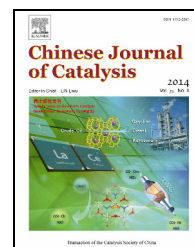


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Review (Special Issue on Rare Earth Catalysis)

Current status and perspectives of rare earth catalytic materials and catalysis

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ABSTRACT

Rare earth elements possess $4f$ orbitals without full electron occupancy and lanthanide contraction. This characteristic results in their unique catalytic performance when they are used as active components or as catalyst supports. Research into and the development of rare earth catalytic materials will significantly promote the high-efficiency utilization of abundant rare earth elements, such as lanthanum and cerium. Currently, rare earth catalytic materials play an important role in such areas as the petroleum chemical industry, the catalytic combustion of fossil fuels, automotive emissions control, the purification of industrial waste air, and solid solution fuel cells. In this paper, we review the application of and recent research progress that has been made on rare earth catalytic materials, including relative theoretical research. The effects of rare earth elements on the structure, activity, and stability of the catalysts of interest are described.

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1. Introduction

Rare earth (RE) elements contain the lanthanide elements with atomic number from 57 to 71, and scandium and yttrium, which have similar electronic structures and chemical properties to lanthanide elements. Rare earth elements possess $4f$ orbitals without full electron occupancy and lanthanide contraction. This characteristic results in their unique chemical properties when they are used as catalysts or catalytic components. This is especially evident for cerium (Ce) and lanthanum (La). Since the middle of the 1960s, the catalytic performance of RE catalytic materials has been studied widely in the world. Their applications in the chemical processing field include the petroleum chemical industry, the catalytic combustion of fossil fuels, automotive emissions control, the purification of industrial waste air, olefin polymerization, and fuel cells (solid oxide fuel cells). Based on their material composition, RE catalytic materials can be divided into the RE composite oxides, RE-noble metal catalysts, RE-zeolite catalysts, and so on. The presence of RE materials in catalysts can improve their ability to store oxygen, the lattice oxygen reactivity of the materials, and the dispersion of active metals on the supports; reduce the noble metal dosage; and enhance their thermal stability. This leads to a significant improvement in catalyst performance.

The applications and recent progress made with RE catalytic materials or in RE catalysis in several important processes related to energy production and utilization, and in environmental protection have been reviewed in this paper. Relative theoretical research and challenges in the development of novel RE catalytic materials have also been discussed.

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2. Catalysts for the petroleum chemical industries

Fluid catalytic cracking (FCC) is an important procedure in petroleum refining, in which zeolite catalysts have been used widely because of their high surface area, highly ordered pore structure, high acid density, shape selectivity, and so on. As early as the 1960s, RE-exchanged Y zeolites were used as cracking catalysts instead of amorphous silica-alumina catalyst, thereby increasing the gasoline yield by more than 10%. This has been termed the revolution of the oil refining industry.

The introduction of RE materials into zeolites can be used to adjust the amount and intensity distribution of the acid sites. The amount and method of RE³⁺ introduction influences the zeolite acid properties significantly and results in different zeolite-based FCC catalyst activities [1,2]. The high Brønsted acidity of RE-Y is related to its high RE content owing to the hydrolysis reaction, RE³⁺ + H₂O ↔ [REOH]²⁺ + H⁺, that occurs in the zeolitic cavities. For example, there is ~17% RE₂O₃ in RE-Y vs. 6%–7% RE₂O₃ in RE-ultrastable Y (RE-USY) and none in USY (RE = Ce or La), and the RE-Y catalyst exhibits a higher FCC activity [3,4].

FCC catalysts are generally used at high temperatures and in hydrothermal environments in the petroleum industry. These conditions usually induce a decline in the crystal degree, a deterioration of the aluminum leaching framework and even a collapse in the zeolite structure, which results in a deactivation of zeolite-based FCC catalysts. The introduction of RE materials into the zeolite results in a retention of the aluminum framework and an improved zeolite structure stability [5–8]. As shown in Fig. 1, La³⁺ has replaced Na⁺ or H⁺ in the Y zeolite and is situated inside the β cage [8]. As a result, it stabilizes the Y zeolite framework and improves the hydrothermal stability.

To produce lead-free gasoline, RE-Y cracking catalysts with high RE content have transited to RE-exchanged ultrastable Y with low RE content. As a result, the olefin content in the FCC gasoline is high (~40%–45%, and up to 65%), which does not conform to current global requirements for the development of clean fuel. In contrast, compared with Y zeolite, ZSM-5 zeolite has a small pore size and can cause the olefin in the gasoline to crack selectively to C₃ and C₄ olefins. This increases the propylene content in FCC gasoline, and is accompanied by a decrease in olefin content [9]. For the RE-exchanged Y zeolite, the

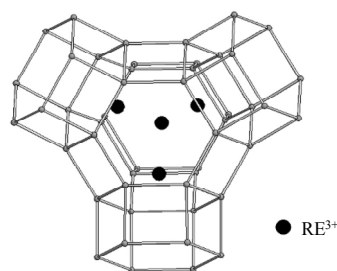


Fig. 1. Distribution of RE³⁺ inside β cage of RE-Y zeolite [8].

introduction of RE material into ZSM-5 zeolites can also effectively adjust the amount and intensity distribution of acid sites to reduce the olefin content in FCC gasoline [10–12]. For example, the ZSM-5 zeolite modified with La possessed more strong acid sites compared with ZSM-5 zeolite. Olefin conversion and propylene selectivity increased in the cracking reaction of FCC gasoline for the La-modified ZSM-5 zeolite, and resulted in an olefin conversion of 74.3%, an olefin mass fraction of 18.2% in cracking gasoline, and a propylene selectivity of 45.9% at 550 °C, at atmospheric pressure and with steam [13]. Similarly, in the post-treatment of naphtha using monolithic catalysts with zeolite washcoat, the introduction of RE material into ZSM-5 zeolite by ion-exchange or precipitation could promote the conversion of olefin in naphtha and also increase propylene selectivity. The gaseous products consisted mainly of up to 60% propylene and C₄ olefin and the propylene yield was ~31%, while the olefin content in naphtha could be reduced to 15% [14].

In addition to their irreplaceable role in zeolite-based FCC catalysts, RE elements are also important co-catalysts, and play an important role in ethanol catalytic dehydration to ethylene [15], lactic acid dehydration to acrylic acid [16], the direct transformation of *n*-butane to iso-butene [17], double bond position isomerization [18] and the acylation of toluene [19]. RE materials can also be used as the main active component in many catalysts. For example, Ce/AlPO-5 showed high catalytic performance in the oxidation of cyclohexane without solvent. As shown in Table 1, at 0.5 MPa O₂ and 140 °C for 4 h, the conversion of cyclohexane was 13.5%, and the total selectivity of cyclohexanol and cyclohexanone was above 92%. However, trace amount of oxidative products were detected over the

Table 1

Catalytic performance of Ce/AlPO-5 for cyclohexane oxidation [20].

Catalyst	Time (h)	Atmosphere (MPa)	Conversion (%)	Selectivity (%)	
				Cyclohexanol	Cyclohexanone
AlPO-5	4	N ₂ /0.5	—	—	—
Ca(A)/AlPO-5	4	N ₂ /0.5	—	—	—
Ca(A)/AlPO-5	4	O ₂ /0.5	13.5	42	50
Ca(A)/AlPO-5 ^a	4	O ₂ /0.5	13.0	40	51
Ca(B)/AlPO-5	4	O ₂ /0.5	12.0	35	58
Ca(C)/AlPO-5	4	O ₂ /0.5	11.5	30	60
Mn/AlPO-5 ⁴²	24	Air/1.0	6.0	19	43
Mn/AlPO-5 ^{42b}	24	Air/1.0	16.5	20	43
CeO ₂	4	O ₂ /0.5	7.0	30	52

Reaction conditions: 18.5 mmol cyclohexane, 10 mg catalyst, at 140 °C.

^a After using repeatedly 4 times.

^b Small amounts (3 wt% cyclohexane) of hydroquinone (free-radical scavenger) added.

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