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ARTICLE

Use of Intraparticle Mass Transfer Parameters as a Design Tool for Catalyst Pellets

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Abstract: A chromatographic method and a dynamic Wicke-Kallenbach method (DMWK) were used to determine the diffusion characteristics of two industrial copper containing catalysts. The first catalyst was used in nitrobenzene hydrogenation to aniline and the second was used in a low temperature water-gas shift reaction. Experimental results show that application of these two methods leads to similar results. Experimental data obtained allow for monitoring changes in the texture of the catalyst grains and intraparticle diffusivity of gaseous reagents at different states of the catalyst activity and use, which can be used as criteria for designing optimal industrial catalyst pellets.

Key words: effective diffusion coefficient; tortuosity; copper catalyst; pellet design

Catalyst shape and grain structure strongly influence their inter-particle and intra-particle heat and mass transfer characteristics and hence their performance in any industrial scale application. Thus, a proper design of a catalyst for industrial scale applications requires not only a proper attention to its catalytic characteristics but also a due attention to its shape and grain structure that allow for a better achievement of the desired heat and mass transfer in the catalyst grains and hence the required catalytic performance in the industrial reactors. Therefore, a purposeful design of industrial catalysts requires not only experience in the area of catalysis but also an in-depth knowledge of the process thermodynamic, kinetic and mechanism of the reaction and mass and heat transfer processes [1].

Inter- and intra-particle mass and heat transfer processes substantially affect the catalytic performance of a heterogeneous catalyst and the proceeding of an industrial scale catalytic reaction [2]. Therefore, optimal performance of a particular heterogeneous catalyst and successful executions of an industrial scale catalytic reaction demand proper attention to the design and formulation of the catalyst structure and its grain formation that allow for optimal inter- and intra-particle transfer processes.

The relevance and influence of mass and heat transfer phenomena on heterogeneous catalytic reaction processes are well established and presented in details in different references [3–6]. Among the important parameters of key importance in all theoretical treatments of catalytic processes are basic quantities related to the mass transfer in the catalyst grain, such as the porosity α, effective diffusion coefficients of reagents D_{eff}, and tortuosity factor τ of the catalyst pores, or simply the tortuosity. To account for the influence of porosity on a diffusion process, the diffusion coefficient must be measured along with the tortuosity. Moreover, critical reviews of experimental methods to measure the effective diffusion coefficients in porous media are also given by different researchers [7–10].

Measurements of effective diffusion coefficients and tortuosity factors of industrial catalysts are usually performed on as received samples prepared by the catalyst producers. However, most catalysts need to be activated by special procedures before their actual use. The transformation of a catalyst into its active form is a complex process that results into changes in the chemical and physical properties of the catalysts accompanied by changes in the textural and mechanical properties of the catalyst grains.

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Under operating conditions, industrial catalysts undergo further considerable changes in their chemical composition, crystal morphology, catalyst's texture, etc. At the same time, catalysts are steadily deactivated by one or more mean and mechanism including coking, sintering, fouling, phase transformation, and others. Such changes strongly affect the catalyst performance as well as the mass and heat transfer processes within the catalyst pellets and in the catalyst bed.

Only limited data are available in the literature on measurements of diffusion parameters such as the effective diffusion coefficient and tortuosity factor of catalyst pores performed on as received catalysts in their oxide state and after being activated in situ by a reduction step, as well as after being used and practically deactivated. Such data can be particularly useful for an optimum design of catalyst pellets.

Thus, the present work is concerned with the effect of the process of catalyst reduction and deactivation on the diffusion characteristics of industrial copper containing catalysts. Two catalyst samples used in two different types of catalytic processes, namely, nitrobenzene hydrogenation to aniline as a process representing typical catalytic organic synthesis, and a catalyst used in low temperature water-gas shift reaction (WGSR) as a typical catalytic process in the ammonia synthesis industry.

1 Experimental

1.1 Catalysts

1.1.1 Copper-based catalyst

The first tested catalyst is a copper-based catalyst used for the hydrogenation of organic compounds, such as nitrobenzene hydrogenation to aniline. It contains 50 wt% Cu supported on activated kieselguhr and promoted with 1.5 wt% Cr_2O_3 and 1.0 wt% Ni. Commercial cylindrical pellets of 5 × 5 mm particle size, 1.25 kg/L bulk density, and 100 kg/cm^2 compression strength were used. The BET area of the catalyst is 119 m^2/g. Samples of various state of the catalyst as outlined below were subjected to diffusion characteristic measurements.

(a) Random samples (200 g) taken from various industrial containers of the oxide form of freshly prepared catalyst.
(b) Reduced samples of freshly prepared oxide catalyst. Samples were reduced in situ in the diffusion cell or the chromatographic column wherever the diffusion measurements were made. Such samples would emulate industrial copper oxide catalysts reduced in situ in the industrial reactor before use.
(c) Random samples of used and practically spent catalyst collected from the discharge of an industrial reactor.

Prior to diffusion measurements, the copper catalysts were first dried in the diffusion cells using argon flow at 393 K for 6 h. For the case of in situ reduced samples, a flow of hydrogen at a gradually raised temperature to 473 K was employed for 3 h after the drying step with argon flow.

1.1.2 Commercial copper-zinc-aluminum oxide catalyst

The second tested catalyst is a commercial copper-zinc-aluminum oxide catalyst used in low temperature WGSR. The catalyst is composed of 38.0 wt% CuO, 27.0 wt% ZnO, 33.0 wt% Al_2O_3, and 2.0 wt% Cr_2O_3. It consists of 6 × 6 mm cylindrical pellets of 1.25 kg/L bulk density and 89.1 m^2/g BET area.

In an industrial application, copper oxide as part of the catalyst composition is reduced in the industrial reactor under a stream of a mixture of hydrogen, carbon monoxide, and nitrogen at elevated temperatures. Thus, the diffusion characteristics in samples of the following different states of the catalyst were carried out.

(a) Random samples (200 g) taken from various industrial containers of the oxide form of freshly prepared catalyst.
(b) Reduced samples of freshly prepared oxide catalyst. Samples were reduced in situ in the diffusion cell or the chromatographic column wherever the diffusion measurements are made.

Prior to diffusion measurements, the WGSR catalyst samples were first dried in the diffusion cells using a flow of argon at 393 K for 6 h. For the case of in situ reduced samples, hydrogen was gradually introduced to replace argon at the end of the drying step with a gradual increase in temperature to 473 K. Sample reduction step was continued for 3 h after the drying step.

1.2 Chemicals

The following laboratory grade high purity gases were used: 99.999% argon dried over a 5A molecular sieve, electrolytic hydrogen purified of traces of oxygen using a Pd catalyst and dried over a 5A molecular sieve, and oxygen dried over a 5A molecular sieve.

1.3 Apparatus

Diffusion measurements were carried out using two of the most popular and reliable experimental diffusion measurement methods, namely the chromatographic method (CM) and the dynamic method of Wicke-Kallenbach (DMWK).

Experimental measurements for both methods were carried out by using a HP 6890 gas chromatograph. Carrier and tracer gas employed in each experiment were first filtered, dried, and their pressure and flow rate regulated before being introduced into the diffusion measurement device (Chromatographic column in the case of CM and diffusion cell in case of DMWK). The diffusion measurements on all samples were carried out in the 293–433 K temperature range at atmospheric pressure.