HRTEM observation of the monoclinic-to-tetragonal (*m*-*t*) phase transition in nanocrystalline ZrO_2

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Motivation

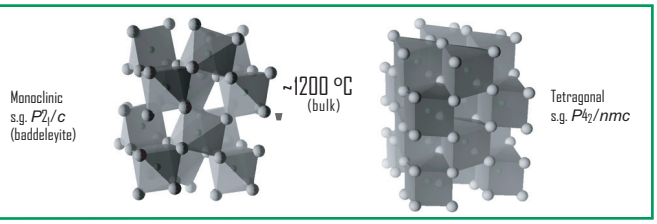
Copper based catalysts supported on ZrO_2 (zirconia) can be used for reactions such as water-gas shift, methanol synthesis, and methanol steam reforming. Zirconia modified with anions such as sulphate is an acid catalyst and became known for its extraordinary activity in low-temperature alkane isomerization [1]; it is also active for a number of other acid-catalysed reactions [2].

Material preparation

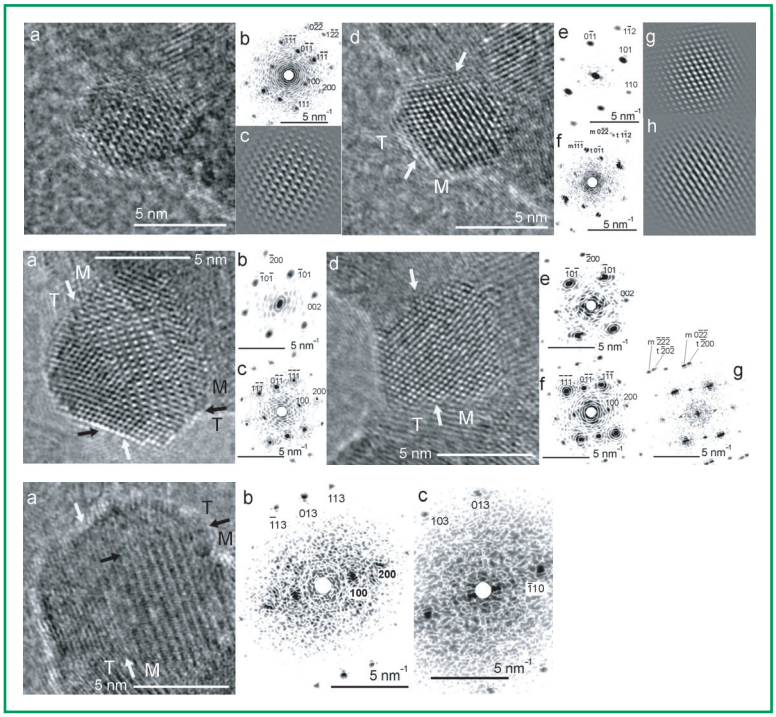
A templating procedure [3] was used for the synthesis of the CuO/ZrO_2 material, which involved the use of a polymer gel template [4]. This particular template was an acrylamide/glycidyl methacrylate polymer formed in an aqueous Tween-60 (Aldrich) solution at 55 °C. After cleaning and solvent exchange to n-propanol the gel was soaked in a zirconium (IV) propoxide (Aldrich, 70 % by mass in n-propanol) solution containing copper(II) acetylacetonate (Aldrich, 2.0 g) for 16 h to give theoretically an 11 % Cu to Cu+Zr mass ratio. The impregnated gel was then placed into a mixture of n-propanol/water (1:1 v/v) and left overnight during which hydrolysis reactions occurred. The hybrid material was dried at room temperature open to the atmosphere, and then calcined at 450 °C (ramp 215 °C*h^{-1}) under a nitrogen then oxygen atmosphere to remove the organic material. Then the powder was heated with the rate of 5 °C per hour up to 250 °C and kept for 10 h at that temperature under normal pressure in a helium atmosphere containing 2 % of hydrogen

Crystallography of ZrO_2

At normal pressure ZrO_2 can exist in three modifications: monoclinic (*m*), tetragonal (*t*), and cubic. In bulk material the $m - t$ transition occurs at about 1200 °C



HRTEM images and power spectra



Orientation relations

m(100) || *t*(110)
m[001] || *t*[001]

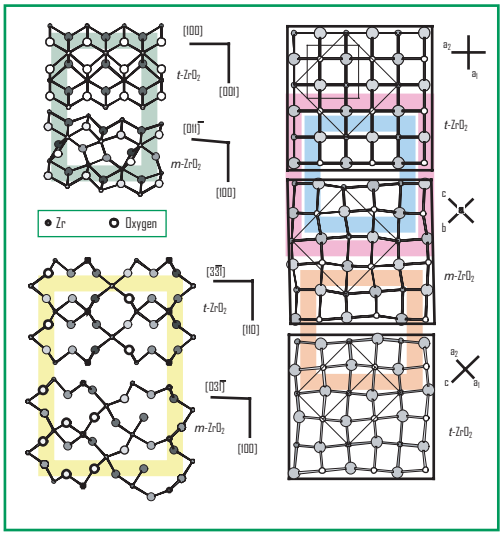
m(100) || *t*(001)
m[100] || *t*[110]
(white arrows in a,d)

m(011) || t(100)
m[100] || t[110]
(black arrows in a)

m(100) || *t*(110)
m[001] || *t*[001]
(white arrows)

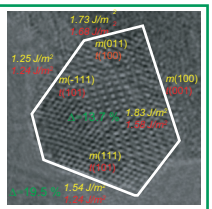
m(013) || *t*(116)
m[001] || *t*[001]
(black arrows)

Habit planes



Surface energies

of the principal planes of *m* and *t* ZrO_2 [5]

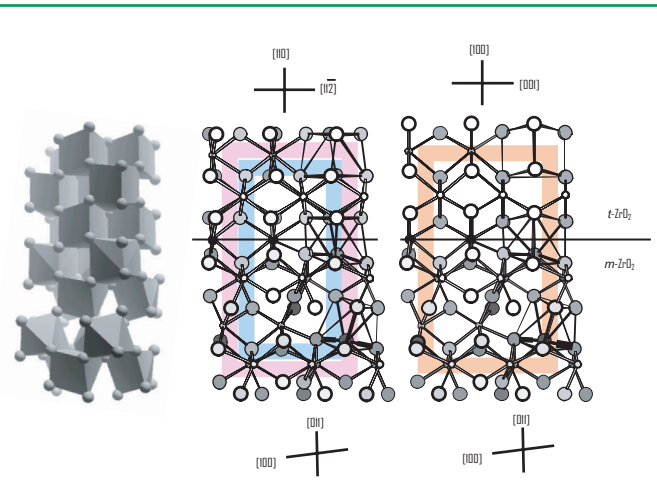


Conclusion

The transition:

- is induced by electron irradiation;
- occurs outside the region of bulk *t*-ZrO_2 thermodynamic stability;
- starts on those surfaces whose transformation provides a maximum gain in surface energy. This confirms the Garvie`s mechanism of the tetragonal phase stabilization [6].

Model of interface



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