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Review

Gas-solid catalytic reactions over ruthenium-based catalysts

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ABSTRACT

Ruthenium (Ru)-based catalysts are widely employed in several types of gas-solid reactions because of their high catalytic activities. This review provides theoretical research on Ru-based catalysts and an analysis of their basic properties and oxidation behavior. There is particular emphasis on Ru-catalyzed gas-solid catalytic reactions, including the catalytic oxidation of VOCs, preferential oxidation of CO, synthesis of ammonia, oxidation of HCl and partial oxidation of CH₄. Recent literature on catalysis is summarized and compared. Finally, we describe current challenges in the field and propose approaches for future development of Ru-based catalysts.

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1. Introduction

Development and use of catalysts has greatly progressed over past decades and they are used for nearly 80% of all chemical production. It is envisioned that future development of existing catalysts or identification of novel materials for the next generation of catalysts will rely on rational design, which requires an understanding of the complete catalytic reaction system at the atomic scale [1]. A better understanding of the atomic-scale structure of a catalyst requires investigation of model catalysts with simple structures, such as single crystalline films or single crystal surfaces [2]. The mechanisms of real catalytic processes are highly complicated and it is difficult to identify the micro-steps in these reactions. Therefore, analysis

of catalytic performance — including the study of elementary reactions steps, reaction intermediates and related topics — is typically accomplished via a combination of surface science and experimental methods. Such studies have led to an in-depth understanding of catalytic reactions under real-life conditions.

Many catalysts, such as noble metals and transition metal oxides, have been explored for gas-solid reactions. Recently, supported ruthenium (Ru)-based catalysts were employed in many gas-solid reactions because of their excellent activities under low temperature and pressure conditions.

This review describes properties of Ru, the oxidation of Ru metal and the theoretical research on Ru-based catalysts. In addition, we explain the gas-solid reactions catalyzed by Ru-based materials. As shown in Fig. 1, the catalytic applica-

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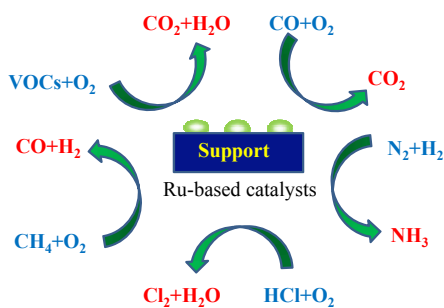


Fig. 1. Gas-solid reactions promoted by Ru-based catalysts.

tions of these materials include the catalytic oxidation of volatile organic compounds (VOCs) [3–5], preferential oxidation of CO (PROX) [6,7], synthesis of ammonia [8], oxidation of HCl (the Deacon process) [9] and partial oxidation of CH₄ [10–12]. Finally, this review summarizes existing problems as well as future developmental trends for Ru-based catalysts.

2. Ru-based catalysts

2.1. Basic properties

Ru is a rare transition metal belonging to the platinum group in the periodic table. The electronic structure of elemental Ru is $4d^75s^1$ and Ru exhibits a rich variety of oxidation states, including +2, +3, +4, +6 and +8. Ru materials are mainly composed of metallic Ru, RuO₂ and RuO₄. The boiling points of these forms are 4100 °C [13,14], 1400 °C and 100 °C [15,16], respectively. The crystal planes of RuO₂ are illustrated in Fig. 2. In the bulk structure of RuO₂ (rutile structure), the Ru atoms bind to six oxygen atoms, forming a slightly distorted RuO₆ octahedron, while the oxygen atoms are coordinated to three Ru atoms in a planar configuration that is consistent with the sp^2 hybridization of oxygen [1].

Volatility at high temperature is recognized as a serious limitation in applications of Ru-based catalysts. In Ru-based catalysts for gas-solid reactions, metallic Ru and/or RuO₂ have been commonly identified as the active species and the reaction temperatures are usually below 400 °C, much lower than the boiling points of Ru and RuO₂. Hence, volatility of Ru species is not observed in most gas-solid catalytic reactions and there have been no reports of this behavior for such reactions.

2.2. Oxidation behaviors

The transition from oxygen adsorption to oxide formation on Ru is structurally complex because of the various phases of

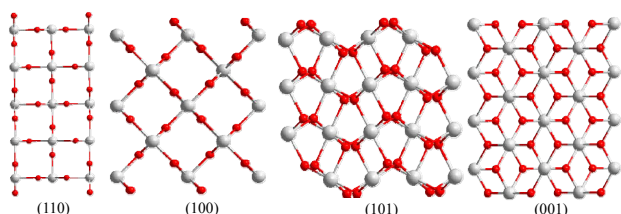


Fig. 2. The crystal planes of RuO₂.

oxygen on the surface [17]. However, the orientation of the RuO₂ depends on the orientation of the Ru. H. Over *et al.* [18] demonstrated that the active part of this “O-rich” Ru phase is RuO₂, which grows epitaxially with its (110) plane parallel to the Ru (0001) surface at high O₂ partial pressure and elevated temperatures. When the Ru (0001) surface is exposed to molecular oxygen under UHV conditions, a (2×2)-O layer and a (2×1)-O overlayer are formed [19]. At much higher concentrations of oxygen, for example, more than 1 000 L at room temperature, the Ru (0001) surface stabilizes two additional phases of chemisorbed oxygen, namely, (2×2)-3O and (1×1)-O [20]. However, Ru (0001) is oxidized by an autocatalytic process, because of formation of oxide nuclei on the Ru(0001)-(1×1)O surface [17]. The autocatalytic reaction indicates that the surface produces its own ‘catalyst’, thus readily dissociating the oxygen molecules and resulting in self-acceleration of the oxidation process [21]. This complexity is characteristic of oxygen chemistry on many transition metal surfaces, as shown in Fig. 3. The oxidation of Ru occurs only under specific conditions and requires a minimum threshold temperature. Goodman *et al.* [22] discovered that formation of RuO₂ on Ru (0001) required, at a minimum, an O₂/CO pressure ratio of 18/10, a temperature of 360 °C, and a reaction time of 700 s. To generate RuO₂, the oxygen must cover a volume of 4 ML and must have at least two layers of the tri-layer structure [23].

2.3. Theoretical research

Relatively simple reaction structures are usually chosen to represent the atomic-scale structure of the catalyst for study. CO oxidation is one of the most extensively studied reactions because it is relatively simple and includes all basic steps of a heterogeneous process, that is, adsorption, diffusion, dissociation, reaction and desorption [24]. In addition, it is also the most important part of the PROX reaction.

Ru has long been known as an exception in the Pt group metals, in terms of its behavior towards the oxidation of CO. Under UHV conditions, Ru is an extremely poor catalyst for oxidation of CO [25], yet its activity becomes greater than that of the other Pt group metals under high pressure and oxidizing conditions [26–28]. The reaction proceeds through the Langmuir-Hinshelwood (L-H) mechanism which requires the chemisorption of reactants before their recombination [28]. Stampfl

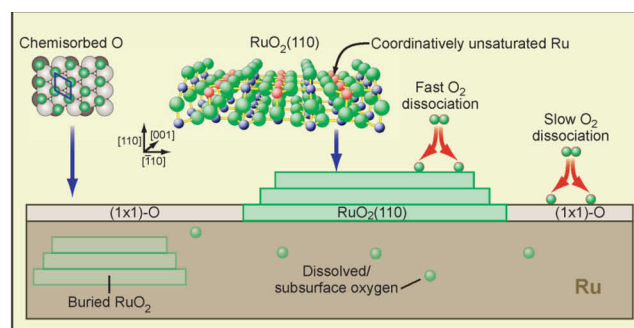


Fig. 3. The rich oxygen chemistry of ruthenium (0001). Reproduced with permission from Ref. [17]. Copyright 2002, the American Association for the Advancement of Science.

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