Abstract

In the scope of this work processes for continuous heterogeneously catalyzed gas-phase reactions under in situ ball milling of a solid catalyst were developed. The oxidation of carbon monoxide was used as a model reaction. In an initial exploratory study to assess the potential of in situ ball milling in heterogeneous catalysis, a set of batch experiments with different metal oxides as catalysts (NiO, Cr₂O₃, Fe₂O₃, Co₃O₄, Mg(OH)₂ and 1 wt.-% Pt/γ-Al₂O₃) were carried out in a high pressure milling vial of a planetary ball mill. After a clearly positive effect of the milling on the catalytic activity of the solid catalysts had been established, selected catalysts were studied in more detail in continuous experiments to provide closer insights into the process. For this purpose a commercial shaker mill (Retsch MM200) was modified and the milling capsule was equipped with a gas inlet and outlet to allow the continuous operation of heterogeneously catalyzed gas-phase reactions. Milling during the catalytic CO oxidation over Cr₂O₃ led to a dramatic increase in the reaction rate. Without milling no conversion of CO to CO₂ could be observed at room temperature over Cr₂O₃. After starting the mill, the reaction rate increased immediately, however, rather long milling times were needed to reach a steady state. When the milling was stopped, the rate rapidly dropped to almost zero with some residual reactivity decreasing over a longer time period. The previous activity could be recovered after restarting the mill. We suggest that the immediate drop in activity after stopping the mill could either be due to a lack of direct impact that induces reactivity, or the rapid vanishing of some defects. Other, more stable defects heal over time periods on the order of minutes. An even slower decay of the catalyst activity after stopping the mill could be observed over metallic gold as catalyst. Whereas gold particles with sizes on the micrometer scale were known to be catalytic inactive before, they show high activity if exposed to the conditions of ball milling.

Comparison experiments in a plug flow reactor over premilled catalysts show that the activity of solid catalysts can be increased by several orders of magnitude, when the reaction is performed during ball milling of the catalyst. Furthermore a method for synthesizing supported gold catalysts with 1 wt.-% and 10 wt.-% gold on the metal oxides Fe₂O₃, Mn₂O₃ and TiO₂ under the conditions of the mechanocatalytic CO oxidation could be developed. The catalysts show high catalytic activity in CO oxidation under ball milling conditions and in a plug flow reactor. However, in order to be comparable with the activity of supported gold catalysts, synthesized by impregnation or co-precipitation, described in literature some modifications of the mechanocatalytic method, like longer milling times, are required.
In a follow-up study on further applications of \textit{in situ} ball milling, the potential in propene oxidation, an industrially interesting reaction to yield important oxygenated products such as acrolein or propene oxide, was investigated for mechanocatalysis. Catalyst screening of different metal oxides and pure metal powders (Ag, Cu) indicated a distinct catalytic activity over CeO$_2$, Cr$_2$O$_3$ and MnO$_2$ towards the formation of CO and CO$_2$; rate oscillations during milling were observed. Abrasion from the steel milling vessels could be eliminated as the cause for the oscillations through substitution by tungsten carbide milling vials.

In order to reach a steady state reaction and improve the catalytic activity, the reaction conditions were modified. By diluting the reaction gas with nitrogen or helium the oscillations could be prevented. Furthermore, it could be demonstrated that the activity of the metal oxides in propene oxidation was higher under mechanocatalytic conditions, compared to a plug flow reactor.