Defective Nb_2O_5-supported Pt catalysts for CO oxidation: Promoting catalytic activity via oxygen vacancy engineering

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A B S T R A C T

We introduced oxygen vacancies into Nb_2O_5 via thermal treatment at 700 °C under oxygen-deficient conditions for different lengths of time. Niobia-supported Pt catalysts were subsequently synthesized using the wet impregnation method with the fabricated Nb_2O_5. The catalytic activity of the synthesized catalysts for CO oxidation exhibited a significant increase from that obtained for a counterpart having the Nb_2O_5 support treated under saturated oxygen conditions (i.e., in air). Moreover, increasing the number of oxygen vacancies was found to increase the catalytic activity. At 150 °C, the TOF calculated for the catalyst with the most oxygen vacancies was 0.36 s^{-1}, which was much higher than that obtained from the catalyst possessing the fewest oxygen vacancies (0.05 s^{-1}). Systematic characterization of the synthesized catalysts revealed the crucial impact of oxygen vacancies and active lattice oxygen on the enhancement of catalytic activity.

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1. Introduction

Metal oxides have been employed broadly as catalyst supports in heterogeneous catalysis because they not only offer essential features such as improved surface area and stability, but also represent active components during the reaction. For the latter purpose, the oxide surface must be able to exchange charge and/or chemical bonds with adsorbed chemical species. Reducibility, which can be described by the cost of oxygen vacancy formation (i.e., the capability to release atomic oxygen from the metal oxide lattice to interact with the adsorbed species) and the consequent tuning of the composition of the metal oxide surface from M_nO_m to M_nO_{m-x} are typical metal oxide properties that satisfy this requirement. The reducibility of metal oxides holds great importance in chemical reactivity for a variety of reactions where lattice oxygen is the source of active oxygen, per the Mars–van Krevelen mechanism [1]. Exploiting this reducibility (i.e., the ability to generate oxygen vacancies in metal oxides) is extremely beneficial for catalytic applications. Among the approaches for improving the reducibility of metal oxides, thermal treatment under reducing or inert atmospheres has gained much attention, because this method is relatively simple and effective. For instance, Chen et al. [2]

synthesized black TiO_2 by thermal annealing of TiO_2 in H_2 gas, which was found to increase solar adsorption for photocatalysis. Likewise, Xie et al. [3] synthesized self–doped perovskite $SrTiO_{3-\delta}$ via thermal treatment at 1200–1400 °C for 20 h under Ar gas, which enhanced the visible light activity for photosynthesis from CO_2/H_2O.

The relative reducibilities of different metal oxides were determined using the hydrogen chemisorption study pioneered by Tauster et al. [4], which found a correlation with the strong metal–support interaction (SMSI) properties (i.e., where the support influences the catalytic reactivity of a metal via charge transfer, metal stabilization, support participation in the reaction, and oxide encapsulation of metal particles). Since then, much scientific research has been devoted to the impact the SMSI effect and reducibility have on catalytic performance [5–8]. Admittedly, metal oxides possessing excellent reducibility, such as TiO_2 [9,10], Fe_2O_3 [11], and CeO_2 [12], have commonly been employed for this purpose. Meanwhile, the practical use of other metal oxides such as Nb_2O_5, which appears to be a reducible oxide [4,13], is still underestimated. Niobium oxides exist naturally with different structures (e.g., stoichiometric, nonstoichiometric, metastable, and mixed) [14]. The many possible structures allow this oxide to change its electrical conductivity, refractive index, and photo-electric properties significantly [15]; thus, these materials have been used as catalysts for various applications. Moreover, niobium oxide is widely known as a solid acid catalyst [15,16], but less