

The study on alkali-promoted Co-Mo/Al₂O₃ catalysts for water–gas shift process*

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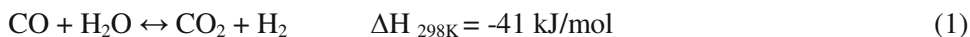
The following contribution presents the results of studies on the effects of alkali metals on the physicochemical properties and the effectiveness of a Co-Mo/Al₂O₃ catalyst for the water gas shift reaction. It has been shown that the addition of alkali metals modifies the properties of Co-Mo catalysts, resulting in a significant increase in activity of catalysts in water gas shift reaction. The greatest effect was observed in the case of sodium-promoted reaction.

1. INTRODUCTION

Shrinkage of natural gas and petroleum resources, their increasing acquisition costs paired with the tendency to reduce the CO₂ emission are the main driving factors for an increasing interest in coal and its thermal treatment processes [1-2]. The contemporary, so-called „Clean Coal Technology” allows a significant reduction of negative environmental impact of processes associated with coal use [3]. Particularly intensive development takes place in the area of coal gasification technology and synthesis gas production processes, which are valuable in syntheses of many important products.

*This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

One of the key stages of processing of coal gasification products is the catalytic water gas shift process, aiming at enrichment of synthesis gases in hydrogen with the simultaneous reduction of carbon dioxide concentration as shown in Scheme 1:



The water gas shift process in synthesis gases produced from natural gas is usually conducted in two stages in an adiabatic reactor on an Fe-Cr-Cu catalyst (high-temperature stage) and a Cu-Zn-Al catalyst (low-temperature stage) [3]. These catalysts are sensitive to sulfur compounds that makes it hardly possible to apply them to the processing of gasification products (containing relatively high concentrations of sulfur compounds). Another problem impeding the use of conventional catalysts is the possibility of formation of carbon deposits on the Fe-Cr-Cu catalyst. In order to eliminate this risk, more expensive enrichment of synthesis gases in water steam, i.e. the performance with a higher steam/gas ratio is necessary [4].

These problems can be solved by the use of molybdenum sulfide catalysts resistant to sulfur compounds (sour shift catalysts) of sufficient activity in a wide temperature range (220–500°C). Using this type of catalysts eliminates the technological problems associated with the presence of sulfur compounds in the synthesis gases. Their presence is even desirable to maintain the catalyst in an active form [5]. The Co-Mo contact also catalyzes the hydrolysis reactions of COS to H₂S and CO₂, and also HCN to NH₃ [6].

The use of such catalysts leads to the improved process economics by:

- reducing excess water steam – better heat performance,
- ability to remove H₂S and CO₂ in one operation,
- simplification of the technological scheme and reducing investment costs.

The Co-Mo catalysts are a subject of many studies and the results show that one way to improve their catalytic activity is doping with alkali metals [7].

This paper presents the results of investigations on the influence of a type of an alkali metal on the basic physicochemical and kinetic properties of Co-Mo/Al₂O₃ catalysts. Catalysts have been investigated by physicochemical methods such as BET and TPR (the temperature-programmed reduction profile), as well as evaluated with respect to their kinetic properties at low pressure of reactants.

2. MATERIAL AND METHODS

Carrier. As a starting material for the preparation of all catalysts an aluminum carrier was used (INS, Al₂O₃, 220 m²/g, Na<120ppm) [8].

Catalysts. A standard catalyst consisting of 16% wt of MoO₃ and 4% wt of CoO and the catalysts (16% wt MoO₃, 4% CoO) promoted by alkali metals (Na, Li, K, Cs) on the aluminum carrier were utilized. The molar ratio of alkali metal to molybdenum was 0.1. Catalysts were obtained by dry impregnation with solutions of ammonium molybdate or ammonium molybdate with the addition of an alkali metal (in the form of nitrates: Na, Li, K or carbonates: Cs) and cobalt nitrate. After each impregnation operation the catalysts were dried and calcined for 4 hours at 500°C. When selecting the method and parameters of preparation of catalysts for water gas shift earlier findings on the catalytic type Co-Mo were used [9]. Before further tests, samples of all catalysts obtained were crushed to fractions of 0.1–0.16 mm.

Methods of work. *The total surface.* The size of the total area of the samples was determined from the N₂ adsorption isotherms at liquid nitrogen temperature, using a SORPTOMATIC camera (FISSONS, Italy).

TPR- The temperature-programmed reduction profile. The reduction of catalyst precursors was studied by the temperature-programmed reduction profile method in a Zielinski's non-gradient reactor [10], in a glass apparatus of own construction [11]. A sample of a catalyst of approximately 100 mg was reduced with a mixture containing about 5% H₂/Ar, at a flow rate of 400ml/min, and the temperature gradient 8°C/min. Water steam, which is the product of the reduction of catalysts was frozen in the temperature of dry ice, and changes in the H₂ concentration were measured by a TCD detector.

Measurements of activity of catalysts for water gas shift at low concentrations of reactants. Catalytic activity measurements were carried out in a non-gradient reactor in the kinetic area at atmospheric pressure at low concentrations of reactants. The speed of the process was measured according to the previously developed methods and apparatus described in this article [12].

3. RESULTS AND DISCUSSION

The surface area of the catalysts under study is presented in Table 1.

Tab. 1. BET surface areas of Co-Mo catalysts.

Catalyst	Co-Mo	(Na)Co-Mo	(Li)Co-Mo	(K)Co-Mo	(Cs)Co-Mo
BET (m ² /g)	180	142	176	156	118

In the case of alkali metal-promoted catalysts a smaller total area in comparison with the Co-Mo reference catalyst could be observed. It seems that a degree of surface development also depends on the type of alkali metal added. In case of Li, there was the smallest (about 3%) decrease in the surface area. The largest decrease by about 35% was observed for the Cs doped catalyst.

Figure 1 illustrates a comparison of the reduction of the Co-Mo catalyst with and without doping with various alkali metals (Na, Li, K, Cs).

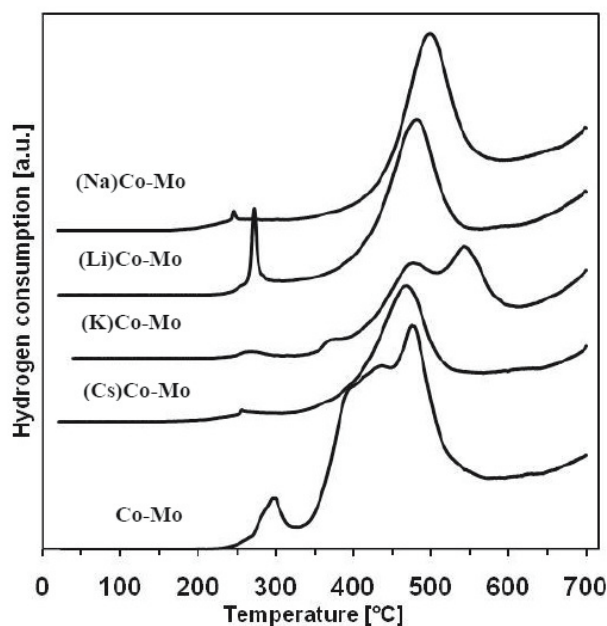


Fig. 1. Plots of temperature-programmed reduction of Co-Mo/Al₂O₃ and Co-Mo promoted catalysts.

The temperature-programmed reduction profile (TPR) of the standard Co-Mo catalyst shows that the reduction starts at about 240°C and occurs in several stages:

- Low-temperature phase (240–320°C),
- Middle-temperature phase (320–550°C),
- High-temperature phase (>550°C).

Low-temperature band with a maximum of 300°C is of relatively low intensity. The dominant phase of the reduction occurs in the range of 350–550°C, as evidenced by the intensive and broad band in the TPR profile. Here one can specify two reducible oxide forms, whose peaks are superposed. The high-temperature reduction phase starts over 550°C, however it was terminated due to technical limitations. The temperature-programmed reduction profiles (TPR) of the Co-Mo catalysts promoted by the lithium metals indicate, that these catalysts are less reducible in comparison with the conventional Co-Mo system. For all the samples tested the presence of several stages of reduction, shifted towards higher temperatures compared to the standard catalyst was observed, which indicates a more complex oxide form of the catalyst precursor. Moreover, in the case of alkali-metal doped catalysts the consumption of hydrogen was lower by 30–50% compared to the reference sample. It may indicate that alkali metals strongly interact with the carrier and molybdenum phase, thereby altering the properties of the Co-Mo systems.

The comparison of activity of alkali-metal promoted Co-Mo catalysts in the water gas shift process is illustrated in Figure 2.

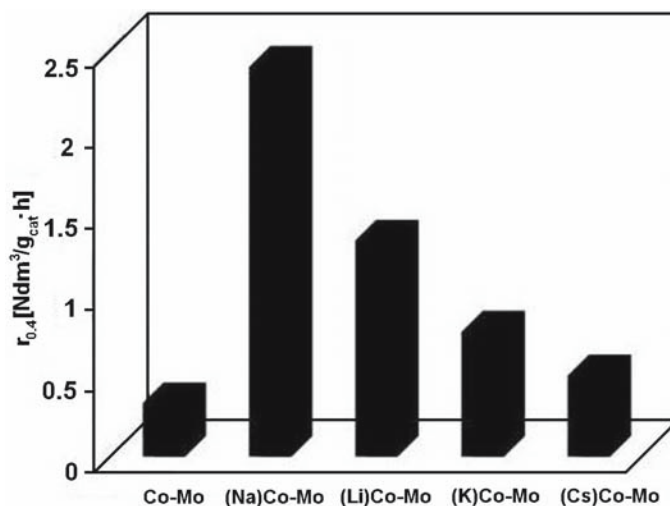


Fig. 2. Activity comparison of Co-Mo catalysts at 350°C.

The above data show that the efficiency of the alkali metal promotion strongly depends on the type of promoter. A very intensive effect – about 5-fold increase in activity – was observed in the case of sodium. A bit lower, but also relatively high catalytic activity growth was achieved for the catalysts doped with Li or K (respectively 3 or 2-fold). The addition of Cs only slightly increases the activity (an increase of approximately 25%). It follows therefore, that the positive effect of promoting the Co-Mo catalyst was achieved for addition of all the alkali metals. The activity of catalysts containing an optimum amount of promoter decreases in a series Na>Li>K>Cs.

Tab. 2. Hydrogen consumption during the reduction.

	Relative [-] hydrogen consumption during the reduction				
	Co-Mo	(Na)Co-Mo	(Li)Co-Mo	(K)Co-Mo	(Cs)Co-Mo
Up to ca. 600°C	428	221	201	167	156
up to ca. 700°C	330	305	305	225	229

Figure 3 shows a dependence of the speed of water gas shift on the surface of Co-Mo catalysts. The data indicate that the level of activity of various Co-Mo catalysts promoted by alkali metals does not correlate with the size of the total area.

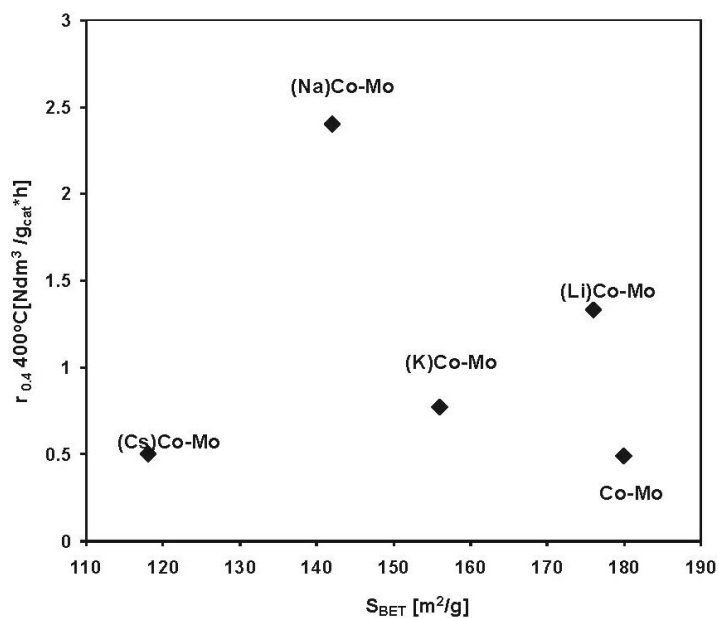


Fig. 3. BET surface area and activity of various Co-Mo catalysts.

4. CONCLUSIONS

The following conclusion can be drawn from our studies:

- addition of alkali metals to the Co-Mo catalysts changes the properties of Co-Mo catalysts,
- decrease in the total area of alkali-metal promoted systems was observed in comparison with the reference Co-Mo catalyst,
- reduction of the oxide precursor forms of the Co-Mo catalysts is a complex process with three distinguishable main stages,
- alkali metal addition decreases the reducibility of the Co-Mo/Al₂O₃ system,
- alkali metal addition significantly increases the activity of the Co-Mo/Al₂O₃ catalysts in water gas shift process,
- the greatest promoting effect was observed for sodium,
- level of activity of individual alkali-metal promoted Co-Mo catalysts does not correlate with the size of the total area.

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