

CATALYTIC OXIDATION OF METHANOL OVER ALKALYEARTH TUNGSTATES

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ABSTRACT

The preparation of oxide divalent alkaliearth tungstate catalysts and the investigation of their catalytic activity in the process of methanol oxidation are under scrutiny in this study. The samples were prepared by the precipitation method and by thermal method. Its catalytic properties were defined using a flow apparatus. The concentrations of methanol as well as those of its oxidation products were examined using the gas – chromatographic method. The results of the present study show that the proposed method leads to the obtaining of active catalysts for complete oxidation of methanol in gaseous phase. The main products of the methanol conversion are carbon dioxide and formaldehyde. The catalytic activity of the tungstates of alkaliearth metals toward the reaction of methanol oxidation depends on the system's composition and strongly increases with the rise of temperature .

Keywords: catalytic, methanol, oxidation, alkaliearth, tungstate.

INTRODUCTION

The searching for and screening of new classes of catalysts is of great importance for the industry [1]. In this connection we carried out a systematic and detailed study of the catalytic behaviour of some tungstates of divalent metals as catalysts toward methanol oxidation. There are some publications and patents of catalysts for selective oxidation of methanol, containing WO_3 or tungstates of di- and trivalent metals [2, 3]. It is also known that the catalytic activity of samples obtained by precipitation and by different heat treatment with respect to reactions, taking place on their surface, is rather different[4-8]. The preparation of oxide divalent alkaliearth tungstate catalysts and the investigation of their catalytic activity in the process of methanol oxidation are under scrutiny in this study.

EXPERIMENTAL

It is known that in aqueous solutions of tungstates there is a complex balance between the different ions of tungstate deeply influenced by pH of the medium, temperature and concentration [9]. Factors like concentration of initial solutions,

order of addition of solutions, temperature and pH during precipitation, stirring, aging of the precipitate and calcination conditions is usually of major importance. The samples studied were obtained by two ways – precipitation method and by thermal decomposition. Precipitation was achieved by slow addition with continues stirring of aqueous solutions of Me(II) nitrate to sodium tungstate heated to 60 – 70 °C at different pH values. Oxides of easily decomposing salts and tungsten trioxides are usually applied. The process takes place to completion at about and above 1000°C. Their phase composition was determined by X-ray, chemical and thermal analysis. The X-ray analysis of the annealed specimens was performed by Phillips diffractometer with Co-K_α radiation. The element analysis of the samples was carried out by Perkin Elmer 3030 atomic absorption spectrophotometer.

The catalytic activity was measured by a flow apparatus at a concentration of the methanol in the alcoholic aerial mixture 4 vol.% ($1.8 \cdot 10^{-3}$ mmol/cm³) at the temperature range of 300 – 450° C. This value of concentration corresponds to the highest degree of methanol concentration in industrial waste gases.

The methanol content was periodically checked using the oil-adsorption method – methanol adsorption on silica gel at 0° C as well as a gas chromatography. The gas analysis was carried out by a Perkin-Elmer Sigma gas-chromatograph. In order to determine the CO₂ (CH₂O)₂O and CH₃OH we used a steel column filled with Porapak Q adsorbent and gas carrier hydrogen. To define CO the steel column was filled with NaX adsorbent with gas carrier hydrogen.

Sample preparation and characterization

Some samples were prepared by using the precipitation method by slow addition with continues stirring of aqueous solutions of Me(II) nitrate to sodium tungstate in temperature range from 20 to 80°C. The pH of initial solutions was maintained constant during the composition process by addition of 10% NH₃ solution or 10% HNO₃. During the precipitation process pH of the solution must be maintained in range of 4.0 to 6,5. A creamy precipitate was formed immediately. The slurry was left under stirring for 30 min. The mixture was heated to dryness on a water bath overnight, the result being white lumps. These lumps were ground up and washed with distilled water in a Büchner funnel. This step was repeated some times. The resulting powder, completely amorphous to X-rays, was heated at 550°C in the air for 6 h . Some samples were prepared by using thermal solid-state syntheses. Oxides of easily decomposing salts and tungsten trioxides are usually applied. The process takes place to completion at about and above 1000°C. X-ray and chemical analysis determined their phase composition. Figure 1. presents X-ray diffraction patterns of the samples treated at 550°C. The well expressed lines in the diffraction patterns at values between $Q = 26.8^\circ$ and 28.2° can be assigned to WO₃.

Catalytic measurements

The catalytic properties were studied in the temperature range between 300-450 T°C. Table 1 presents the distribution of the reaction products depending on the content of the catalytic samples. The catalytic activity of all samples reaches its

maximum at about 450°C. The results can prove that the highest activity show the samples prepared by precipitation method. Probably thermal treating at about 1000°C of the samples prepared by thermal synthesis has a negative effect on catalytic properties of catalysts. The extent of the oxidation process to CO is substantial only for MgWO₄ and BaWO₄, prepared by thermal method. Side reactions are more important at low reaction temperature and low methanol conversion.

Table 1. Catalytic activity and selectivity of alkali earth tungstates toward methanol oxidation

Catalyst	T°C	X ₁	X ₂	X ₃	Selectivity	Total
CaWO ₄ Precipitation method	300	-	1.0	1.2	54,2	2.2
	350	-	1.5	1.2	54,2	2.2
	400	-	2.9	4.6	61,0	7.5
	450	-	11.2	8.2	42,2	19.4
SrWO ₄ Precipitation method	300	-	1.5	1.8	54,3	3.3
	400	-	3.9	3.0	43,4	6.9
	450	-	4.2	6.8	61,8	11.0
BaWO ₄ Precipitation method	350	-	4.3	3.7	46,3	8.0
	400	-	6.2	3.9	38,6	10.1
	450	-	9.5	4.3	31,2	13.8
MgWO ₄ Thermal method	300	-	2.2	2.5	53,2	4.7
	350	-	4.7	5.8	39,7	14.6
	400	0.2	8.9	7.1	43,8	16.2
	450	0.2	12.2	7.7	38,2	20.2
CaWO ₄ Thermal method	300	-	1.3	3.4	72,4	4.7
	350	-	3.2	8.0	71,4	11.2
	400	-	8.2	14.4	62,5	22.6
	450	-	19.3	16.0	45,3	35.3
SrWO ₄ Thermal method	300	-	2.6	4.0	60,9	6.6
	350	-	4.7	19.4	80,5	24.1
	400	-	10.6	20.3	65,6	30.9
	450	-	28.6	14.8	34,3	43.1
BaWO ₄ Thermal method	300	-	-	2.1	100,0	2.1
	350	-	-	3.1	100,0	2.1
	400	0.2	6.4	10.5	61,4	17.1
	450	0.2	11.2	26.3	69,8	37.7

X₁, X₂ and X₃ – degrees of conversion of methanol (%) to CO, CO₂ and CH₂O

It is known that the mechanism of methanol conversion over oxide catalysts is a redox type mechanism. In this context, the steps of such catalytic system were the object of several investigations. The reduction of the catalyst bulk by methanol only seems to occur at temperatures higher than 230 °C while the reoxidation only starts at temperatures higher than 270 °C. The reduction and reoxidation rates increase when temperature rises.

CONCLUSIONS:

- The different samples of systems Me(II)/WO₃ were obtained by precipitation method and by thermal method. The samples prepared by thermal method have a negative effect on catalytic properties.
- Methanol conversion over oxide catalysts is a heterogeneous process, redox type mechanism. The main products are CO₂ and formaldehyde and major by-product is always CO.
- The catalytic activity of the samples toward the conversion of methanol to CO₂ strongly increases with the rise of temperature from 300-450 °C.

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