Effect of Titanium Doping on the Structure and Catalytic Activity of Molybdenum Dioxide for the Reforming of Liquid Hydrocarbons

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Abstract

Molybdenum dioxide (MoO_2) has demonstrated potential not only as a heterogeneous catalyst but also as electrode material in lithium ion batteries and fuel cells. MoO_2 exhibits high catalytic activity towards the reforming of complex liquid hydrocarbon fuels, such as n-dodecane, jet-A fuel and gasoline. Along with the high catalytic performance, MoO_2 has also displayed high coking resistance and excellent sulfur tolerance, which are key properties in fuel reforming catalysts. The excellent catalytic properties combined with the mixed ionic and electronic conductivity exhibited by MoO_2 have led to the use of this metal oxide as an effective anode material in solid oxide fuel cells. However, stability problems prevent the widespread use of this oxide in commercial applications.

In the present work, MoO_2 was doped with titanium (Ti^{4+}) by using a novel solution-based synthesis method followed by hydrothermal reduction, rather than using a conventional high-temperature solid-state reaction. Nano-sized Ti-doped MoO_2 particles with Ti/Mo ratio of 0, 0.03 and 0.05 were prepared. X-ray photoelectron spectroscopy (XPS) performed on the Ti-doped MoO_2 sample showed that the Ti dopant is present in the Ti^{4+} form. XPS depth profile analysis indicated the presence of Ti^{4+} even in the bulk of the sample, in agreement with the data obtained by using Rietveld refinement on X-ray and neutron powder diffraction patterns showed changes in both the lattice parameters and the Mo-Mo interatomic distance upon doping, suggesting the substitution of Mo^{4+} by Ti^{4+}. Transmission electron microscopy and laser scattering showed that the particle size ranges from 20 to 40 nm. Elemental mapping obtained by scanning electron microscopy with energy dispersive spectroscopy showed homogenous distribution of the dopant.

Attenuated total reflectance-Fourier transform infrared spectroscopy revealed that the solubility limit of the synthesized Ti-doped MoO_2 was reached at Ti/Mo ratio of 0.5, indicating that the bulk thermodynamic solubility limit can be exceeded at the nanoscale.

The Ti-doped MoO_2 sample after annealing in N_2 at elevated temperatures showed the absence of phase changes. High temperature annealing caused increase in the crystallite size and decrease in the surface area most of which comes from the mesoporous structure. X-ray photoelectron spectroscopy analysis suggested the formation of a core-shell structure where the core is formed by the MoO_2 and the shell by the Ti-doped MoO_2. The interaction of Ti-O-Mo was observed by using Fourier transform infrared spectroscopy. Temperature-programmed reduction combined with thermogravimetric analysis carried out on the annealed samples indicated that the presence of Ti^{4+} dopant caused a delay in the onset reduction temperature of MoO_2, which is associated with an increase on the energy of activation barrier imposed by the reduction process. These observations were confirmed using in situ X-ray powder diffraction and led to conclude that Ti-doping improves the stability of MoO_2 when exposed to strong reducing environments. The Ti-doped MoO_2 also showed higher catalytic stability towards the reforming of n-dodecane than undoped MoO_2, which may be related to the decreased oxygen mobility in MoO_2 as a result of the doping.

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