyst Modification

The result shown in *Fig. 3* is the optimum product distribution that can be achieved on a γ -alumina catalyst by reaction optimization. To increase the yields, the initial selectivity for the desired product has to be increased by a modification of the catalyst. To avoid a time-consuming catalyst screening, a good understanding of the nature of the active sites and the adsorbed reaction intermediates is necessary. For the catechol methylation, FT-IR experiments have been performed to determine the structure and orientation of catechol and methylated catechols on γ -alumina. This catalyst reacts with a large number of chemical compounds to give chemisorbed species which can be studied by IR spectroscopy to yield information about the adsorbed species as well as the adsorption sites themselves [13]. It has been shown that catechol is strongly chemisorbed on the surface of the catalyst (phenol resists evacuation at 450° according to *Taylor and Ludlum* [13]). A comparison of the IR spectra of catechol in the gas phase and catechol chemisorbed on γ -alumina (at 300°) is illustrated in *Fig. 4*. The region of the OH-stretching frequencies is strongly perturbed: the bands at 3730 and 3688 cm^{-1} disappear (the two

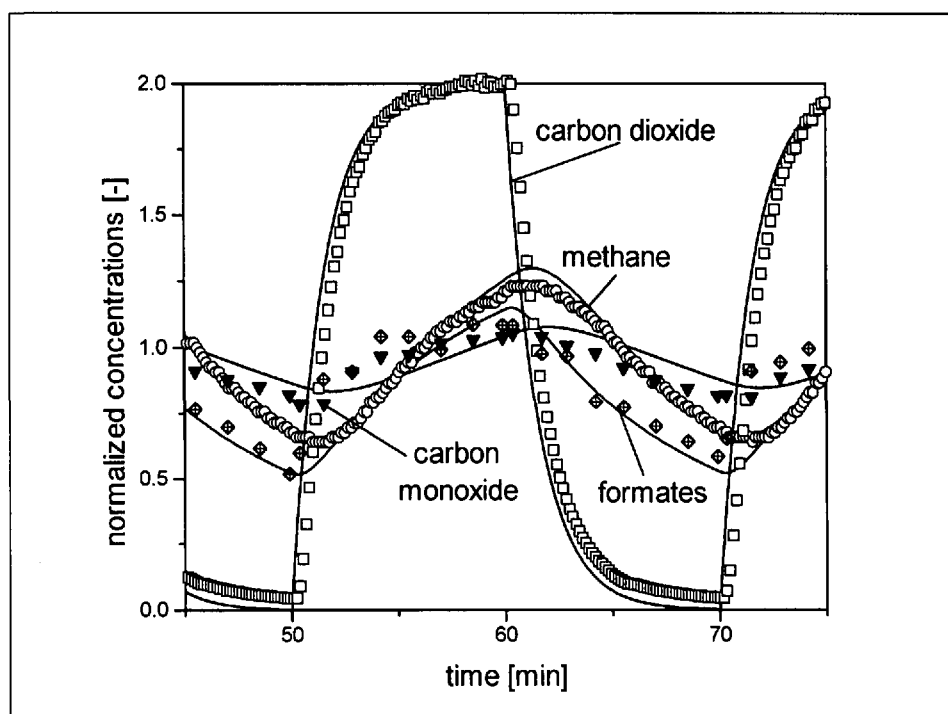
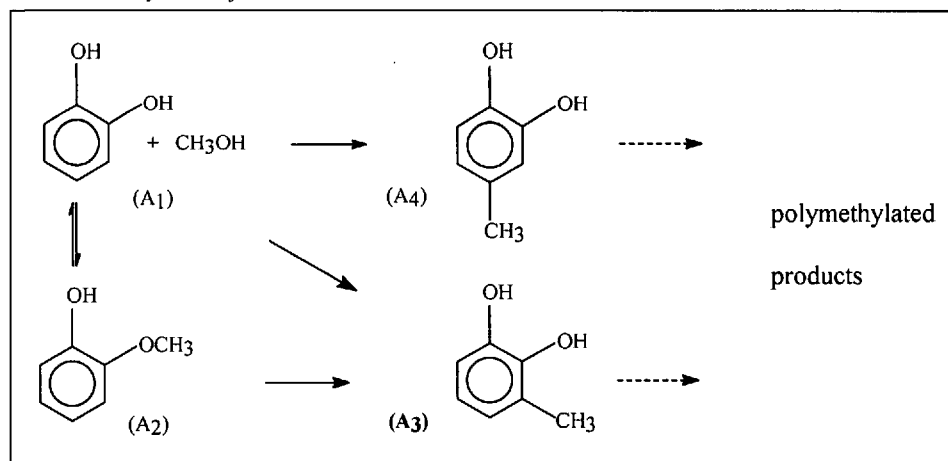


Fig. 2. Response curves to periodic CO_2 feed variations (split = 0.5, period = 20 min, CO_2 amplitude = 10%, feed = 40% H_2 , 8.0 mbar H_2O , He carrier, $T = 383$ K, Model: formate dissociation to adsorbed carbon monoxide and inert CO reservoir on the surface of the catalyst [11])

Scheme. Methylation of Catechol with Methanol



highest-frequency hydroxy bands for γ -alumina) when catechol is chemisorbed on the surface. This indicates that these two OH groups take part in the chemisorption of catechol and that the activity and selectivity of the catalyst can be modified by modification of the acidic and basic properties. Mg^{2+} cation, incorporated into γ - Al_2O_3 , can markedly modify the polarization of the lattice and consequently influence the acidic and basic properties of the surface which control the mechanism of the reaction [14]. Pure γ -alumina from *Engelhard* (Al-3982) was used as starting material. The modified catalysts were prepared by wet capillary impregnation with aqueous solutions of magnesium nitrate salts.

The catalytic activity of Mg^{2+} -modified alumina decreases with increasing Mg^{2+} content in the samples. This can be explained by the loss of acidity of pure alumina through the addition of the basic element. Literature reports [6][14–16] show that acidic oxides such as V_2O_5 , SiO_2 , and Al_2O_3 are active for methylation reaction below 400°. Basic catalysts such as MgO are active only beyond 500°. The selectivity $s_{3,0}$ is strongly dependent on the Mg^{2+} content (*Fig. 5*). It increases with Mg concentrations up to 7.5%, passing through a maximum of 0.65. 3-Methylcatechol becomes the main product at low conversion. It is worthwhile to note that only the relative formation of guaiacol and 3-methylcatechol are affected by the per-

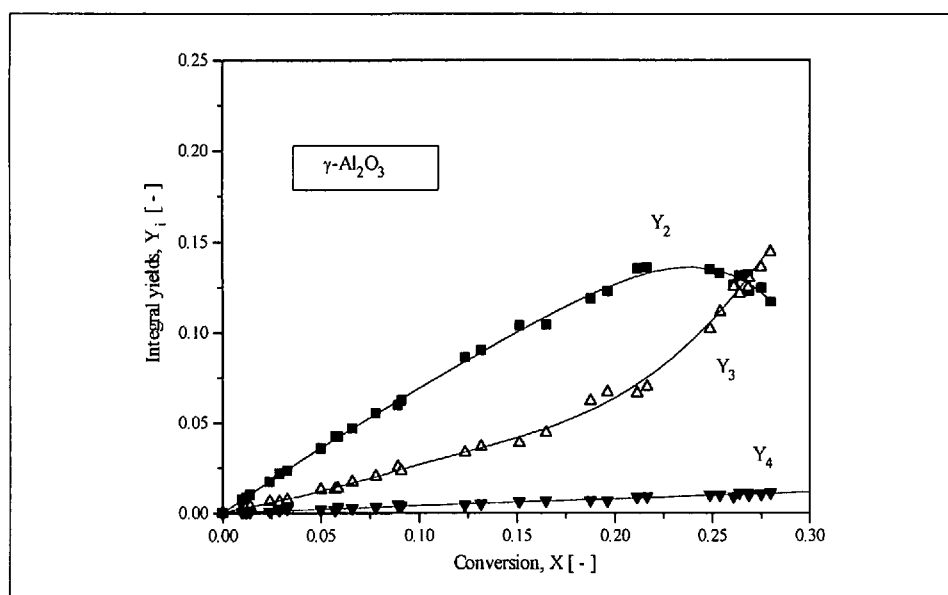


Fig. 3. Yields of monomethylated products as a function of catechol conversion at 260°. Y₂ = guaiacol, Y₃ = 3-methylcatechol, Y₄ = 4-methylcatechol.

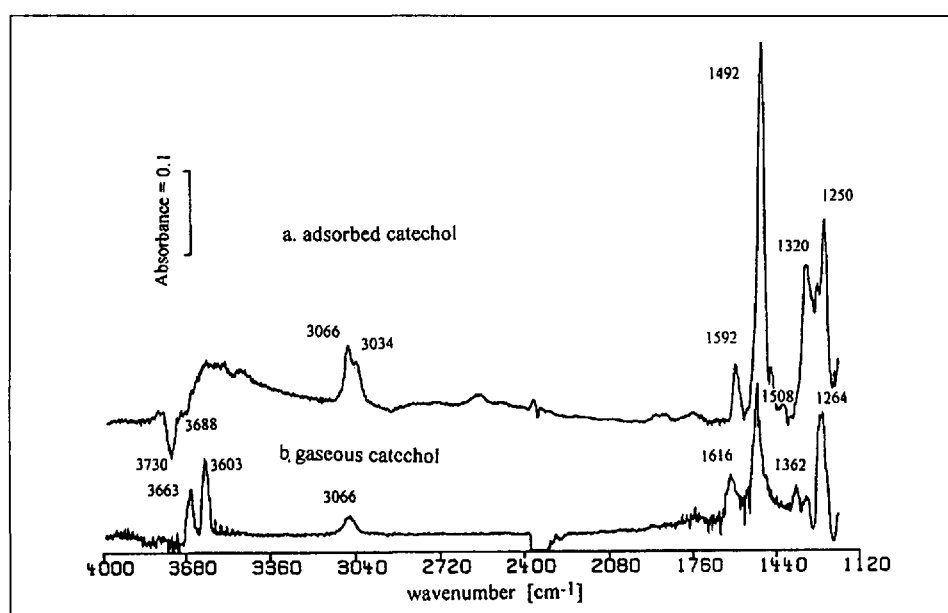


Fig. 4. IR spectra of catechol in the gas phase and catechol chemisorbed on γ -alumina at 300°

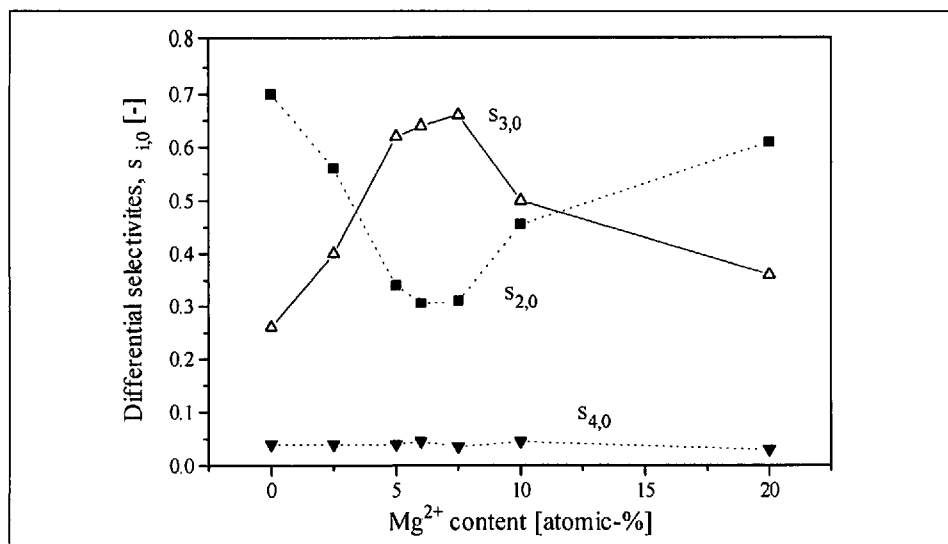


Fig. 5. Initial selectivity of the monomethylated isomers as function of Mg²⁺ content of a doped γ -alumina catalyst at 270°. s_{2,0} = guaiacol, s_{3,0} = 3-methylcatechol, s_{4,0} = 4-methylcatechol [8].

centage of Mg²⁺ added to alumina, O-alkylation is reduced in favor of C-alkylation, but the ring methylation stays preferentially 3-selective.

For the studied catechol methylation reaction the catalyst structure and surface properties can explain the catalytic behavior. As mentioned above, the reaction at 260–350° has to be performed over the acid catalysts. It has been shown, by FT-IR experiments, the strong adsorption of catechol on Lewis sites of the γ -Al₂O₃ surface. These sites control the reaction mechanism. Mg²⁺ cations in the γ -Al₂O₃ structure reduce the acidity of the surface. This causes an increase in the energy needed to activate adsorbed MeOH and results in the decrease of the observed catalytic activity. Since the catalyst structure remains the same type, it is possible to control the surface acidity by varying the amount of cation added. The strength and amount of active sites on the surface influence the catechol-adsorbed structure as well as the ring polarization and, therefore, determine the O/C-alkylation ratio.

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