Metal Oxide Nano-Sheets with (111) Surfaces as Catalysts and Catalyst Supports

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Introduction

MgO and NiO have a typical rocksalt structure and possess a high melting point and high ionic character. Although the stoichiometry and crystallinity change little, the morphology can vary in shape, particle size and surface structure. The (100) facet of the rocksalt structure is unambiguously the most stable due to its low surface energy, therefore, it is normally a product after cleavage and is unaminously the surface demonstrated by current wet chemical preparations. Numerous studies have demonstrated that the shape and size of crystalline MgO and NiO are highly influential on the adsorption properties and the configuration of surface species formed during chemical adsorption. Furthermore, nanoscale MgO has been reported to be extremely effective for the destructive adsorption of numerous environmental toxins and several chemical warfare agents (VX, sarin, mustard gas)[1]. However, the (111) surface consists of alternating polar monolayers of oxygen anions and metal cations and thus, a strong electrostatic field perpendicular to the (111) surface is created [2]. Such a surface has provided a prototype for the study of surface structure and surface reactions, which drew great attention for both experimental and theoretical studies [3,4]. These studies imply the importance of size and shape control in metal oxide synthesis for its applications, as it is not only the surface area that matters, but also the surface chemistry. Here, we will present recent work demonstrating the preparation, characterization and catalytic properties of metal oxide nanosheets with (111) surfaces as well as their application as catalyst supports [5-8].

Materials and Methods

Synthesis: An example of a typical synthesis of the MgO nano-sheet structure [5], 1.0 g of Mg belt was dissolved in absolute methanol under a static argon atmosphere. After the Mg belt totally dissolved, 4-methoxy-benzyl alcohol (BZ) was added to the mixture in the ratio Mg : BZ = 2 (molar ratio), after stirring for 5 h, H_2O (molar ratio of 2 with respect to Mg) was dissolved into 30.0 ml methanol and was added dropwise into the system under stirring, the mixture was stirred for 12 h before being transferred to an autoclave. The autoclave containing the reaction mixture was purged with Ar for 10 min, and then a pressure of 10 bars Ar was imposed before initiation of heating. The mixture was heated to 265 °C and maintained for 15 h continuously, then, the vapor inside was vented (thereby removing the solvent in the supercritical state). A dry white powder was collected and calcined with a ramp rate of 3 $°C\cdot min^{-1}$ to 500 °C, then maintained at 500 °C for 6 h. The ultra-fine white powder produced from the above contains solely the MgO nano-plates possessing the (111) surface on the edges.

Results and Discussion

Metal oxides with (111) surfaces can be prepared through a facile self-assembly process following a thermal treatment. For example, the MgO(111) nano-sheets possessing the exposed (111) plane as a main surface have a thickness typically between 3 and 5 nm. Study by in-situ DRIFT spectroscopy of MgO(111) nano-sheets suggests that hydroxyl groups, oxygen vacancies and surface oxygen anions exist on the surface and the (111) surface may be stabilized by hydroxyl groups. DRIFTS and TPD studies of CO_2 adsorption reveals that there are large amounts of medium strength basic sites which can be attributed to high concentrations of surface O^{2-} Lewis base species. DRIFTS and TPRS studies of methanol reveals that, in contrast to the commercial metal oxides (MgO or NiO), the NiO and MgO(111) nano-sheets are highly reactive and strongly basic. The surface oxygen defects and oxygen anions are the main active sites for methanol decomposition [7, 8]. Methanol can be readily decomposed and the surface C=O species formed can be oxidized quickly at low temperature by the high concentration of oxygen anions on the surface of MgO(111) nano-sheets, which demonstrates that the MgO(111) nano-sheets have potential application in fuel cells and methanol based alternative energy technologies. Additionally, MgO(111) nano-sheets also demonstrate ultrahigh activity for the base catalyzed Claisen-Schmidt condensation and biodiesel transesterification [5, 6]. The structure and function relationships have also been investigated by in-situ DRIFTS studies of adsorption and reaction of benzaldehyde and acetophenone and the reaction intermediates observed.

Significance

The metal oxide (111) nanosheets possess a novel surface that can be utilized for low temperature methanol decomposition, and Lewis base catalysis (for example, biodiesel transesterification). Additionally, use of these surfaces as supports for nanoparticles of gold indicate very different catalyst/support interactions as compared to the (100) surfaces.

References

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