



Effect of flash calcined alumina support and potassium doping on the activity of Co–Mo catalysts in sour gas shift process

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ABSTRACT

Potassium promoted Co–Mo catalysts supported on flash-calcined alumina for sour WGS process have been prepared. The oxide form of samples has been characterized by ICP-OES method, N₂ adsorption, temperature-programmed reduction (TPR) and the sulfides form after the catalytic activity test by means of XPS. Catalytic activity measurements were carried out in gradientless reactor in a kinetic region at low partial pressure of reagents.

A strong effect of the promoter addition sequence to the support has been observed. The highest activity in the WGS process was determined for the potassium promoted Co–Mo/Al₂O₃ catalyst with a K/Mo ratio of 0.06 obtained by a simultaneous impregnation of flash-calcined alumina with aqueous solution of K and Mo salts. Potassium addition significantly changes reducibility and decreases total surface area of catalysts. XPS results show that the catalyst activity is correlated with the surface concentration of Mo⁵⁺ and Co–Mo–S species. Potassium addition enhances the formation of such species. The method of potassium incorporation to the catalyst has been suggested and its optimal content has been determined. The catalyst obtained can be implemented in industrial processes of hydrogen and syngas production from feedstocks with high sulfur content.

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1. Introduction

Raw synthesis gases (syngases) prepared by coal gasification are valuable intermediates, which, after appropriate processing, can be applied in methanol, dimethyl ether and liquid hydrocarbons syntheses [1–4]. However, coal and its gasification products contain relatively high amounts of sulfur compounds and other substances, which are very strong poisons to typical metallic catalysts (especially based on copper, nickel and iron) used in the syngases processing. The presence of sulfur-rich components rules out the application of standard catalysts used in the conversion of other raw materials containing a lower content of sulfur compounds, e.g. natural gas [3,5,6]. Therefore, new sulfur-resistant catalysts for the conversion of coal gasification products are still developed.

The water gas shift reaction (WGS),



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is one of the processes requires more resistant catalysts [7,8]. In this case, the replacement of standard WGS catalysts (e.g. Fe–Cr–Cu and Cu–Zn–Al) with modern sulfur-resistant ones can result in elimination of an initial desulfurization stage, a decrease of steam requirements and higher degrees of conversion by much lower steam/gas ratios than in the classical solutions. The application of sulfur-resistant catalysts can considerably simplify a technological scheme of coal-based syngas production by the removal of acid gases (H₂S and CO₂) in one step by means of absorption methods, e.g. Rectisol [9,10]. In Fig. 1 two solutions for syngas or hydrogen manufacturing from coal, where WGS is a key stage, are compared. Path A illustrates the classical two-stage WGS process, whereas path B involves multistage sour gas shift performed on sulfur-resistant catalysts.

The most effective catalysts for WGS of sulfur-contaminated feedstocks are molybdenum sulfide catalysts doped with cobalt or nickel, supported on alumina [8,11] or magnesia–alumina [11–13]. The formula of the proposed Mo-containing catalysts is similar to that for the catalysts used in hydrodesulfurization (HDS) processes [14–17] or in mixed alcohol synthesis (MAS) [18,19].

The Co–Mo oxysulfides are considered as an active phase of sour gas shift catalysts. According to Chen et al. [20] the promoting effect of cobalt is attributed to the easier formation of active