Nanocrystalline perovskites prepared by reactive grinding

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Perovskite mixed oxides with exceptionally high specific surface areas can be fabricated for use as efficient catalysts in a wide variety of chemical applications.

Some perovskite-type mixed oxides have long been recognized as very active oxidation catalysts with many potential applications, but unfortunately have been limited by the low specific surface area (SSAs) of these materials. This is due to fabrication methods using high temperature techniques that induce sintering, effectively also reducing their SSA. Several years ago, my colleague André Van Neste and I realized that the ball-mill was a very convenient reactor for the synthesis of perovskite-type mixed oxides from the single oxides of the constituent metals. With our method, the solid-solid reactions involved in synthesis can be performed close to room temperature (≈ 40°C) which has significant consequences for the surface properties of the solid products. Moreover, by controlling the gas phase within the mill with gaseous or solid grinding additives, materials with exceptionally high SSAs can be fabricated. For example, Figure 1 shows the SSA values of several perovskite mixed oxides of general formula ABO₃ (with different cations at positions A and B) that were produced using our reactive grinding technique.

Another advantage of reactive grinding is that it produces mixed oxides consisting of agglomerates of nanocrystalline domains. Their SSA can be increased by partial detachment of the nanoparticles, which yields a looser agglomerate. The resulting solid exhibits nanoparticle properties without the drawbacks of potentially hazardous airborne nanoaerosols. Another interesting property of these agglomerates is the presence of a high density of nanoscale grain boundaries. As oxygen mobility is usually higher in grain boundaries, their occurrence is especially important for the catalysis of redox reactions. Recently, we were able to show that the B-transition metal atoms present in ABO₃ perovskite grain boundaries were easier to reduce to the zero-valent state in this phase and that our approach could be used for the preparation of supported transition metals.

From these experiments, we concluded that nanocrystalline perovskites (NCP) could be used as catalysts in redox reactions and also in reactions catalyzed by metals. Over the last few years, we have been exploring the catalytic properties of these systems in such reactions. A company (Nanox Inc., Québec, QC, Canada) was also created to exploit this technology under an exclusive license from Laval University. Over the last few years, with the help of the Nanox team, we have studied a variety of NCP catalytic applications.

One study investigated the oxidation of volatile organic compounds by La/Co-based perovskites. Kinetic experiments on the gas phase oxidation of n-hexane by oxygen allowed us to describe a reaction mechanism involving the participation of a surface oxygen species adsorbed on surface oxygen vacancies ($\alpha$-O₂). The oxidation of methane was then shown to proceed via another mechanism involving the participation of $\beta$-oxygen species originating from the bulk of the crystal. These results were subsequently used by the Nanox team to develop an outstanding diesel oxidation catalyst.

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Sulphur compounds being almost ubiquitous in fuels, we also investigated the catalytic activity of NCPs prepared by reactive grinding for CH₄ oxidation and their unique ability to resist SO₂ contamination. Similar properties were observed in the case of CO₂ during the catalytic wet air oxidation (CWAO) of stearic acid. Using our understanding of the CH₄ deactivation mechanism, we are now attempting to develop efficient NCPs for use in the CWAO of municipal waste waters. Interestingly, the oxidation rate was shown to be related to the oxygen storage capacity as well as to oxygen mobility, which was again shown to be associated with grain boundaries.

In other studies, the catalytic properties of NCPs in gas phase redox reactions were also utilized to develop catalysts for the reduction of NO and NOₓ species, the main pollutants produced by combustion engines. It is indeed notorious that the three-way catalyst of catalytic mufflers can not efficiently reduce NOₓ under so-called lean burn conditions, i.e. in the presence of excess oxygen. We investigated NCPs consisting of Co, Fe, or Mn associated with Cu or Pd at the B site, all prepared by reactive grinding, as catalysts for the reduction of NO by propene. Our results showed that they functioned as very active catalysts at low feed oxygen concentrations. Since their properties were found to be complementary to that of Ag-based catalysts, we also optimized NCP mixtures with Ag/Al₂O₃. Recent results are rather spectacular with high NO conversions at high space velocity over the range of 0-10% feed oxygen content.

We are also interested in using NCPs to fabricate supported metal catalysts. For example, we recently investigated the catalytic performance of hydrogen-treated LaCoₓCu₁₋ₓO₃ in the synthesis of higher alcohols from CO+H₂ gas mixtures. We found again that reactive grinding yielded high SSA materials with good catalytic properties. Although not yet systematically investigated, the Fischer-Tropsch process should also be efficiently catalyzed by Co or Fe-based nanoperovskites.

To conclude, our findings clearly show that NCPs are exceptional materials with a promising future for a wide variety of chemical catalysis applications.

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References