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Ce–K-promoted Co–Mo/Al₂O₃ catalysts for the water gas shift reaction

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ABSTRACT

The effect of doping traditional Co–Mo/Al₂O₃ catalysts with Ce and K on their catalytic activity for the water gas shift reaction in coke oven gas was investigated. Doped Co–Mo/Al₂O₃ catalysts were prepared by adding different amounts of Ce and K (CeO₂, K₂O, and CeO₂–K₂O ~10 wt%) by a wetness impregnation method and characterized by BET specific surface area measurements and scanning electron microscopy (SEM). The characterization results reveal that CeO₂ addition mainly produced an electronic effect and aided to disperse the active ingredient. At the same time, the synergistic effect between Ce and K contributed to the catalytic activity. Activity tests showed that Ce–K-promoted Co–Mo/Al₂O₃ catalysts exhibited greater activity and selectivity than Co–Mo–Ce/Al₂O₃ catalysts and Co–Mo–K/Al₂O₃ catalysts. The maximum promotion of the water gas shift reaction was observed when 3.0 wt% CeO₂ and 6.0 wt% K₂O were added.

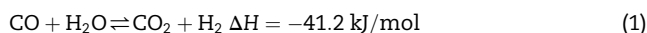
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1. Introduction

“Dual gas resources” polygeneration systems (or IGCC systems) based on CH₄ reforming with CO₂ are important for clean coal technology based on gasification gas and coke oven gas (COG) as feed stocks for the production of syngas [1,2]. In reforming processes, the large quantity of H₂ in coke oven gas is heated from ambient temperature to above 950 °C, consuming substantial amounts of energy [3]. Additionally, a substantial amount of H₂ is wasted because of hydrogen oxidation [4]. If CH₄-rich gas could be separated from COG and then reformed with CO₂ in the gasification gas, the global efficiency of the reforming process would be improved, and the H₂ consumption would be reduced. The separation of CH₄-rich gas from coke oven gas is challenging because of the complexity of the components of COG [5]. Through the water gas shift (WGS) reaction of COG, both H₂ and CH₄ can be easily

separated from the mixture, and the yield of H₂ can be increased.

Carbon control in IGCC systems has gained increasing awareness, and emphasis is now on the optimization of the water gas shift (WGS) reaction. The WGS reaction converts CO into CO₂, consuming one mole of steam and producing one mole of hydrogen in the process:



When the temperature is increased, the equilibrium conversion level is decreased because the WGS reaction is exothermic. To retain a high conversion at a low temperature, a catalyst must be used.

The WGS reaction has a long history as an important industrial catalytic process for coal-based ammonia synthesis and hydrogen production. The WGS reaction is used to increase the H₂ content and reduce the CO content of

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synthesis gas by steam reforming [6,7]. Industrially, the WGS reaction is performed in two steps with two classes of catalysts: a high-temperature shift over an iron oxide-promoted ($\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$) catalyst, and a low-temperature shift over a copper oxide-promoted (CuO--ZnO) catalyst [8,9]. Although these catalysts can be used with coal-based syngas, there are still some barriers for CO conversion in COG that contains a high concentration of tar and multiple forms of sulfur (e.g., hydrogen sulfide, carbonyl sulfide and thiophene). Because these types of catalysts are sensitive to sulfur, Co–Mo catalysts that are sulfur-tolerant are preferred because they are more active and can be used in a wider temperature range without sulfur poisoning [10]. Because of the low catalytic activity of conventional Co(Ni)–Mo hydrotreating catalysts, there have been several attempts to improve the catalytic performance of these catalysts [11,12]

Metals such as Pt, Pd, Rh, Ru and Au added to a Co–Mo support result in high WGS activities over a wide temperature range [13,14]. Of these metals, Pt and Au are the most promising promoters of the WGS reaction because of their better catalytic activity at a low temperature; however, they are rare and expensive. Many new types of catalysts containing metals that are less expensive and more abundant are being developed. Numerous studies have shown that a combination of two metals can provide good WGS reaction activities. Many bimetallic systems have been studied for numerous reactions, and bimetallic systems have been shown to increase the rates of WGS reactions [15–20]. Among the second metals that have been used to form bimetallic catalysts, ceria-based mixed oxides have been actively studied as the best candidate so far. One potential method to enhance the catalytic activity of CeO_2 as a WGS catalyst is to use multiple metals in combination with Ce rather than using Ce alone.

Ceria is a crucial component of three-way, automotive and emission-control catalysts, partly because it augments the activity of precious metal catalysts for the water gas shift (WGS) reaction. Although the use of this metal has been known for many years, the need for active WGS catalysts for nontraditional applications, including fuel processing for fuel cells, has renewed the interest in examining ceria-supported metals. Ceria-based catalysts may be good candidates for improved water gas shift activities because of their strong interactions with the active metal and because of the facile transition between Ce^{3+} and Ce^{4+} [21–26]. In addition, CeO_2 has a high oxygen-storage capacity (OSC) because of its oxygen vacancy that is closely linked to its water gas shift activity [27–31]. Recently, many scientists have paid considerable attention to ceria loaded with precious metals (Pt, Pd, Au and Rh) [32–34]. However, because of the high cost and instability of these precious metals, more attention has been focused on cheap alkali metals and transition metals, including potassium [35–38].

Alkali metal additives promote the WGS activity of molybdenum-based catalysts. Potassium is one of the best promoters for Co–Mo/ Al_2O_3 WGS catalysts, and K_2CO_3 appears to be the most suitable potassium source for catalyst preparation [39]. Industrially, Al_2O_3 -supported K–Mo catalysts promoted by Co or Ni are widely used as sulfur-tolerant WGS catalysts that also tolerate small amounts of O_2 , HCN and C_6H_6 in the feedstock [40]. V. Kettmann et al. [41] reported that the

addition of K_2CO_3 to a commercial Co–Mo/ Al_2O_3 hydrodesulfurization (HDS) catalyst leads to a catalyst with WGS activity that maintains some HDS activity. Krupay and Amenomiya [16] reported that potassium on alumina weakens the bond between the oxygen and the surface. Kantschewa and Kordulis reported that all alkali cations except Li^+ inhibit the reduction of Mo(VI) to Mo(V) and induce the transition from octahedral to tetrahedral coordination symmetry of Mo(VI) at 673 K [39,42]. However, the weak binding of the alkali metal promoter of industrial catalysts adversely affects the catalyst stability. At higher operation temperatures, potassium loss occurs more readily [39–42]. Therefore, the development of a potassium-stabilizing component for potassium-containing catalysts can solve this practical problem.

The WGS reaction over Co–Mo catalysts has been extensively studied. However, few studies have been conducted with $\text{CeO}_2\text{--K}_2\text{O}$ -modified Co–Mo catalysts. Our initial investigation found that the $\text{CeO}_2\text{--K}_2\text{O}$ increased the WGS reaction rate after it had been doped on Co–Mo/ Al_2O_3 . In this paper, we report on the enhancement of WGS reaction rates when Ce–K is doped on Co–Mo/ Al_2O_3 catalysts. These catalysts were prepared by the incipient-wetness impregnation method and characterized by the BET specific surface area and scanning electron microscopy (SEM).

2. Experimental

2.1. Catalyst preparation

The Co–Mo–K/ $\gamma\text{-Al}_2\text{O}_3$, Co–Mo–Ce/ $\gamma\text{-Al}_2\text{O}_3$ and Co–Mo–Ce–K/ $\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared by successive aqueous incipient-wetness impregnations. The $\gamma\text{-Al}_2\text{O}_3$ support (particle size 3.0–4.0 mm) was treated by heating in air at 450 °C for 2 h prior to impregnation to eliminate surface impurities. For sequential impregnation, the molybdenum salt ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) and potassium salt (K_2CO_3) were introduced first. The impregnated support was then dried at 120 °C for 2 h and calcined at 450 °C for 2 h. Finally, the sample was impregnated with a cobalt salt ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$). The tree series of catalysts were denoted Co–Mo– $\text{Ce}_m\text{--K}_n$, Co–Mo– Ce_m and Co–Mo– K_n , where m and n represent the mass ratio of the promoter/the catalyst. All obtained catalysts contained 3.0 wt% of CoO and 10.0 wt% of MoO_3 .

2.2. Catalytic activity measurements

The WGS experiments were conducted in a fixed-bed reactor with 15.0 ml of catalyst. The apparatus consisted of a fixed-bed stainless steel reactor (1.6 cm inner diameter) inside an electric furnace. The temperatures at the top and the bottom of the catalyst bed were monitored, and the difference between the two temperatures was less than 2 °C for catalyst beds at a GHSV of 2000 h^{-1} . The GHSV was calculated based on the volume of the catalyst alone.

Before the activity tests, the samples were sulfidated in situ at 300 °C for 4 h with a mixture of $\text{CO}/\text{H}_2/\text{H}_2\text{S}$ (45.0/50.0/5.0, v/v/v) and then cooled to 200 °C within the same gas flow. The feed gas consisted of 9.7% CO, 30.0% CH_4 , 60.0% H_2 , and 0.3% H_2S (a typical composition of COG). The catalytic reaction was

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