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SPECTRAL ANALYSIS OF THE VARIOUS COMPONENTS OF AN AUTO CATALYST

Abstract: This paper presents a study reaction comparison who was carried out in a glass continuous-flow reactor at atmospheric pressure. The inlet gas contained $8.1\ vol.\%\ CO$ in Ar (Messer MG Chimco Gas). The WGS reaction was carried out in the temperature range $270-400°C$, space velocities (GHSV) from 2000 to 3000 h^{-1}, H_2O/CO ratio = 3 (vapour/gas = 0.27) and in the presence of $2\ vol.\%\ H_2S$. The converted mixture was controlled continuously by an Infralyt 200 spectral gas-analyser recording online CO and CO_2 contents in $vol.\%\ (\pm 1.5)$ at the reactor outlet. The research presented in this paper has obvious practical potential. The whole experiment was directed to the activity of low Ni- content catalyst and what is the effect of alkali addition when the reaction is performed at atmospheric pressure and higher H_2S content in the reaction mixture. Improvement of engine characteristics both by reducing harmful quantities emitted and by increasing power were confirmed by analyzes made in a vehicle inspection station.

Key words: Sulphur-tolerant catalysts, spectrophotometre, catalytic materials, atomic ratio.

1. INTRODUCTION

The widely used hydrodesulphurization catalyst, Co-Mo-Al$_2$O$_3$ and Ni-Mo-Al$_2$O$_3$, manifested activity in the water-gas shift reaction (WGSR) when Sulphur was present in the reaction feed. The alkali addition improved their catalytic action [6].

The industrial Fe-Cr and Cu-Zn catalysts, used in the WGS steps of NH$_3$, CH$_3$OH and H$_2$ production are strongly Sulphur sensible [4].

In a shell's patent however, it was demonstrated that not only presulphided NiO-Mo O$_3$/clay catalyst was active in WGSR but also solely 6% NiO/clay [3], [5].

The sample were studied in the 225-300 °C temperature range, 31 bar pressure, H$_2$O/gas=1.35 and 0.4% H$_2$S in the feed [2].

It presents some interest to study if the activity of low Ni- content catalyst is of practical interest and what is the effect of alkali addition when the reaction is performed at atmospheric pressure and higher H$_2$S content in the reaction mixture [1].

2. EXPERIMENTAL STUDY

Sample preparation. The catalysts 1 wt. % NiO/Al$_2$O$_3$ (1Ni)and 3 wt. % NiO/Al$_2$O$_3$ (3Ni) were synthesized by the method of incipient wetness imprenation of the careeier ($\gamma-Al_2O_3$ BASF D10-10,225 m^2/g 0.605 cm^3/g) with an aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ (p.a., "Chemapol").[18] The impregnation was followed by drying at 105°C for 2 h and calcination at 450°C for 2 h [6].

The potassium deposition was performed at an atomic ratio $K/Ni=2$ by impregnation of the calcined 1 Ni and 3 Ni with aqueous solutions of K_2CO_3 (p.a., "Chemapol"). The obtained samples, denoted as $K1Ni$ and $K3Ni$ were dried and calcined again. The chemical composition and specific surface area of the samples are given in Table 1.

Table 1

Chemical composition and specific surface of the $(K_2O)NiO/Al_2O_3$ samples

Sample	Content (wt %)		Specific surface	
	NiO	K2O	calcined	tested
Al2O3	-	-	231	-
1 Al2O3 / Ni/Al2O3	1.02	-	229	-
Ni/Al2O3 K1Ni/Al2O3	1.02	1.3	221	-
3 Ni/Al2O3 Ni/Al2O3	3.01	-	228	226
Ni/Al2O3 K	3.01	3.8	188	199

For comparison 5 $wt.\%\ K_2O/Al_2O_3(K)$ and 5.1 $wt.\%\ MoO_3/Al_2O_3(Mo)$ samples were prepared according to the same procedure using aqueous solution af K_2CO_3 (p.a., "Chemapol") and $(NH_4)Mo_7O_{24} \cdot 4H_2O$ (Fluka, puriss).

Before the activity test the samples were presulphided in a fix bed reactor with continuos flow containing 6 $vol.\%\ H_2S$ in H_2.

2.1. Methods

Mass-gas analysis was performed on a MS-10 spectrometer. Diffuse reflectance (DR) spectra of the samples in the 250-2500 nm range were recorded on a Beckman 5270 spectrophotometre equipped with a DR spectra accessory. $BaSO_4$ was used as the reference in the near infrared (NIR) region, and the $\gamma-Al_2O_3$ carrier in the UV-VIS region.

The specific surface area of the investigated samples was determined by a modified BET method using low temperature adsorption of air.

2.2 Catalytic activity

The reaction was carried out in a glass continuous-flow reactor at atmospheric pressure. The inlet gas contained 8.1 $vol.\% CO$ in Ar (Messer MG Chimco Gas, see figure 1). The WGS reaction was carried out in the temperature range $270 - 400°C$, space velocities (GHSV) from 2000 to 8000 h^{-1}, H_2O/CO ratio = 3 (vapour/gas = 0.27) and in the presence of 2 $vol.\% H_2S$. The converted mixture was controlled continuously by an Infralyt 200 spectral gas-analyser recording online CO and CO_2 contents in $vol.\%$ (± 1.5) at the reactor outlet [7].

Fig. 1 Catalytic equipment- glass continuous-flow reactor at atmospheric pressure [6]

3. RESULTS AND DISCUSSION

Under the applied test conditions $\gamma - Al_2O_3$ and 5 $wt.\% K_2O/Al_2O_3$ samples manifested 0.8 and 7.5% conversion, accordingly, at 400°C and 2000 h^{-1} for 2 h. This indicated that activity might be neglected.

Figures 2 and 3 illustrate the results of activity test of 1Ni, K_1Ni and K_3Ni samples, respectively expressed as conversion of CO versus different temperature and space velocities.

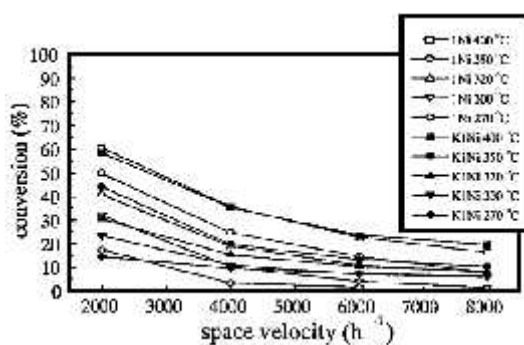**Fig. 2** Catalytic activity of samples at different temperatures and different GHSV

It can be seen that all the samples reached maximum conversion at 400°C and 2000 h^{-1}, 3Ni and K_3Ni manifested activity close to conversion equilibrium values.
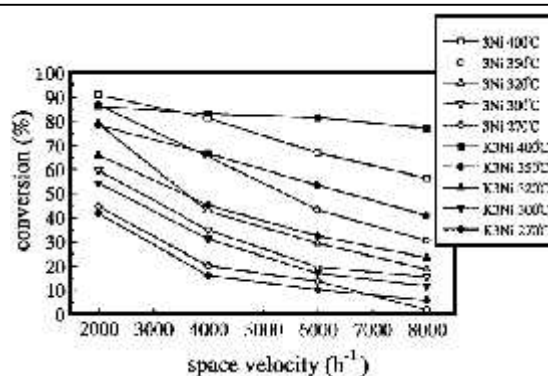

Fig. 3 Catalytic activity of samples at different temperatures and different GHSV

The activity of 1Ni and K_1Ni was lower and no influence of potassium association was observed. The potassium addition to 3Ni had no effect at lower space velocities too, however, at higher space velocities and high temperatures (400, 350°C) its effect was more remarkable. The chemical formula underlying the conversion of the mixture is defined in equation 1, where CO is monoxide carbon, CO_2 – carbon dioxide, H_2 - hydrogen and H_2O - water.

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{1}$$

In industrial application of WGS reaction the space velocities of the inlet gas mixture are between 3000 and 4000 h^{-1}. At these values it was clearly evident that potassium addition did not change the catalytic activity in the temperature range between 270 and 400°C (Fig. 4). It could be also seen that 5.1 $wt.\% MoO_3/Al_2O_3$ exhibited the same activity as 1 $wt.\% NiO/Al_2O_3$.

It was reported that the activity of $Fe - Cr$ industrial catalysts (380°C and atmospheric pressure) was considerably lowered by the addition of $0.2\% H_2S$ in the reaction feed. It may be outlined that $(K)3Ni$ catalytic materials proved to be good Sulphur-tolerant catalysts for high temperature WGSR.
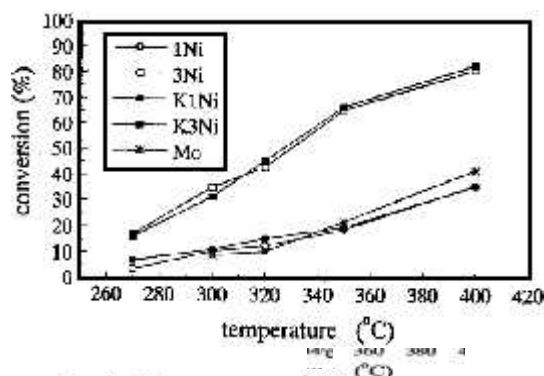

Fig. 4 Catalytic activity of $(K_2O)NiO/Al_2O_3$ and MoO_3/Al_2O_3 samples at different temperatures, GHSV 4000 h^{-1}

Same attempts were undertaken in order to elucidate the nature of the active forms using diffuse reflectance

spectra measurements on 3Ni and K3Ni samples in the visible region. The absorption bands of 1Ni and K1Ni are not presented because of their low intensity. The UV and NIR ranges were omitted a non-informative.

The spectrum of dried light-greenish 3Ni sample is characteristic of $Ni^{2+}(Oh)$ surrounded by $OH(H_2O)$ ligands with bands at 380, 645 and 725 nm (Fig. 4)[5]. In the spectrum of greenish 3Ni sample calcined in air the band of $Ni^{2+}(OH)$ at 400 nm and the doublet $Ni^{2+}(Td)$ at 580 and 620 nm, typical of the NiO/Al_2O_3 system, are registered (Fig. 5). The K addition in the selected ratio $K/Ni = 2$ did not provoke spectral changes (Fig. 5). Practically both spectra coincide.

After the test 3Ni and K$_3$Ni samples became light grey-greenish. The shallow bands of $Ni^{2+}(Td)$ and (Oh) on the high background line pointed to the idea of Ni^{3+} presence on the surface[6]. The higher background of absorption in the K$_3$Ni sample is most probably due to the higher content of Ni^{3+} ions (Fig. 5, 6). The figure 7 and 8 show in extenso absorption in the K$_3$Ni sample.
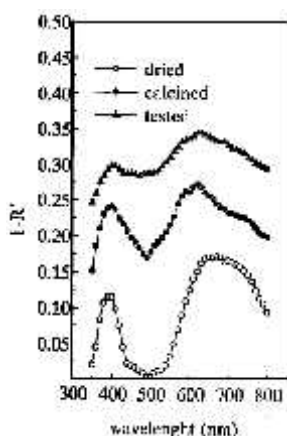

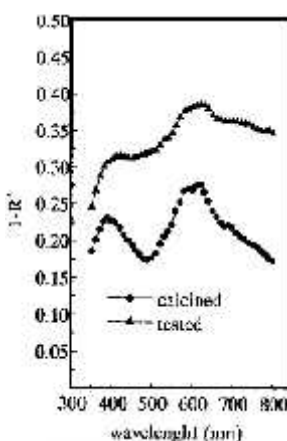**Fig. 5** DR spectra of dried, calcined in air and tested 3Ni sample

Fig. 6 DR spectra of calcined in air and tested K$_3$Ni sample

The electron $Ni^{2+} \leftrightarrow Ni^{3+}$ plays a key role in the catalytic act of WGS reaction.

Then, the registration of Ni^{3+} in tested 3Ni and K$_3$Ni samples may be correlated with their considerable activity.
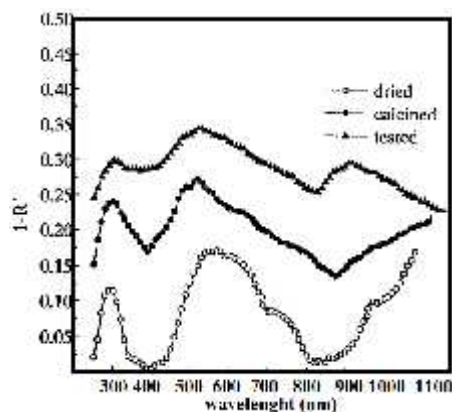

Fig. 7 DR spectra of dried, calcined in air and tested 3Ni sample-extenso
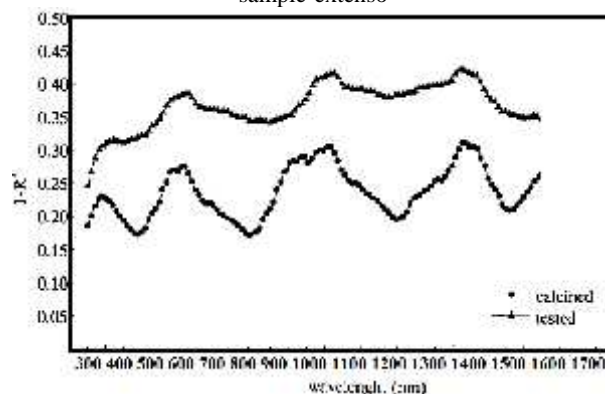

Fig. 8 DR spectra of calcined in air and tested K$_3$Ni sample-extenso

In addition, the enhanced conversion values of K$_3$Ni at High temperatures and space velocities relative to 3Ni may be spectaculated with the higher Ni^{3+} content registered in this sample.

4. CONCLUSIONS

The results of DR spectra of the tested samples after reduction with H$_2$ (Fig. 9) are similar to those in fig. 10 and confirm the above assumption about the role of Ni^{3+} in WGS reaction. The lack of CH$_4$ in the reaction products is the most convincing evidence that metallic Ni did not provoke methanation of CO as a secondary route of the reaction even if it was present during the test.

After test all the sulphided samples are black in colour in the absence of H$_2$S. It may be due to the presence of metallic Ni, Ni$_2$O$_3$, or Ni sulphides (oxysulphides). XRD of the high Ni loading samples (10Ni and K$_{10}$Ni) revealed no metallic Ni. XPS results indicated that no sulphur containing species were present on the surface of 3Ni and K3Ni samples [2], although some inactive sulphur remained in the bulk [7].

The reaction medium is more oxidative than reductive because of the higher CO/H$_2$O ratio than stoichiometric one. Then it can be supposed that the black colour of the samples after test is due to Ni^{3+}. Most surprising are the changes in the black sulphided samples after test in the presence of H$_2$S in the feed. The most active catalysts 3Ni and K$_3$Ni underwent minor changes. They became light grey-greenish and the

shallow bands of Ni^{2+} (Td) and (Oh) on the high background line pointed to the idea of Ni3+ presence on the surface.

The high loaded 10Ni and K_{10}Ni samples became greenish in colour mixed with some dark particles. Intense bands of Ni2+ (Td) and Ni2+ (Oh) appeared, see fig. 11.

In the K_{10}Ni sample they are more intense and with better resolved doublet of Ni^{2+} (Td) at 580 and 620 nm and a shoulder of Ni^{2+} (Oh) at 720 nm. As it was discussed above, 10Ni and K_{10}Ni activity was not higher than the activity of 3Ni and K3Ni samples (Figs. 1 and 2). Then it can be concluded that these spectacular changes in Ni state are related to the inactive part of the deposited nickel.
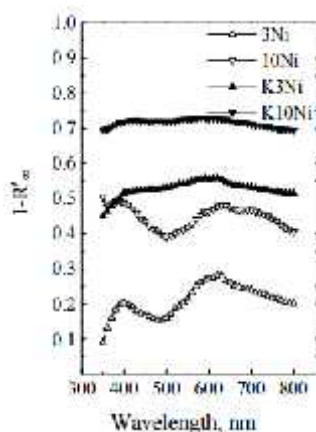

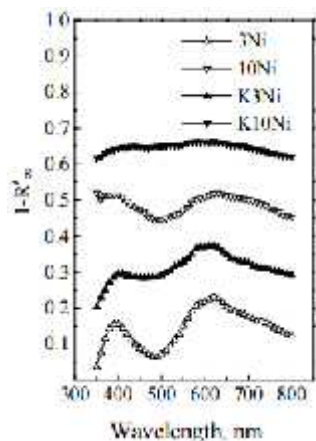**Fig. 9** DR spectra of tested samples after pretreatment in hydrogen

Fig. 10 DR spectra of tested samples after pretreatment in Ar

Based on the obtained results, the following conclusions can be drawn:

• The presence of H2S in the feed stream did not poison NiO/Al2O3 catalysts in WGS reaction. Surprisingly, this presence makes potassium promoting useless.

• The increase in Ni loading did not enhance the catalytic activity related to the amount of deposited Ni.

• Potassium addition enhanced the catalytic activity if the catalysts were thermally pretreated in Ar flow, reduced by H2, or sulphided and the reaction proceeded in the absence of H2S in the feed. It seems that K stabilises the Ni3+ state under reaction conditions. This

would be a favorable phenomenon if the electron transfer $Ni^{2+} \leftarrow Ni^{3+}$ were assumed to be involved in the WGS reaction mechanism.

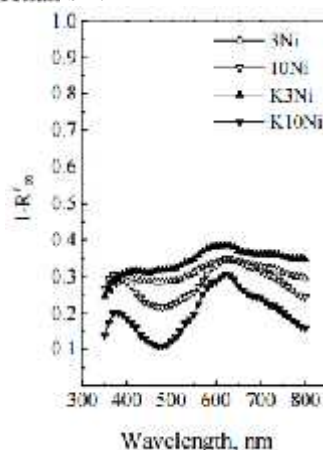**Fig. 11** DR spectra of samples, presulphided and tested in the presence of H2S in the feed

This study can be applied in both the construction of new automotive catalysts and large factories chimney.

Knowledge

In this paper, the calculation performed on the studied part of the doctoral thesis with name "Systems for waste reduction resulting from the combustion process in engines".

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