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TEMPERATURE-PROGRAMMED SURFACE REACTIONS OF METHANOL ON COMMERCIAL Cu-CONTAINING CATALYSTS

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Temperature-programmed reaction spectroscopic studies reveal two main transformation routes of methanol adsorbed on commercial Cu-containing catalysts. First the reverse methanol synthesis reaction (hydrolysis) $CH_3OH + H_2O = CO_3 + 3H_2$; a second route is not connected with CH_3OH synthesis and it includes bimolecular interaction of methanol giving methyl formate. The conversion of the latter compound results in the formation of CO, and other intermediates often postulated in methanol synthesis.

1. Introduction

Industrial methanol synthesis from $CO/CO_2/H_2$ mixture over Cu-containing catalysts proceeds only [1] via CO_2 hydrogenation

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O, \qquad (1)$$

as established by kinetic studies [2] and isotope labelling [3,4]. The main steps of detailed mechanism of the methanol synthesis have been detailed in ref. [5].

At the same time the steady-state methanol decomposition results in CO and H_2 formation as the main products, and only during the initial transient process does the production of $CO_2 + 3H_2$ mixture dominate [6]. To understand this phenomenon one must examine the detailed properties of the expected intermediates. As the synthesis mechanism includes the reactions of strongly adsorbed species [5], temperature-programmed reaction spectroscopy (*tprs*) is an appropriate technique. Earlier [7] on the basis of this method we showed that there is no strong adsorption neither of CO nor of H_2 on the CO reduced Cu-containing catalyst; the H_2 evolution during *tprs* run comes from oxidation of reduced surface centres by strongly adsorbed H_2O.

2. Experimental

All the experiments were performed in a quartz tube, which could be used both as flow reactor and as a vacuum cell, connected to a single pole mass-spectrometer MX-7301, an evacuation system and a gas admission system. The tube was also provided with the temperature-regulating device, permitting measurements to be made under isothermal conditions or in linear heating regime (25–30 ° C/min) up to 500 ° C.

Two sets of SNM-1 type (Cu-Zn-Al oxide) commercial catalyst were examined. The first included the samples with standard activity. The samples of the second set were deactivated during the exploitation in methanol synthesis process at 5 MPa pressure.

The catalyst's pretreatment (see ref. [7]), included calcination in air stream (350 ° C), evacuation (250 ° C, 10^{-4} Torr), reduction in CO/He or H_2/He mixture flow (250 ° C), evacuation (100 ° C), exposition in the gaseous reagent medium (5–10 Torr) and evacuation followed by *tprs*. The pumping rates (cm^3/sec) during the *tprs*-run were 210 (H_2), 60 (CO), 50 (CO_2), 60 (H_2O). Graphic integration of the *tprs*-curves was made.

3. Results and discussion

For reliable interpretation of the *tprs*-spectra the experimental procedure was employed, including chemical testing of the samples, followed by the analysis of spectra's transformations, analogous to [8].

First we focus on the surface characterization of the initial reduced samples. Figure 1 shows the *tprs*-spectrum of the catalyst, reduced by carbon monoxide. This is an unexpected spectrum because the H_2 peak is observed along with the interpretable peaks of CO_2 (T_{max} = 300 ° C) and H_2O (350 ° C). Besides, the CO peak is absent though the sample contacted gaseous carbon monoxide all the time up to evacuation.

As shown in [7] the CO_2 and H_2O peaks result from the desorption of corresponding surface species during temperature rise. The H_2O species is the residue of so-called "biographical" water, which retains on the catalyst's surface

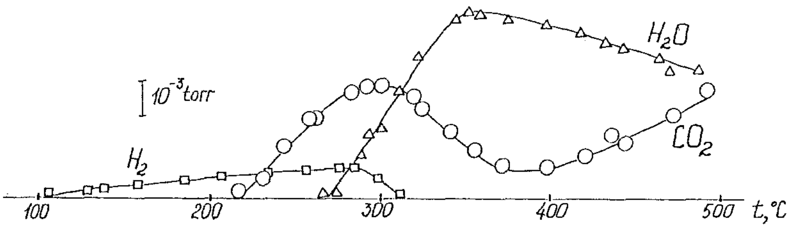

Fig. 1. *tprs*-spectrum of catalyst (0.1 g) reduced with CO/He (20/80) mixture at 250 ° C, 20 mins (CO-sample).

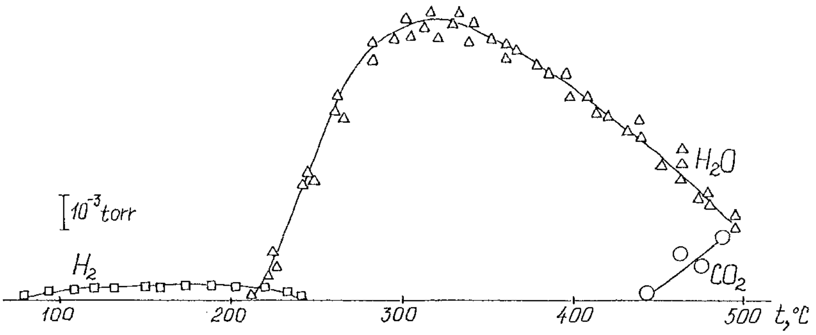

Fig. 2. *tprs*-spectrum of catalyst (0.1 g) reduced with H_2/He (20/80) mixture at 250 °C, 20 mins (H_2-sample).

after reduction process when its amount decreases due to the shift-reaction. The CO_2 species originates from carbon dioxide, which is produced during the reduction and then becomes adsorbed on the surface. The H_2 profile, as mentioned above, is formed due to partial oxidation of catalyst by strongly adsorbed H_2O [7], which acquires surface mobility in *tprs*-conditions. Strong adsorption of CO and H_2 does not occur on reduced surface which contains CO_2 and H_2O adsorbed species [7].

Figure 2 shows the *tprs*-spectrum of the catalyst after reduction in hydrogen. No CO_2 evolution is observed and consequently no CO_2 species are detected. The H_2O peak is shifted to a lower temperature ($T_{max} = 320\,°C$) and its area (directly proportional to H_2O surface coverage) is circa two times that of the corresponding peak on fig. 1. Thus reduction of the sample with H_2 results in additional uptake of water. Simultaneously the comparison of H_2 peak areas on figs. 1 and 2 shows decrease in H_2 evolution. This result would be strange in terms of the model of desorption of strongly adsorbed H_2. Evidently the conditions of reduction with H_2 are much more favorable than that of reduction with CO as far as adsorption of hydrogen is concerned. This result is, moreover, in good agreement with the statement about the reaction of H_2O with reduced surface centres as a main source of H_2 evolution during the *tprs*-run (CO is more effective reducing agent than H_2). Thus peak of H_2 in *tprs*-spectra of both CO and H_2 reduced samples does not come from the adsorption of this gas.

Summarizing, surface of catalyst reduced with H_2 (H_2-sample) is solely H_2O covered while after CO reduction (CO-sample) adsorbed species consist of H_2O and CO_2.

Now we consider methanol conversion on samples of various origins. Figures 3 and 4 show typical *tprs*-spectra obtained with methanol vapour adsorbed on H_2- and CO-samples respectively. The lack of CO peak ($T_{max} = 260\,°C$) in spectrum on fig. 3 is their main difference. As already pointed out, H_2O surface coverage of the H_2-sample is circa twice that of CO-sample. Thus the formation of CO may come from methanol conversion in deficiency of strongly adsorbed H_2O. Actually

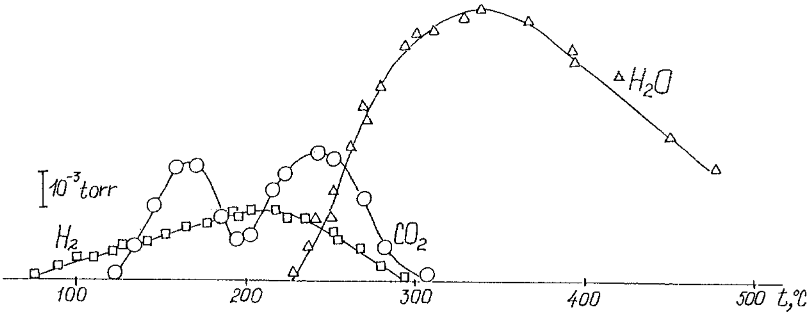

Fig. 3. *tprs* following CH_3OH adsorption on H_2-sample at 100 ° C, 10 mins.

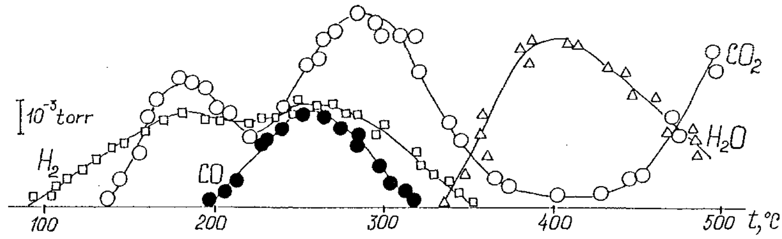

Fig. 4. *tprs* following CH_3OH adsorption on CO-sample at 100 ° C, 10 mins.

(fig. 5) the pretreatment of CO-sample with water vapour results in elimination of CO peak from the *tprs*-spectrum. Evidently, the H_2O peak comes from desorption of residual H_2O surface species. To find out the sources of H_2 and CO_2 formation we examine the ratio of evolved gases amounts (table 1).

As to the H_2-sample exposed in methanol vapour the ratio of evolved H_2 and CO_2 is 2.8. This value approximately corresponds to stoichiometric ratio (3.0) of the reverse methanol synthesis reaction (see eq. (1)). At the same time the reaction with the surface hydroxyl groups (ratio 2.5) can also take place:

$$CH_3OH + OH_S = CO_2 + 2.5H_2. \qquad (2)$$

The reactions (1) and (2) are likely to describe methanol conversion on this sample to the full. There are two CO_2 peaks in the *tprs*-spectrum which reveal the existence of two types of adsorbed species.

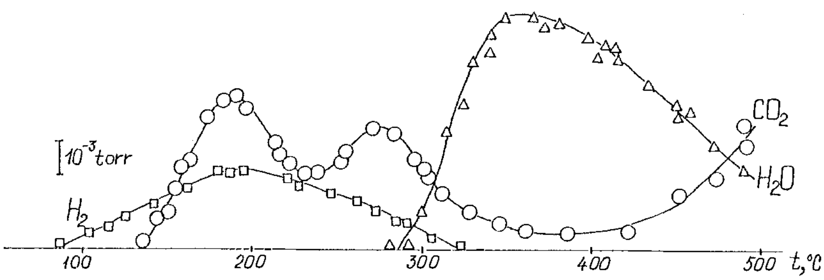

Fig. 5. *tprs*-spectrum of CO-sample successively treated with H_2O and CH_3OH vapour at 100 ° C, 10 mins.

Table 1
The composition of *tprs*-spectra of the samples of SNM-1 catalyst treated with different gaseous agents

Reducing gas	Gaseous agent		Ratio H_2/CO_2	Components of *tprs*-spectra ($n * 10^{-17}$, molcls/m^2)							
	1	2		H_2		CO_2		H_2O		CO	
				n	t_{max} °C	n	t_{max} °C	n	t_{max} °C	n	t_{max} °C
H_2	CH_3OH	–	2.8	6.1	210	2.2	170 250	8.0	340	0.0	–
CO	CH_3OH	–	2.7	12	180 260	4.4	180 290	3.0	400	1.2	260
CO	H_2O	CH_3OH	2.5	7.7	180	3.1	190 280	5.0	350	0.0	–
CO	HCOOH	–	1.0	6.6	190 270	6.3	170 280	5.0	350	0.0	–
CO	$HCOOCH_3$	–	1.6	10	180 280	6.2	180 280	3.0	400	1.5	270

The *tprs*-profile of CO_2 in the spectrum of the CO-sample after successive exposition in H_2O and CH_3OH vapour (fig. 5) is analogous to that on fig. 3. Interpretation of the H_2/CO_2 ratio in this case is unclear due to possible substitution of the initial CO_2 species (see fig. 1) by H_2O and/or by CH_3OH during the treatments. However even if we presume that substitution does not take place at all, the obtained ratio 2.5 shows that reactions (1), (2) again represent methanol conversion. Thus in excess of H_2O on the surface the reverse methanol synthesis (RMS) reaction occurs during *tprs*-run after adsorption of CH_3OH.

We now analyze the sources of CO evolution in H_2O deficiency (fig. 4). The direct methanol decomposition, according to equation:

$$CH_3OH = CO + 2H_2 \qquad (3)$$

can not take place as the reverse reaction–the methanol synthesis from CO and H_2 does not occur on this catalyst [1].

Another potential origin of CO evolution during the *tprs*-run may be decomposition of surface formate, which is often postulated as intermediate in CH_3OH synthesis process e.g. [9]. According to [10] surface formate is readily obtained after adsorption of HCOOH, and its decomposition results in H_2 and CO_2. However in deficiency of surface H_2O species decomposition of formate, resulting in H_2 and CO may occur [11]. Figure 6 shows a typical *tprs*-spectrum obtained with HCOOH vapour adsorbed on CO-sample. The spectrum does not contain a CO component. Thus during the *tprs*-run decomposition of surface formation in H_2O deficiency does not give carbon monoxide.

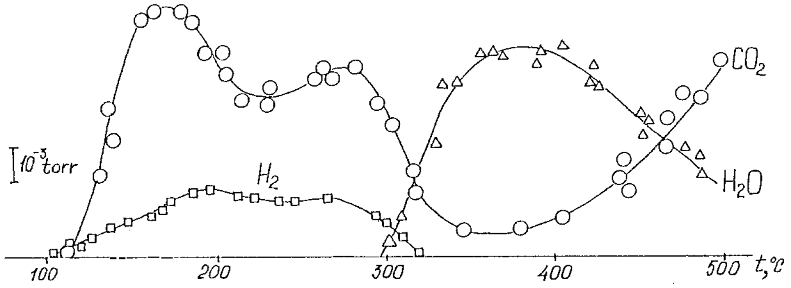

Fig. 6. *tprs* following HCOOH adsorption on CO-sample at 100 ° C, 10 mins.

Deficit of H_2O on catalyst surface favors the bimolecular conversion of adsorbed CH_3OH resulting in the formation of methyl formate:

$$2CH_3OH = HCOOCH_3 + 2H_2. \qquad (4)$$

This reaction was observed in steady state process [6,12]. Decomposition of $HCOOCH_3$ gives CO according to eq. (5) or (6)

$$HCOOCH_3 = 2CO + 2H_2 \qquad (5)$$

$$HCOOCH_3 = CO + CH_3OH \qquad (6)$$

depending upon the catalyst type [13,14]. Either reaction in combination with reaction (4) virtually presents methanol transformation, reversal to CH_3OH synthesis form CO and H_2. Nevertheless the latter reaction cannot take place if only because of small equilibrium concentration of methyl formate under the specified conditions. The possibility of such a transformation is therefore not contrary to the statement that CO_2 is immediate precursor to methanol during the synthesis.

In this connection we discuss the *tprs*-spectrum of CO-sample exposed in $HCOOCH_3$ vapour (fig. 7). It is similar to that on fig. 4 in general. The difference relates to the low-temperature part of the spectra. The *tprs*-spectrum of the CO-sample exposed in CH_3OH (fig. 4) shows that H_2 appears by 40–50 ° earlier than CO_2. The exclusive evolution of H_2 may come only from reaction (4) with methyl formate retained on the surface. This reaction starts at 90 ° C and

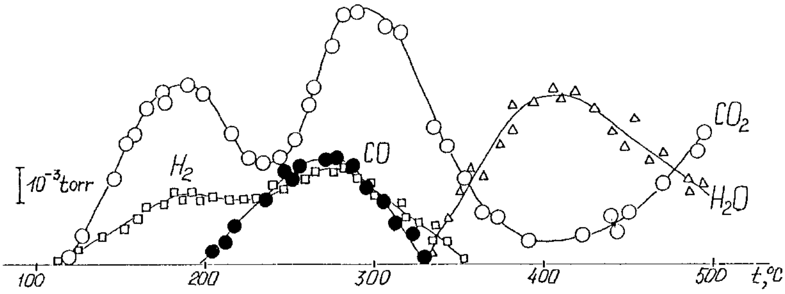

Fig. 7. *tprs* following methyl formate adsorption on CO-sample at 100 ° C, 10 mins.

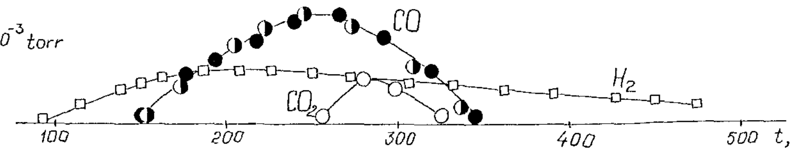

Fig. 8. *tprs* following CH_3OH adsorption on deactivated catalyst reduced with CO/He (20/80) mixture at 250 ° C, 20 mins; half-filled points–Co profile following methyl formate adsorption at 100 ° C, 10 mins.

130–140 ° C decomposition of $HCOOCH_3$ can be detected via CO evolution, as the latter reaction is the only source of CO.

In the spectrum of the $HCOOCH_3$-treated sample (fig. 7) evolution of CO_2 and H_2 begins simultaneously, analogous to that exposed in formic acid (fig. 6). This confirms that along with methyl formate conversion according to eqs. (5) and (6) the saponification of adsorbed $HCOOCH_3$ occurs resulting in formation of CH_3OH and HCOOH. Direct detection of formic acid among the products of methanol conversion during the *tprs*-run was made in [10]. Further hydrolysis of CH_3OH (RMS reaction) and decomposition of HCOOH result in formation of CO_2 peak and, in part, H_2 peak. The ratio of amounts of the developing gases is in accordance with the stoichiometry of a.m. reactions.

Evidently it is methyl formate that is primarily formed from adsorbed methanol during *tprs*-run. Further transformations of $HCOOCH_3$ and residual CH_3OH proceed in H_2O deficiency and competition for it. Thus the initial surface coverage of H_2O determines the route of methanol conversion, and one can expect considerable difference in *tprs*-spectra of CH_3OH-treated samples of various genesis.

We now discuss the spectra obtained when the *tprs*-run is carried out after the synthesis in high-pressure installation. Samples were transferred from reaction system to vacuum unit tube, where treatment with CO flow and exposure in CH_3OH vapour were performed, similar to standard pretreatment prior to the *tprs*-run (see above).

Samples with standard activity give spectra analogous to that on fig. 4 of the catalyst that was not explored in the synthesis process. Totally different *tprs*-spectra are observed on deactivated samples as presented by fig. 8. Only small amounts of CO_2 and no H_2O are evolved during the run, whereas liberation of CO and H_2 is considerable. The CO peak in the spectrum is identical to that

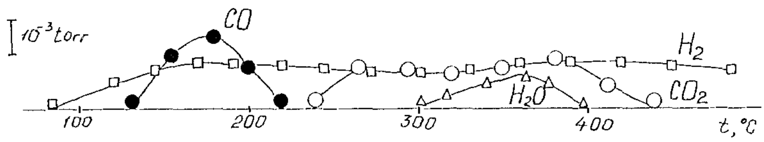

Fig. 9. *tprs* following CH_3OH adsorption on deactivated catalyst reduced with CO/He (20/80) mixture at 250 ° C, 20 mins and treated with H_2O vapour at 100 ° C, 10 mins.

detected after reduction with CO and exposure in methyl formate (fig. 8). The treatment with water vapour prior to exposure in CH_3OH does not result in a visible increase of the CO_2 peak (fig. 9).

Consequently the catalyst deactivated in methanol synthesis process loses activity in RMS reaction, while its activity in production (reaction (4)) and decomposition (reaction (5)) of methyl formate is conserved. Obviously reactions (4) and (5) proceed on active centres, which are different from those of methanol synthesis.

4. Conclusions

The two routes given in the abstract are valid for the transformation of adsorbed methanol. The second yields methyl formate, which undergoes further transformations that are critically dependent upon the surface concentration of H_2O.

In the absence of water the direct decomposition of $HCOOCH_3$ dominates, giving CO and H_2. This situation occurs e.g. in steady state process of methanol conversion [6,12]. In the presence of H_2O saponification of methyl formate is favoured, resulting in the production of methanol and formic acid, and ultimately in CO_2 and H_2. This reaction probably gives rise to the surface formate that has been detected under in situ conditions of the CH_3OH synthesis process by Amenomiya and Tagawa [15].

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