

Water–gas shift activity of K-promoted (Ni)Mo/ γ -Al₂O₃ systems in sulfur-containing feed

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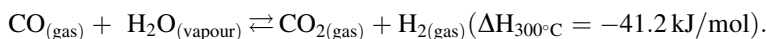
Abstract The effect of potassium additive on the catalytic activity of nickel–molybdenum alumina-supported systems has been studied by varying the molybdenum content within 5–18 mass% MoO₃, reaction temperature from 180 to 400 (500)°C, and steam to gas ratio of 0.3, 0.7, and 1. It has been established that potassium reduces the activity of one-component Mo-containing samples, while, independent of molybdenum loading, nickel promotes activity within the whole temperature range studied and extends the temperature range of catalytic activity by about 70°C to lower reaction temperatures. A symbatic or additive, or antibatic catalytic behavior was observed with NiMo-containing samples depending on the atomic Ni/Mo ratio and temperature range. Potassium, being a third component in tri-component KNiMo-containing samples, enhances the water–gas shift (WGS) activity depending on the atomic K/(Ni + Mo) ratio. The activity approaches the equilibrium conversion degree in the interval of 320–500 °C. A decrease in the specific surface area of calcined and tested samples relative to the bare support shows close values indicating that the overall dispersion of the species is not changed during the catalytic test. Close examination indicated that the sample containing K₂O, NiO, and MoO₃ of 4.9, 2.5, and 12.7 mass%, respectively, was found to be the most suitable catalyst for water–gas shift reaction with sulfur containing feed since it attains equilibrium conversion even at 300 °C, and at a low steam to gas ratio of 0.3 atm. This catalyst demonstrates a stable and reproducible catalytic activity as inlet gas loading is increased.

Keywords Water–gas shift reaction · CO conversion · Hydrogen production · Alkali additive · NiMo catalyst

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Introduction

The reaction of converting carbon monoxide by water vapor, well known for more than a century, is an important stage in the production of ammonia and methanol that ensures purification of the synthesis gas from carbon monoxide and provides additional quantities of hydrogen for further application [1–5]:



The water–gas shift (WGS) reaction as a process of hydrogen production has become increasingly important due to current interest in fuel cells [6, 7].

The use of fossil fuels such as coal and heavy oil as alternative carbon sources for production of synthesis gas is related to the problem of developing sulfur-resistant catalysts because the syngas generated during the gasification contains a considerable amount of sulfur that causes deactivation of conventional WGS catalysts. In the future, world energy demand will require renewable sources of hydrogen to reduce pollution. Biomass and carbon-based waste products are very promising sources of carbon to produce syngas; however, they also contain sulfur. Therefore, the need of improved sulfur-resistant WGS catalysts remains yet important for both cases of conventional and alternative fuel sources.

High-temperature (350–450 °C) iron-chromium WGS catalysts are known to lose their activity on increasing the sulfur content in the reaction mixture. Small quantities (50 ppm) have an insignificant effect, while at a higher sulfur content (>1000 ppm), the activity decreases nearly twofold, but it could be restored completely after removing the sulfur from the feed. Unlike the iron-chromium catalyst, a low-temperature (190–250 °C) commercial copper-zinc WGS catalyst is poisoned irreversibly by sulfur. It can operate only at about 0.1 ppm H₂S or even less in the reaction mixture [1].

In this connection, there has been a continuing interest in catalysts, which are active in the presence of sulfur compounds [8–10]. Sulfided Mo-based supported systems have been designed as sulfur-resistant WGS catalysts. A major part of the studies are related to the structure and activity of Co-Mo catalysts, both unpromoted [11–15] and promoted by alkaline metals [16–20]. To our knowledge, unpromoted Ni-Mo catalysts [21, 22] or that promoted by alkaline metals [23] are so far less investigated. This fact directed us to study systematically the state of (K)(Ni)Mo/ γ -Al₂O₃ catalysts as one-, bi- and tri-component samples [24–27].

Introduction of potassium and nickel was found to provoke different kinds of oxidic surface species on calcined precursors by varying the molybdenum content within the range of 1–4 atoms Mo/nm² support [28]. These oxidic species are presumed to generate different WGS activity.

The present work is aimed at further studying the effect of potassium on the catalytic activity of (Ni)Mo/ γ -Al₂O₃ systems in relation to molybdenum content, reaction temperature, and steam to gas ratio. The results will allow the selection of the most appropriate sample as a promising catalyst candidate for WGS reaction in the sulfur-containing feed.

Experimental

Sample preparation

One-component 5Mo, 10Mo, 14Mo, 18Mo, Ni, and K samples were synthesized by incipient wetness impregnation of γ -Al₂O₃ (BASF D10-10, particle size of 0.4–0.8 mm) with aqueous solutions of the corresponding salts. Then the samples were dried at 105 °C for 2 h and calcined in air at 450 °C for 2 h. The theoretical loading of the samples corresponds to 5.1, 9.7, 13.9, and 17.7 wt% MoO₃ (1, 2, 3, and 4 atoms Mo/nm² support), 3.0 wt% NiO (1.1 atoms Ni/nm² support), and 5.0 wt% K₂O (2.9 atoms K/nm² support).

Bi- and tri-component samples were prepared from calcined one-component molybdenum samples by consecutive loading of nickel or/and potassium. The samples are listed in Table 1. Details of the preparation procedures have been reported elsewhere [28].

Table 1 Composition and specific surface area of the calcined and tested samples

Sample	Content (mass%) ^a			SSA (m ² g ⁻¹)		SSA decrease (%)	
	MoO ₃	NiO	K ₂ O	SSAc ^b	SSAt ^c	calc.	test.
γ -Al ₂ O ₃				231	198		14.3
K			4.88	153	125	67.5	36.9
Ni		3.01		228	184	1.3	7.1
5Mo	5.03			208	133	10.0	32.9
10Mo	9.51			189	127	18.2	35.9
14Mo	13.70			181	123	21.7	37.9
18Mo	17.45			159	121	31.2	38.9
K5Mo	4.78		4.92	175	131	24.2	33.8
K10Mo	9.06		4.85	168	128	27.3	35.4
K14Mo	13.08		4.89	167	125	27.7	36.9
K18Mo	16.68		4.90	129	118	44.2	40.4
Ni5Mo	4.90	3.02		207	174	10.1	7.6
Ni10Mo	9.19	3.05		183	158	20.1	20.2
Ni14Mo	13.28	2.98		187	142	19.0	24.2
Ni18Mo	16.90	3.03		181	131	21.7	33.9
KNi5Mo	4.68	2.76	4.90	171	145	26.0	26.8
KNi10Mo	8.83	2.68	4.92	157	139	32.0	29.8
KNi14Mo	12.74	2.54	4.85	152	124	34.0	36.9
KNi18Mo	16.23	2.49	4.87	135	113	41.6	42.9

^a Content: measured by ICPES

^b SSAC: SSA values after calcination, reported in [28]

^c SSAT: SSA values after returning to the initial reaction conditions (400 °C, 4000 h⁻¹ and s/g = 0.3) at the end of the activity test

Catalytic activity

A quartz-glass continuous flow reactor was charged with 0.7 g ($\cong 1 \text{ cm}^3$) of catalyst with 0.4–0.8 mm particle sizes in the calcined state and the free space above it was filled up with quartz glass particles of 1.0–1.25-mm size for homogenization of the mixture. The amount of catalyst and the particle size were selected based on preliminary tests aimed at establishing conditions, where mass transfer effects are eliminated. The samples were presulfided in situ through simultaneous sulfidation and reduction by 6 vol.% H_2S in H_2 at 400 °C for 2 h at GHSV of 2000 h^{-1} . The reaction mixture, containing 8.1 vol.% CO in Ar (Messer MG Chimco Gas), was bubbled through the water saturator-evaporator. The catalytic activity tests were performed at atmospheric pressure by means of gaseous mixture of $\text{CO}/\text{H}_2\text{S}/\text{Ar} = 7.8/2/90.2$ vol.% in two modes:

- (i) Decreasing the reaction temperature in the range of 400(500)–180 °C at steam/gas ratio (s/g) 0.3 and GHSV = 4000 h^{-1} ;
- (ii) Varying the steam/gas ratio (s/g = 0.3, 0.7, 1) at 400 °C and GHSV = 4000 h^{-1} . The ratio was realized by increase of the temperature in the saturator-evaporator thus changing partial pressure of the saturated water vapors.

The steady-state activity was established gaining the constant conversion value at each reaction temperature and each steam/gas ratio achieved realized.

The deactivation of each sample under study was verified by going back to the initial reaction conditions (400 °C and 4000 h^{-1}) by the end of each catalytic test. The converted mixture was controlled continuously by an Infracal 2100 spectral gas-analyser recording online CO and CO_2 content as vol.% at the reactor outlet.

Characterization

Specific surface area measurements were carried out by the single point BET method through Micromeritics Instrument, FlowSorb 2300, based on N_2 adsorption from N_2/He mixture (30/70) at the boiling temperature of liquid nitrogen –196 °C.

Component content in the samples was determined by inductively coupled plasma emission spectrometry (ICP-ES) through model JY38 Jobin–Yvon analyzer by dissolving the samples in dilute mineral acids.

Mass-gas analysis of the outlet gas mixture was performed on a MS-10 spectrometer with precision of 1×10^{-4} vol.%.

A Pay Unicam SP 1950 spectrometer was used in regime of emission for determination of the potassium content in condensed water after the reactor.

Results and discussion

Specific surface area (SSA)

Table 1 lists SSA values of the samples after calcination (SSAc) and after going back to the initial reaction conditions (400 °C, 4000 h^{-1} and s/g = 0.3) by the end

of the activity test (SSAt). In general, the table shows that the surface area values for the bare support and for all the studied samples after the test are smaller than that for the samples after calcination. In addition, the SSA of the bare support and the studied samples is decreased on increasing the Mo loading after calcination and after test. Careful inspection indicates that the bare support exposes a lower surface area, by 14%, after test. On the contrary, deposition of potassium alone (K sample) provokes the most significant decrease in SSAC of the bare support (68%), while the deposition of nickel (Ni sample) reduces moderately the area by 14%. This peculiarity is also preserved in the bi-component NiMo samples, both in the calcined and tested state. Under reaction conditions, the surface area is most strongly modified (33–39%) in the case of Mo samples. The values are close to those of the K sample, of all the KMo samples, and of the KNiMo samples with higher Mo content (KNi14Mo and KNi18Mo). It should also be noted that in the samples with highest Mo loading (18Mo, K18Mo) and in the tricomponent KNiMo set, the decrease in SSAC and SSAt relative to the bare support shows close values. It means that the overall dispersion has not been changed despite the fact that the precursor oxidic species are transformed in sulfidic, oxysulfidic, and sulfate species as well as that polysulfides and paramagnetic sulfur appear on the surface in the reaction redox environment (CO, H₂O, H₂S, H₂, and CO₂ agents), as it has been stated in Ref. [27].

All these results reflect the complex effects of molybdenum content and addition of potassium, which are more pronounced than that of addition of nickel, on sample texture both in the calcined and tested states

Effect of reaction temperature on WGS activity

Initially, the catalytic activity of the one-component samples (Ni, 5Mo, 10Mo, 14Mo, and 18Mo) has been followed by lowering the reaction temperature down to 10% conversion (Fig. 1). It is evident that the one-component samples do not attain equilibrium conversion values. The highest activity was registered at 400 °C with the 18Mo and Ni samples (85%) and 14Mo (78%). The activity of all the samples decreases on lowering the temperature down to 8–15% CO conversion at 250 °C. The samples of low Mo content (5Mo and 10Mo) manifest similar low activities within the whole temperature range. The catalytic activity of the samples of higher Mo content (14Mo and 18Mo) is greater and comparable at all reaction temperatures. The Ni sample, in spite of low nickel amount, practically completely repeats the pattern of CO conversion over the 14Mo and 18Mo samples. It should be noted that the bare γ -Al₂O₃ support and the K sample demonstrate measurable activity at a temperature higher than 450 °C. The support reaches CO conversion of 5% at 500 °C while the one-component K sample attains 24% (Fig. 2).

Introduction of potassium as a second component decreases the activity of all bi-component KMo samples (atomic ratio K/Mo = 0.9–3.1) compared to corresponding one-component Mo samples, which is more pronounced at higher temperatures and higher atomic K/Mo ratios (Fig. 1). Evidently, potassium addition in the range of K/Mo = 0.9–3.1 does not cause any promoting effect on the activity of the Mo/ γ -Al₂O₃ system.

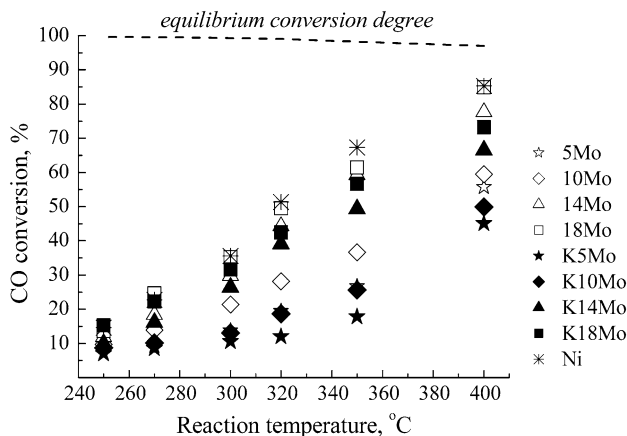


Fig. 1 Catalytic activity of one-component Ni- and Mo- and bi-component KMo samples at various reaction temperatures, $s/g = 0.3$, $GHSV = 4000 \text{ h}^{-1}$

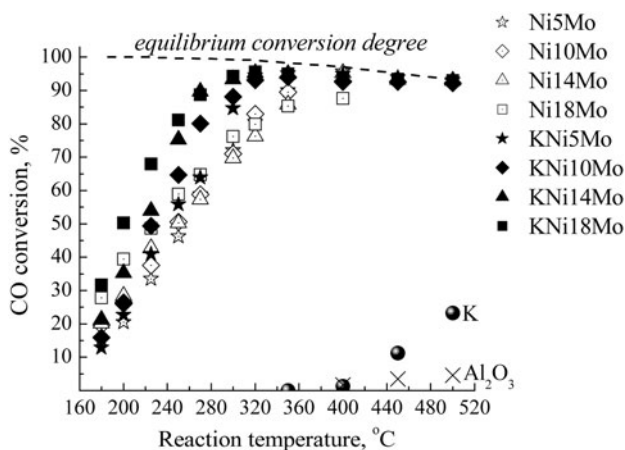


Fig. 2 Catalytic activity of bi-component NiMo- and tri-component KNiMo samples at various reaction temperatures; $s/g = 0.3$; $GHSV = 4000 \text{ h}^{-1}$

In contrast to potassium addition, nickel deposition on the Mo samples leads to an increase in the conversion values close to the equilibrium one at 400 °C whereas the NiMo samples manifest some activity (16–28%) even at 180 °C (Fig. 2). The unexpectedness of this result is that the increase in activity and its extension to lower reaction temperatures is practically the same one independent of molybdenum content in the range of the Ni/Mo ratio of 0.3–1.1.

The close values of conversion of the one-component Ni, 14Mo, and 18Mo samples (Fig. 1) bring about an interest to define the character of catalytic behavior of the nickel additive to molybdenum in the bi-component NiMo systems. Estimation was done based on the ratio (R) of the activity (CO conversion degree)

of the bi-component samples to the sum of the activities (CO conversion degree) of the corresponding one-component samples, i.e.

$$R = \frac{\text{Activity}_{\text{M1M2}}}{\text{Activity}_{\text{M1}} + \text{Activity}_{\text{M2}}}$$

A sybatic effect between the components will be present if the ratio is higher than unity. The behavior will have an additive character if R is equal to one and it will be antibatic if R is lower than unity. Evaluation according to this formula reveals the complex nature of the effect of Ni addition to Mo samples regarding reaction temperature (Fig. 3). It is sybatic in the 250–300 °C temperature range ($R = 2.12$ – 1.14) and additive in the 300–330 °C interval ($R = 0.95$ – 1.04), while it becomes antibatic within 330–350 °C ($R = 0.77$ – 0.92) with deviation of $\pm 6\%$ of CO conversion degree. It should be noted that the sums of activities of the one-component samples exceed the equilibrium conversion values of the temperatures of the latter range.

The catalytic activity of the tri-component KNiMo system was studied on extending the temperature range up to 500 °C in order to consider also the activity of the bare support and the one-component K sample. Depending on the K/Ni + Mo atomic ratio, introduction of potassium to the NiMo samples as a third component enables approaching the equilibrium conversion (Fig. 2). The decrease in activity starts at 300 °C for KNi5Mo ($\text{K/Ni} + \text{Mo} = 1.5$) and KNi10Mo ($\text{K/Ni} + \text{Mo} = 1.1$) and at 270 °C with KNi14Mo ($\text{K/Ni} + \text{Mo} = 0.8$) and the KNi18Mo sample ($\text{K/Ni} + \text{Mo} = 0.7$). Lowering the temperature down to 200–180 °C causes the tri-component KNiMo and bi-component NiMo samples to exhibit comparable activities. Evidently, the promoting action of potassium is manifested in the 250–320 °C range. No contribution of support and K alone was observed.

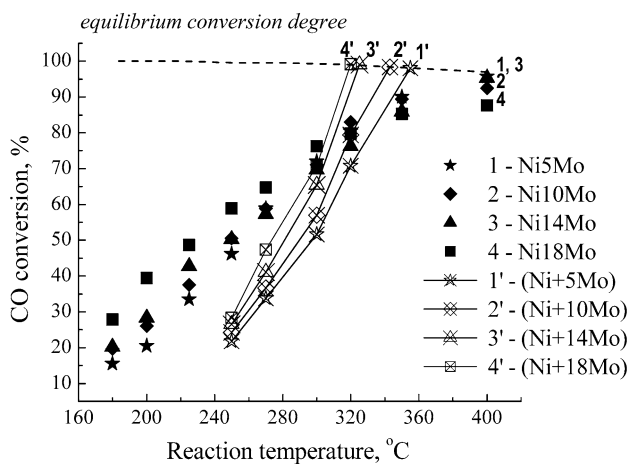


Fig. 3 Comparison of CO conversion degree for the bi-component NiMo system with the sum of the separate CO conversion degrees of Ni and Mo samples at various reaction temperatures, $s/g = 0.3$, $\text{GHSV} = 4000 \text{ h}^{-1}$

The pattern of the catalytic performance of the samples under study was practically the same if the activity is represented as catalyst productivity (mol CO/h) related to specific surface area of the examined samples (Fig. 4a–d). The order of catalytic activities is also the same if the productivity is related to the specific surface area of the calcined samples, because of the monotonous decrease in the SSAC and SSAT values. The result will be similar if the conversion calculated as mol CO/h is related to the weight of the catalysts, because one and the same quantity, approximately (0.7 g), of the samples was charged into the reactor.

An attempt was made to correlate the activity results with the nature of the species formed on the oxidic catalyst precursors during the calcination step [28].

The increase in catalytic activity of the one-component molybdenum samples with the increase in molybdenum content of the oxidic precursor may be related to a change in the coordination of the Mo^{6+} ions by analogy with pioneering studies [29, 30]. It was found that the Mo^{6+} ions are in *Td* surrounding by oxygen ligands, i.e. molybdate structures of the type MoO_4 at low molybdenum content (sample 5Mo corresponding to 1 at Mo/nm^2 support). At higher molybdenum contents (samples 10Mo, 14Mo, and 18Mo matching 2, 3, and 4 atoms Mo/nm^2 support, respectively), the Mo^{6+} ions appear in *Oh* surrounding associated with the formation of polymolybdate $(-\text{MoO}_6)_n$ structures, i.e. a combination between heptamolybdate

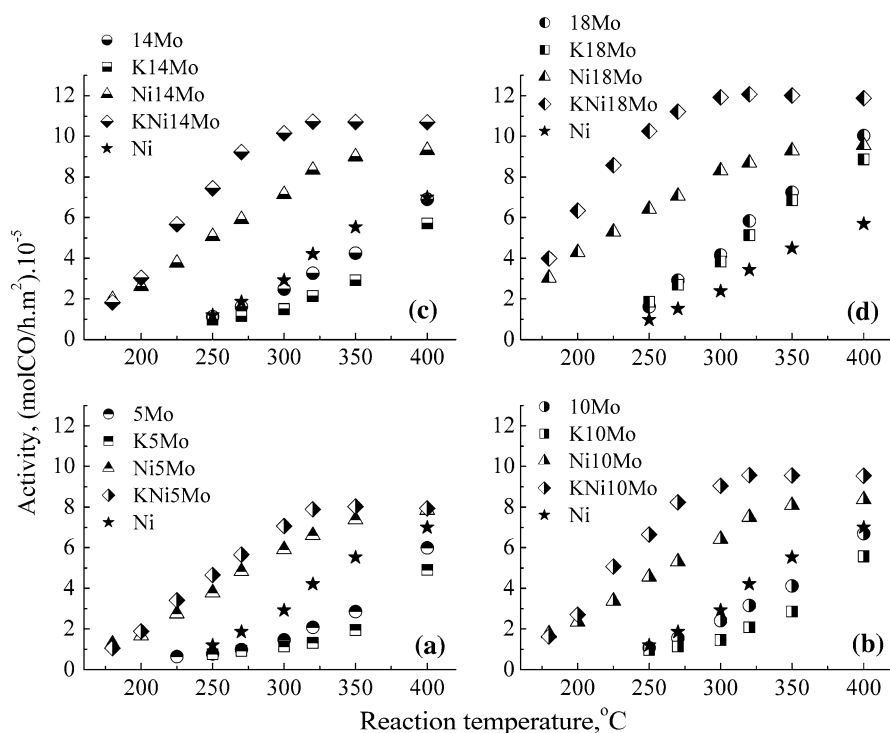


Fig. 4 Catalyst productivity of (K)(Ni)Mo-containing systems related to the specific surface area of the tested samples: **a** (K)(Ni)5Mo; **b** (K)(Ni)10Mo; **c** (K)(Ni)14Mo; **d** (K)(Ni)18Mo

($\text{MoO}_7\text{O}_{24}^{6-}$) and octamolybdate ($\text{Mo}_8\text{O}_{26}^{4-}$) structures [28]. The Mo polymeric species prove to be favored oxidic precursors of the active species in the WGS reaction. This statement is supported by a negative effect of K addition on the activity of the Mo samples. This may be categorically assigned to the formation of surface species, analogous to potassium molybdate (K_2MoO_4) in KMo samples, related to a change from an octahedral to tetrahedral ligand surrounding of the Mo^{6+} ions [28, 31]. The monomeric molybdenum tetrahedral species prove to be unfavorable precursors of the active species in the WGS reaction.

The comparable values of the activity of the NiMo samples are at variance with diffuse reflectance spectroscopy data on oxidic precursors [28]. These data indicate that, depending on the atomic Ni/Mo ratio, surface Ni–Mo–O species with different number of Mo-oxo and Ni-oxo entities are being formed during calcination. Evidently, further procedure of activation by sulfidation and reaction creates the same kind and quantity of active surface species independent of parent oxidic entities.

The observed positive effect of K presence on the NiMo catalyst, depending on the Mo content, i.e. the K/Ni + Mo ratio, cannot be assigned to the $\text{Mo}^{6+}(\text{Oh}) \rightleftharpoons \text{Mo}^{6+}(\text{Td})$ partial transition of the polymeric species into the monomeric ones in the oxidic precursor since the KMo samples possess lower activity than the Mo ones. This effect cannot be related to domination of the $\text{Ni}^{2+}(\text{Td})$ species over the $\text{Ni}^{2+}(\text{Oh})$ ones in the oxidic precursor [28] either, because a previous paper has established that KNi samples were not so active as the Ni catalysts [32].

An explanation of the obtained results is searched in the extent of interaction between the components during the calcination step that causes formation of K–Ni–Mo–O species on the support surface of the oxidic precursors. An indirect confirmation of this statement is provided by FTIR spectroscopy [28]. The highest activity of the samples of atomic K/Ni + Mo ratio ≤ 0.8 is associated with complete interaction of the K^+ ions with the rest of components, as demonstrated by the absence of the characteristic ν_3 band of the CO_3^{2-} ions which proves that all ‘potassium ions are bonded’. The partial interaction between the K^+ ions and the rest of components in the samples of atomic K/Ni + Mo ratio > 0.8 is evidenced by the presence of CO_3^{2-} ions. It is related to the existence of ‘free potassium ions’ available to form surface potassium carbonate. The surface coverage by K–Ni–Mo–O species as oxidic precursors is not complete and sufficient and the samples manifest minor activity.

It is generally accepted that differences in the state of the components of the oxidic precursors predetermine to some extent the differences in the structure and behavior of the active species. This was illustrated in our previous studies based on XPS and EPR characterization of the tested samples [27]. It was found that molybdenum reducibility was the highest and sulfur lability was the lowest in the case of the bi-component KMo system, their values being intermediate in the NiMo system, while in the tri-component KNiMo system molybdenum reducibility was the lowest and sulfur lability was the highest one. It was claimed that both the molybdenum reducibility, i.e. the $\text{Mo}^{4+}/(\text{Mo}^{5+} + \text{Mo}^{6+})$ and $\text{Mo}^{4+}/\text{Mo}^{5+}$ ratios, and the sulfur lability (sulfide to sulfate ratio, i.e. stability of the S^{2-} species to oxidation) represent informative indices in relation to the catalytic properties of the

Mo-containing systems in the WGS reaction. A concomitant presence of potassium, nickel, and molybdenum favours the formation of oxysulfide molybdenum species associated with the highest catalytic activity of the tri-component system observed at the lower reaction temperatures.

The trend of changes in oxidation (reducibility) and sulfidic (sulfur lability) states of molybdenum related to the catalytic activity of the Mo, KMo, NiMo, and KNiMo systems points to a regenerative (redox) mechanism of the WGS reaction taking place in the case of sulfided Mo [33, 34] and Co-Mo catalysts [13]. It may be stated that the effect of alkali presence is related to the K ion affinity to (Ni)Mo in forming surface K–(Ni)–Mo–O species. The sulfide and oxysulfidic derivatives of this ‘bound’ K exhibit different adsorptive, dissociative, and desorptive behavior toward reactants as CO, H₂O, H₂S, CO₂, and H₂ thus affecting in some way the WGS reaction. This statement is partially supported by chemisorption measurements of CO, H₂, and O₂ on K–MoO₃/γ-Al₂O₃ catalyst [35]. The authors reported that a higher temperature, normally 300 °C, is necessary to attain appreciable chemisorption. The adsorption capacities of the reactants on the sulfided samples are suppressed on addition of potassium to molybdenum. Another support is through an IR spectroscopy study of CO chemisorption on KNiMo/Al₂O₃ catalysts [23]. Here, the authors have concluded that the behavior of oxidized KNiMo/Al₂O₃ was very similar to that reported previously for K₂CO₃/Al₂O₃ system [36]. The species were by far ‘more complex’ on the reduced KNiMo/Al₂O₃ catalysts, but partially were very similar to those of the oxidized form. Carbonyl groups appear on the reduced and sulfided NiMo/Al₂O₃ catalysts. They are no more registered on KNiMo/Al₂O₃ after identical sulfidation treatment. In return, bands confirming the presence of formate species appear.

One may suppose that the interaction of the basic potassium ion with the OH groups on the surface of the amphoteric γ-Al₂O₃ support yet during the impregnation and drying steps [16, 23], should also affect the WGS reaction by changing the acid–base properties of the system.

Certainly, the latter are important in the case of a typical WGS reaction on potassium-promoted Al₂O₃ [37] proceeding at 400–600 °C, low space velocity, and atmospheric pressure. A mechanism of consecutive surface formate formation on potassium and its decomposition to CO₂ and H₂ has been accepted as the authors established that the reaction rate is proportional to the surface concentration of formate. Kancheva et al. [36] have also considered surface formate species an intermediate in the typical WGS reaction. No changes in the oxidation state of the components take place. A similar pattern of activities was obtained in the present study where potassium also increases the activity of the bare γ-Al₂O₃ in the WGS reaction at high temperatures and low space velocities (Fig. 3). Consequently, the same mechanism without changes of the oxidation state of the components may be accepted for the WGS reaction with sulfur presence in the feed in the case of potassium-promoted alumina. It should also be emphasized that, according to literature data, the different nature of the *ads*-CO species (carbonyl, formate, carbonate, and carboxylate) is determined by the surface coverage, temperature, and the presence of other components [5].

It may also be supposed that the so-called ‘free’ K ions, namely excess of potassium ions, bonded only to the γ -Al₂O₃ surface in the low content KMo and KNiMo samples (K/Mo > 1.2 and K/Ni + Mo > 0.8) that generate surface CO₃ entities [28], would be able to participate as well in the WGS reaction to increase the yield of CO₂ and H₂. This assumption may be declined on the basis of the following experimental data: (i) a decrease in activity of all the KMo catalysts rather than an increase of activity of the Mo series (Fig. 1); (ii) contrary to expectations, the increase of activity of the KNi5Mo and KNi10Mo samples relative to Ni5Mo and Ni10Mo at low reaction temperatures is insignificant (Fig. 2); (iii) an important enhancement of activity is documented for the KNi18Mo sample relative to Ni18Mo in the temperature range studied (Fig. 2), despite the fact that no CO₃ bands were registered, i.e. no ‘free’ K ions are available on the surface of the KNi18Mo sample [28]; (iv) in addition, the KNiMo catalyst manifests a fairly good reproducibility of activity both on lowering and increasing the reaction temperature (Fig. 6). The latter demonstrates the same reaction pathway, that is, the decisive role of potassium interaction with the rest of components affecting the oxidation state of molybdenum and sulfur lability.

One more source of CO₂ and H₂ could be the decomposition of K-Dawsonite [KAlCO₃(OH)₂] phase under mild conditions by co-precipitation as it was reported in Ref. 38 or under relatively high pressure of an equimolar mixture of CO₂ and steam [39]. K-Dawsonite is unlikely to be formed during preparation and reaction under the conditions applied in the present study: impregnation of Al₂O₃ instead of co-precipitation of K and Al salts, low potassium content (5 wt% K₂O), atmospheric pressure, and high H₂O/CO molar ratio.

In our opinion, it can be concluded that the significant basicity of alkali-promoted aluminas that CO₂ uptake does not determine WGS reaction proceeding. In this work, K ions are added after the deposition of Mo and Ni on alumina. Hence, a competition is taking place between the affinity of K to Mo and Al during the impregnation, drying, and calcination steps. As a result, the effect of basicity reflects on the ability to interact more or less with the (Ni)Mo oxidic and sulfidic states by changing the oxidation state of Mo and the lability of the sulfidic species, the latter two being dependent on molybdenum content and the presence of another additive (Ni).

In the present study, it may be envisaged that the sulfide and oxysulfide Ni–Mo and particularly the K–Ni–Mo entities realize an optimal surface bond strength and coverage of the different surface species (–CO_x, –OH, –O, –OS, –SH, –S, and vacancies) and, consequently, high WGS activity at low temperatures.

Effect of the steam/gas ratio on the WGS activity

In view of the fact that the KNiMo system proves to be the most suitable sulfur-resistant catalyst for WGS reaction, the influence of the steam/gas ratio on the catalytic activity was studied by means of the tri-component samples (Fig. 5a–d). On the one hand, the WGS reaction stoichiometry requires increased concentrations of the reaction products on increasing the concentration of steam. On the other hand, increased amounts of water vapor favor the oxidation or decomposition of the sulfur

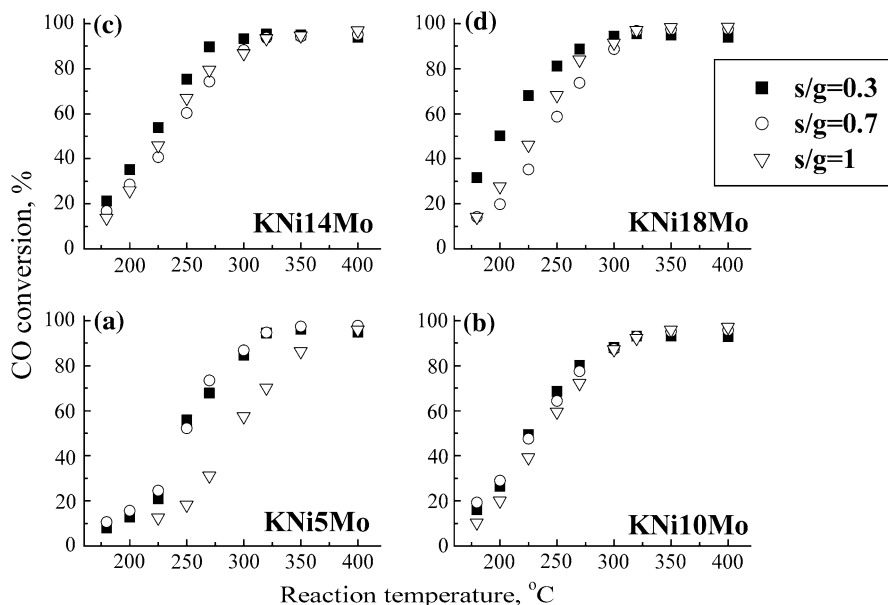


Fig. 5 Influence of the steam to gas ratio ($s/g = 0.3, 0.7, 1$) on the catalytic activity of the KNiMo samples at various reaction temperatures, $GHSV = 4000 \text{ h}^{-1}$: **a** KNi5Mo; **b** KNi10Mo; **c** KNi14Mo; **d** KNi18Mo

species. Here, results from experiments reported so far with $s/g = 0.3$ and molar $\text{H}_2\text{O}/\text{CO}$ ratio of 2.8 are compared with studies carried out with steam to gas ratio of 0.7 and 1 and molar $\text{H}_2\text{O}/\text{CO}$ ratio of 4.9 and 5.9, respectively. The latter two values of the steam/gas ratios were selected in accordance with that used for industrial realization of WGS reaction with classical high-temperature Fe–Cr and low-temperature Cu–Zn catalysts [5].

The catalytic activity of all the samples at 400 °C is independent of the steam/gas ratio values, which are the same and comparable to the equilibrium conversion degree. It is evident from the figure that the influence of the amount of steam in the feed mixture is observed on lowering the reaction temperature and the effect is different for the individual tri-component samples. Obviously, except for the case of KNi5Mo, on raising the amount of water vapor the activity of the sample is not affected. The value of 0.3 for the steam/gas ratio was found to be the most appropriate for the WGS reaction to proceed in the presence of sulfur. The obtained results about the influence of the steam amount in the feed are in accordance with literature data [13, 34], namely, that the presence of H_2S enables the high WGS activity of the catalyst at lower steam/gas ratio. These findings offer an option to accomplish the conversion of CO by reduced steam to gas ratio values, which is economically reasonable.

It is clear from the current studies that the composition of the KNi14Mo sample can be accepted as optimal, because of its comparable catalytic activity with

KNi18Mo in the range 270–500 °C, close to the equilibrium conversion degree and due to molybdenum content (see Table 1).

Stability tests

The comparable values of conversion after going back to GHSV 4000 h⁻¹ at the end of every test at each reaction temperature with all the studied samples indicated that no considerable physicochemical changes in the active forms of the catalysts had occurred during the test. The stability of the catalytic behavior of KNi14Mo sample was also examined in two different modes:

- (i) lowering and rising the reaction temperature of one and the same sample in the 400 °C–180 °C range at a steam to gas ratio of 0.3 and GHSV of 4000 h⁻¹ (Fig. 6);
- (ii) increasing the space velocity by three steam/gas ratios and reaction temperature of 400 °C (Fig. 7). It is evident that the catalytic performance of the KNi14Mo sample is stable and reproducible after varying the temperature several times. The preserved high activity at increasing space velocity (Fig. 7) indicates also good stability of the active species on the surface of the KNi14Mo catalyst.

Mass-gas and colorimetric analysis

Despite online recording of CO and CO₂ at reactor outlet, which ensured the material balance of the reaction, the presence of nickel in the samples causes some doubt that the high CO conversion is due to hydrogenation of carbon monoxide by hydrogen to methane as reaction product of WGS reaction. For this purpose, the outlet gas mixture after the catalytic tests of all Ni-containing samples was collected

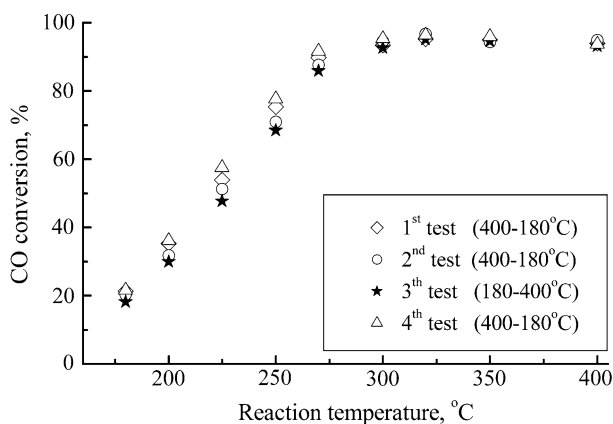


Fig. 6 Stability of the catalytic performance of the KNi14Mo sample on lowering and rising the reaction temperature at $s/g = 0.3$ and $GHSV = 4000 \text{ h}^{-1}$

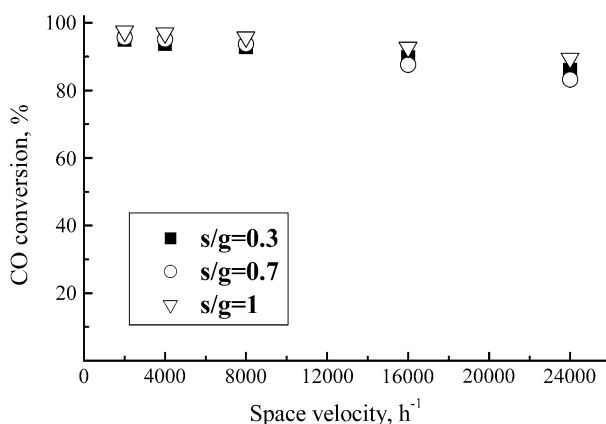


Fig. 7 Catalytic performance of the KNi14Mo sample at 400 °C versus various space velocities at $s/g = 0.3, 0.7$, and 1

and analyzed. The data show that methane content was ≤ 0.006 vol.%. This result confirmed that it is only the WGS reaction that takes place.

The presence of potassium in the samples raises the question about potassium stability on the catalyst surface in view of the high reaction temperature in the presence of water vapor. For this purpose, the excess of water vapor was collected in the condenser at the outlet of the reactor and analyzed colorimetrically. Results show that potassium content (about 1–1.4 $\mu\text{g/ml}$) was extremely low compared to potassium amount in the samples (4.05 mass% K). It reflects the potassium stabilization by interaction with the support and the other components in all K-containing samples.

Conclusions

A systematic study of the water–gas shift activity of K-promoted (Ni)Mo/ $\gamma\text{-Al}_2\text{O}_3$ supported systems in sulfur-containing feed pointed to the following conclusions about the effect of molybdenum content and presence of potassium and nickel on the catalytic performance.

All the catalysts manifested a stable catalytic activity, verified by going back to the initial reaction conditions by the end of every test at each reaction temperature, which indicates that no considerable physicochemical changes occurred in the active forms of the catalysts during test.

Introduction of potassium reduces the catalytic activity of the one-component Mo-containing systems (KMo samples). In contrast, nickel promotes the activity of the one-component Mo samples to the same extent in the whole temperature range studied, independent of Mo loading, and extends the temperature range of catalytic activity to lower reaction temperatures. Ni addition provokes sybatic, additive or antibatic effect on the catalytic activity depending on the atomic Ni/Mo ratio and the temperature interval.

Potassium promotes the WGS activity of the tri-component KNiMo-containing system, depending on the K/Ni + Mo ratio, the activity attaining equilibrium conversion in the 320–500 °C temperature range. The decrease in the surface area of the calcined and tested samples relative to the bare support shows close values indicating that the overall dispersion of the species is not changed during test.

The trend of changes in oxidation (reducibility) and sulfidic (sulfur lability) states of molybdenum related to the catalytic activity of the K-promoted (Ni)Mo/ γ -Al₂O₃ systems points to a regenerative (redox) mechanism of the WGS reaction in sulfur-containing feed.

Close examination indicated that the sample containing K₂O, NiO, and MoO₃ of 4.9, 2.5, and 12.7 mass%, respectively, was found to be the most suitable catalyst for water–gas shift reaction with sulfur containing feed since it attains equilibrium conversion even at 300 °C, and at a low steam to gas ratio of 0.3 at atmospheric pressure. This catalyst demonstrates a stable and reproducible catalytic activity as inlet gas loading is increased.

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