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Hysteresis phenomena in heterogeneous exothermal catalytic reactions and methods for decreasing the overheating of catalyst nanoclusters

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Hysteresis in hydrogenation reactions has been found for the first time. A concept of the local overheating of active nanoparticles in a catalyst due to hindered reaction heat removal has been suggested to explain the origins of the appearance of a hysteresis loop.

The temperature hysteresis in heterogeneous catalysis is observed if a reaction parameter (reaction rate or degree of conversion) measured in the course of increasing temperature does not match the same parameter measured on decreasing temperature. As a result, a hysteresis loop appears, where the ascending and descending branches of the temperature plot do not coincide. Hysteresis can be explained by the existence of a number of steady states in a catalytic system,[1] phase transitions in the catalyst,[2] changes in the surface state of the adsorbed component,[3] the removal of admixtures that can hinder the reaction from the metal surface,[4] *etc*. These data are scattered, and the scope of reactions where the hysteresis effect has been studied is narrow. In most cases, this is the oxidation of CO[3,5,6] and methane.[7–12]

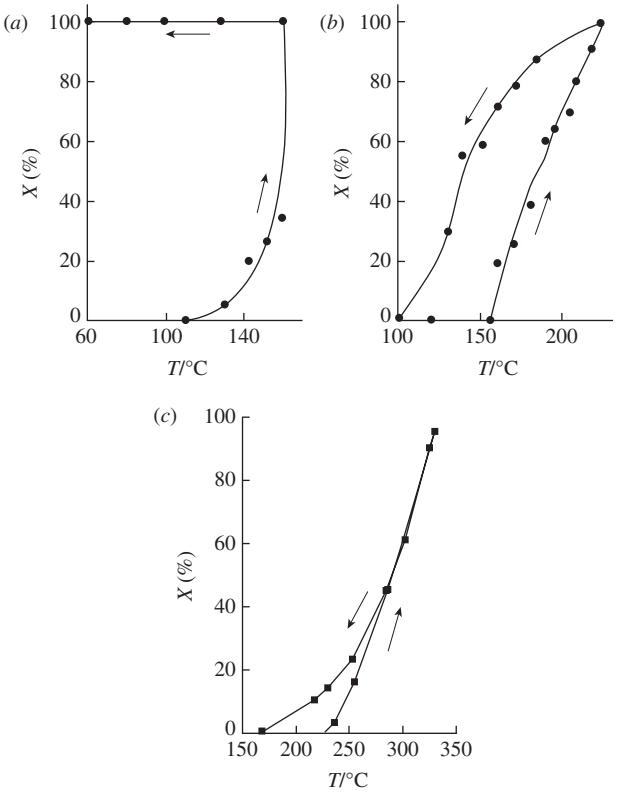

Figure 1 Temperature plot of CO degree of oxidation on the (*a*) 12.7% Mn_3O_4/64.3% Al_2O_3/23.1% CaO, (*b*) 35% NiO/$CaAl_2O_4$ catalysts and (*c*) on Pt foil. The arrows show reactor heating (↑) or cooling (↓).

Previously,[13,14] we suggested concept of temperature hysteresis due to the overheating of catalyst clusters. This is important for industrial chemistry since overheating leads to premature catalyst inactivation and thermal explosions of reactors.

The tests were carried out under atmospheric pressure in a custom-built semiautomatic gradient-free catalytic setup that ensured the adjustable supply of gaseous components, temperature variation in small steps (about 1 K) and sampling for GLC analysis. The flow rate of the reaction mixture (8% CO in air) was 6 $dm^3\ h^{-1}$.

The oxidation of CO (ΔH = –283 kJ mol^{-1}) with atmospheric oxygen manifested a distinct temperature hysteresis.

At a CO concentration of 12% [Figure 1(*a*)], a self-sustaining reaction mode is observed where after the supply of heat is discontinued, the reactor temperature remains at ~60 °C due to heat evolution, and this effect does not disappear for ~48 h. The same behaviour was observed on CuO obtained by the decomposition of copper hydroxocarbonate.

A different temperature plot of CO conversion is observed on platinum foil: hysteresis is almost absent [Figure 1(*c*)].

The hydrogenation of CO was carried out on a 35% NiO/$CaAl_2O_4$ catalyst and Ni (wire). Figure 1(*b*) shows that CO oxidation on the 35% NiO/$CaAl_2O_4$ catalyst is accompanied by a temperature hysteresis. An even more pronounced effect is observed in CO methanation (ΔH = –206 kJ mol^{-1}) on this catalyst [Figure 2(*a*)].

The shapes of the temperature plots in the fundamentally different reactions of CO oxidation and hydrogenation are nearly the same.

The reactions of CO oxidation and methanation are exothermic. It was interesting to compare the temperature dependences

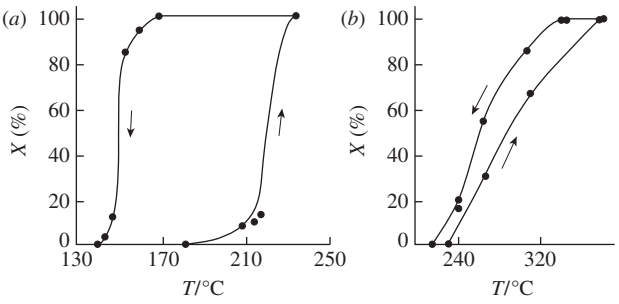

Figure 2 Temperature plot of the degree of CO methanation on (*a*) 5% NiO/$CaAl_2O_4$ and (*b*) Ni wire.

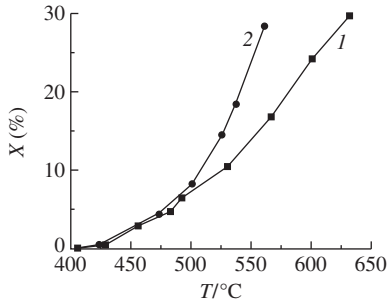

Figure 3 Isobutane dehydrogenation on the (*1*) (0.6% Pt + 2% Sn + 1% K)/Al_2O_3 and (*2*) 6.5% Cr/Al_2O_3 catalysts.

of these reactions with that of an endothermic reaction of isobutane dehydrogenation (ΔH ~ 130 kJ mol^{-1}).

Unlike oxidation and hydrogenation, no signs of hysteresis were observed on the temperature plots in this case: the ascending and descending branches coincided (Figure 3).

To eliminate catalyst overheating, heterogeneous catalysts based on metallic meshes were developed.[15] A stainless steel mesh made of 50 μm wire was used as a metallic carrier for the oxidation of CO.

Figure 4(*a*) shows the temperature plots of the degree of CO conversion on CuO/mesh and CuO/Al_2O_3/mesh samples. The presence of an alumina layer between copper oxide and the steel mesh hinders heat removal and thus enhances the hysteresis effect.

The addition of He, which has a high thermal conductivity, considerably decreases the width of the hysteresis loop in full agreement with our concept of hysteresis phenomena. The cooling reaction mixture (curve *2*) contained 6% CO, 14% O_2, 55% N_2 and 25% He with CuO (malachite) as a catalyst.

The temperature hysteresis in CO oxidation with atmospheric oxygen on copper oxide applied to a steel mesh increases if a heat-insulating alumina interlayer exists between the CuO layer and the mesh. This fact also confirms the local overheating of active ensembles as a reason for temperature hysteresis.

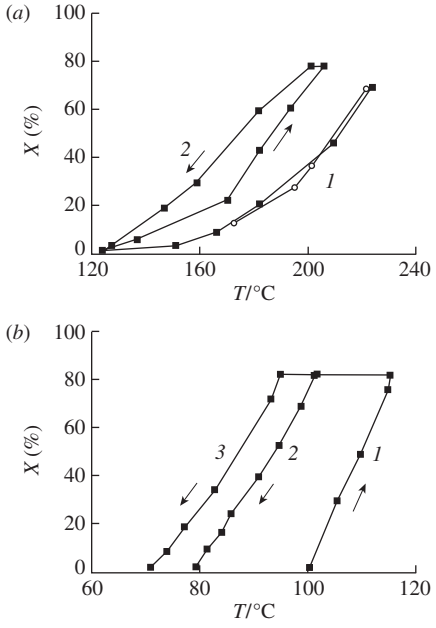

Figure 4 Plots of (*a*) the degree of CO oxidation on (*1*) CuO/mesh and (*2*) CuO/Al_2O_3/mesh samples *vs*. temperature; (*b*) variation in temperature hysteresis on replacement of a fraction of atmospheric nitrogen with helium: (*1*) heating, (*2*) cooling in the reaction mixture with He and (*3*) cooling in the reaction mixture.

The use of a catalyst on a steel wire mesh and the addition of helium provide a more efficient heat removal for an exothermal reaction and improve the process conditions.

If steady states existed in the system, a gradual temperature variation would result in a qualitative fast transition of the system with other kinetic laws; hence, a different reaction rate would be observed, though the reactor temperature did not change. This cannot explain a sharp difference between exo- and endothermal reactions. Furthermore, transitions between different steady states should occur instantaneously and no stable intermediate points on the temperature plots could be obtained in this case. This reason was used as evidence against the explanation of hysteresis effects by the multiplicity of steady states. We believe that, in an exothermal heterogeneous catalytic reaction, an increase in the temperature accelerates reactions on active catalyst clusters to such an extent that the released heat does not have enough time for dissipation by heat transfer. The most important way of heat dissipation is thermal conductivity through the catalyst bulk.[16] However, the majority of catalysts belong to dispersed solids where contact thermal conductivity is hindered, and the smaller the particle size in a granular material, the lower the thermal conductivity.[17] Less porous materials have a higher thermal conductivity coefficient than highly porous ones, and bulk metals possess the highest thermal conductivity [hysteresis is absent or insignificant in this case, Figures 1(*c*) and 2(*b*)].

Due to insufficient heat removal, the actual 'point' temperature of a catalyst cluster where the reaction occurs becomes considerably higher than the average temperature in the catalyst layer (it is usually called the reaction temperature). Because of local catalyst overheating, the degree of conversion becomes higher than the value observed at the temperature measured by a thermocouple. This increases heat evolution and hence the catalyst temperature even more, and, as a result, the degree of conversion in a very narrow measured temperature range increases rapidly. As the temperature changes, the excess heat that does not have enough time to get dissipated due to insufficient heat removal makes the reaction occur at a higher actual temperature than the value measured by the thermocouple. Furthermore, we cannot rule out that less active catalytic sites that could not be active in the absence of overheating participate in the reaction. Because of that, the degree of conversion is maintained at a higher level. Hysteresis does not disappear on increasing the time of the experiment with a stable catalyst to 72 h or more. Note that the observed hysteresis is not a unique phenomenon. For example, concentration hysteresis was observed in deep methane oxidation on a $Pt/\gamma\text{-}Al_2O_3$ catalyst.[18]

The above phenomena are related to insufficient heat removal, but this effect may be additionally shaped by changes in the fine structure of catalyst nanoparticles, adsorption characteristics and changes in reaction rate related to these parameters.[19–21]

In conclusion, temperature hysteresis in hydrogenation reactions has been discovered. A suggested concept of local overheating of active nanoparticles in a catalyst due to hindered reaction heat removal gives a noncontradictory explanation of the origins of the appearance of a hysteresis loop.

Application of a catalyst on a steel wire mesh and addition of helium provides efficient heat removal for an exothermal reaction and reduces catalyst overheating and the width of the hysteresis loop.

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