Abstract

In the field of heterogeneous catalysis, the concept of mechanocatalysis – i.e. the application of mechanical force during a catalytic reaction – remains almost unexplored. In this work, the continuous preferential oxidation of CO in an excess of H\textsubscript{2} (CO-PROX) was carried out by means of mechanocatalysis. By \textit{in-situ} ball milling of metal oxides or copper / metal oxide mixtures, an increase in the CO oxidation rate by several orders of magnitude was achieved. Over mixtures of Cu powder with Cr\textsubscript{2}O\textsubscript{3}, considerable CO oxidation activity was achieved at temperatures as low as -40 °C, while undesired side reactions, such as H\textsubscript{2} oxidation, were largely suppressed. During ball milling, the CO oxidation rate was up to 4 orders of magnitude higher than over the pre-milled catalyst in a conventional flow reactor. At low temperatures < 70 °C, both CO conversion and CO\textsubscript{2} selectivity increased with decreasing temperature, corresponding to an apparent activation energy $E_A \approx -4 \text{ kJ mol}^{-1}$. Due to the high selectivity in the ball mill compared to flow reactor experiments, the drastic increase in activity during milling can not be explained by thermal effects alone. Instead, we postulate that during milling, CO oxidation takes place selectively on mechanically induced, short-lived active sites. With the assumption that these active sites are surface defects, a simple kinetic model was proposed to explain the negative $E_A$. According to this model, the slower healing rate of defects at low temperatures results in a higher defect concentration. Thus, a negative $E_A$ can be expected if the temperature dependence of the defect healing rate is greater than that of the CO oxidation rate. The drastic and highly selective, mechanically induced enhancement of a particular reaction in comparison to undesired side reactions is a novel discovery which highlights the potential of mechanocatalysis in the field of heterogeneous catalysis.

As a side project, highly active nano-Au/TiO\textsubscript{2} catalysts were prepared by ball milling of Au powder and commercial TiO\textsubscript{2} under reaction conditions. The activity of these catalysts with regards to CO-PROX was comparable to benchmark Au/TiO\textsubscript{2} catalysts which were prepared by conventional methods such as deposition precipitation. This novel “top down” approach of preparing supported nano-Au catalysts by ball milling has several key advantages. Most importantly, the preparation is carried out in a single step without the need for Au(III) precursors or solvents.