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Hydrosulfurization of Methanol on Y_2O_3–TiO_2–ZrO_2 Catalysts*

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Y_2O_3-TiO_2-ZrO_2 catalysts, where the contribution of oxide components ranges from 0 to 100 mol %, have been studied for their catalytic performance in methanol hydrosulfurization. Their activity and selectivity have shown a strong dependence on acid-base properties which, in turn, changed with catalyst composition. High yttria content favors selectivity to methanethiol, while catalysts highly active for the formation of dimethylsulfide were those containing 8 mol % Y_2O_3. The latter composition, which boosted selectivity to $(CH_3)_2S$, has created favorable conditions for the generation of acid centers in chemically mixed oxides as concluded on the ground of ESR studies and acidity measurements.

Key words: methanol hydrosulfurization, methanethiol, dimethylsulfide, yttria, titania, zirconia

Catalytic reaction between methanol and hydrogen sulfide (methanol hydrosulfurization) was the subject of many studies performed on oxides and sulfides of different metals and later on zeolites as well [1]. The reaction leads to the formation of methanethiol and/or dimethyl sulfide as the main products. Both products are of importance to practice, particularly methanethiol, which is used for the manufacture of methionine – an additive to chicken fodder.

Studies of the reaction of methanol hydrosulfurization have brought into conclusion that activity and selectivity depend on the relation between the number, concentration and strength of acid centers on the one hand and those of basic centers on the other [2,3]. The catalyst used in practice for synthesis of methanethiol is KWO_4/Al_2O_3 on the surface of which basic sites predominate [1]. Although the mentioned catalyst is characterized by a high conversion and selectivity to methanethiol at 593 K, it loses its activity as a result of thermal changes, caused by heat released in this exothermic reaction. Recent reports point to the advantage of the application of zirconia modified by sodium and molybdenum ions as a catalyst for methanol hydrosulfurization [2,3].

Activity and selectivity of catalysts for methanethiol formation depends, to a considerable extent, on the kind of hydrogen sulfide species involved in the reaction with

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*Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

chemisorbed methanol. On catalysts bearing Brønsted acid sites on their surfaces, the reaction proceeds between methoxy groups and hydrogen sulfide from the gas phase and/or associatively adsorbed on catalyst surface [4–6]. If, however, Lewis acid-Lewis base pair sites are present on the surface of catalyst, then dissociative chemisorption of hydrogen sulfide occurs and HS^- ions interact with methoxy groups which results in the formation of methanethiol [7]. The latter catalysts show higher selectivity to methanethiol, while dimethyl sulfide can form as a result of the interaction between methoxy groups and methanethiol adsorbed associatively on basic centers [8]. Such a way of dimethyl sulfide formation requires an optimum energy to bind methanethiol to the catalyst surface, which infers a suitable relation between the strength of Lewis acid and Lewis base centers. The mentioned relation in the aspect of its effect on activity and selectivity of catalysts has been discussed by several researchers and concerning oxide catalysts in particular, in [2]. According to Mashkina *et al.* [9], strong basic sites are indispensable for achieving high selectivity to methanethiol.

This study was aimed at determining how the addition of yttria to zirconia and/or titania can affect selectivity and activity for methanol hydrosulfurization. Both number [10] and strength [10–14] of Lewis base centers on zirconia surface is higher than on titania. On the other hand, Lewis acidity of titania is higher than that of zirconia, therefore, the introduction of basic oxide such as Y_2O_3 could be a factor enabling to control acid-base properties of TiO_2 and ZrO_2 in a desired direction. Catalytic performance in methanol hydrosulfurization depends not only on acid-base properties of a catalyst surface, but also on H_2S content in the feed. Since the excess of hydrogen sulfide is conducive to methanethiol formation (which is the product of higher importance to practice), we have carried out our measurements at the molar ratio of $H_2S:CH_3OH = 2:1$.

EXPERIMENTAL

The experiments were conducted using three series of catalysts: two binary oxides $Y_2O_3–ZrO_2$ and $Y_2O_3–TiO_2$ and a ternary system $Y_2O_3–TiO_2–ZrO_2$ in which the component content was in the range from 0 to 100 mol %. The catalysts were prepared by co-precipitation with ammonia using the metal chlorides as starting materials. The precipitates were dried at 105°C for 24 h and calcined at 500°C for 4 h. Catalyst labels include a number representing yttria content (in mol %), while letters are standing for relevant oxides (Y – Y_2O_3, Ti – TiO_2, Zr – ZrO_2) which made balance to 100 mol %. The proportion between titania and zirconia in the ternary system was equimolar. Surface area and pore volume of the catalysts were measured on an ASAP 2010 sorptometer. The reactions between methanol and hydrogen sulfide were carried out in a flow system at 623 K. The reactor was loaded with 0.2 g of catalyst (0.5–1.0 mm) followed by a 4-hour activation at 673 K in helium flow. A mixture consisting of hydrogen sulfide (1.5% by volume), methanol (0.75 % by volume) and helium as a carrier gas passed through the catalyst bed at a flow rate of 0.0042 m^3/h. The reactants and reaction products were analyzed on a gas chromatograph model SRI equipped with flame ionization and flame photometric detectors.

RESULTS AND DISCUSSION

The system $Y_2O_3–ZrO_2$ has been extensively investigated since a recent discovery of a new promoting effect in catalysis, so-called NEMCA (Non-Faradaic Electrochemical Modification of Catalytic Activity) [15–19]. In the above electrochemical promotion it plays the role of a solid electrolyte, in which the conductivity is almost entirely caused by transport of oxygen ions in a lattice with anion vacancies and the rate of organic compound oxidation reaction can increase by 100 times compared to that without promoting. Contrary to the keen interest in yttria-zirconia system application to electrochemical reactors, the reports on its acid-base properties and activity for reactions of acid-base catalysis are scarce [20–24]. So are studies of catalytic properties of Y_2O_3–TiO_2 and Y_2O_3–TiO_2–ZrO_2 systems [25,26]. No attempts at all were reported at using yttria–zirconia and/or titania systems as catalysts for conversions of sulfur compounds.

Surface areas of yttria and titania, as results from Fig. 1, are of about 120 m^2/g, whereas that of zirconia is considerably smaller. However, the addition of yttria to zirconia (up to about 55 mol %) brings about a considerable increase in surface area. Even bigger increase occurs on addition of yttria to titania. No such an effect is observed in the case of the introduction of Y_2O_3 into TiO_2–ZrO_2.

In Fig. 2 methanol conversion on yttria, zirconia, titania and titania-zirconia catalysts in hydrosulfurization of the above alcohol was presented as a function of time on stream. For the sake of comparison, commercial catalysts CRS-31 and KA-201, based on titania and alumina, respectively, were also examined in the above reaction. Since during three hours on stream no essential changes in conversion and selectivity were observed for the catalysts, except for CRS-31, both methanol conversion and

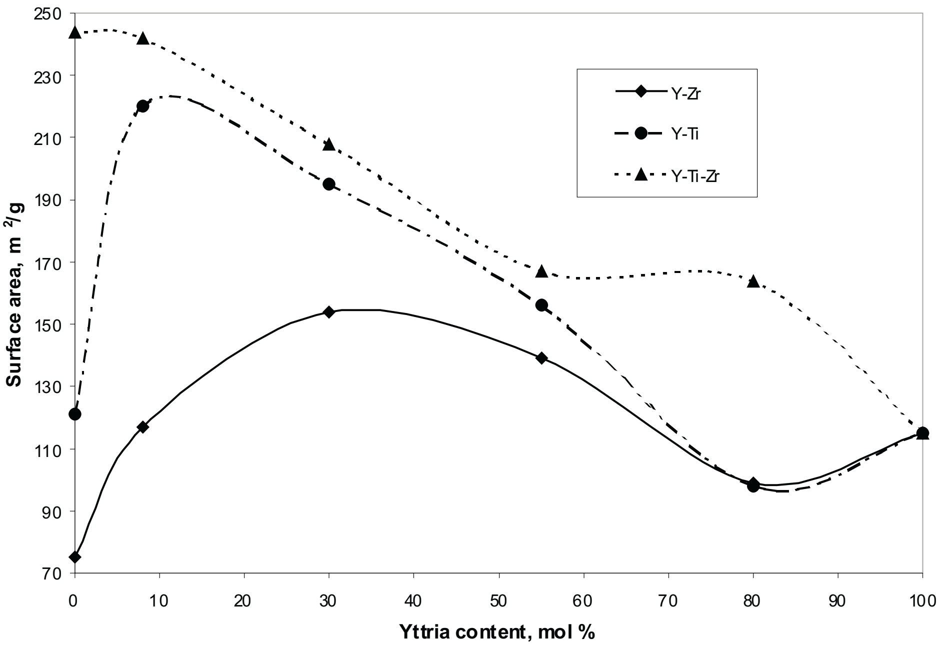

Figure 1. Surface area of yttria-containing catalysts as a function of Y_2O_3 content.

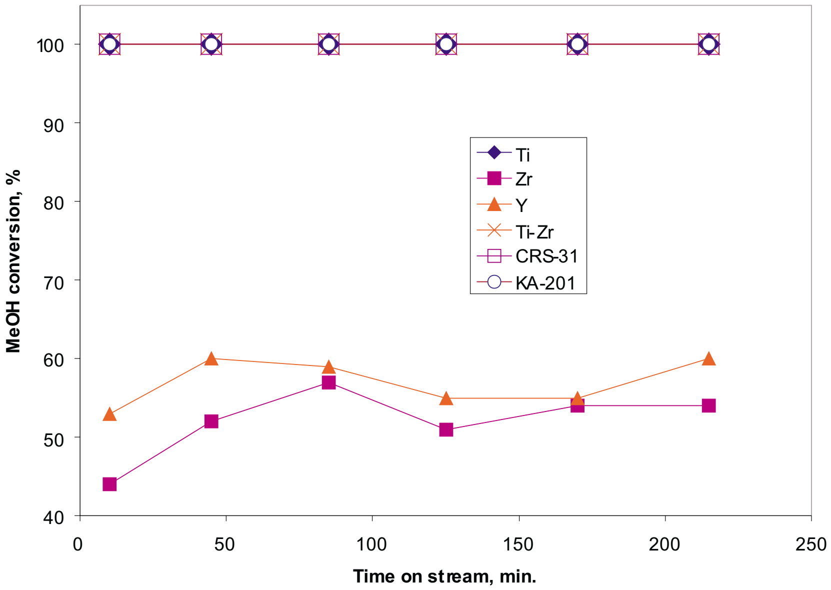

Figure 2. Methanol conversion on titania (Ti), zirconia (Zr), titania-zirconia (Ti-Zr), CRS-31 and KA-201 catalysts.

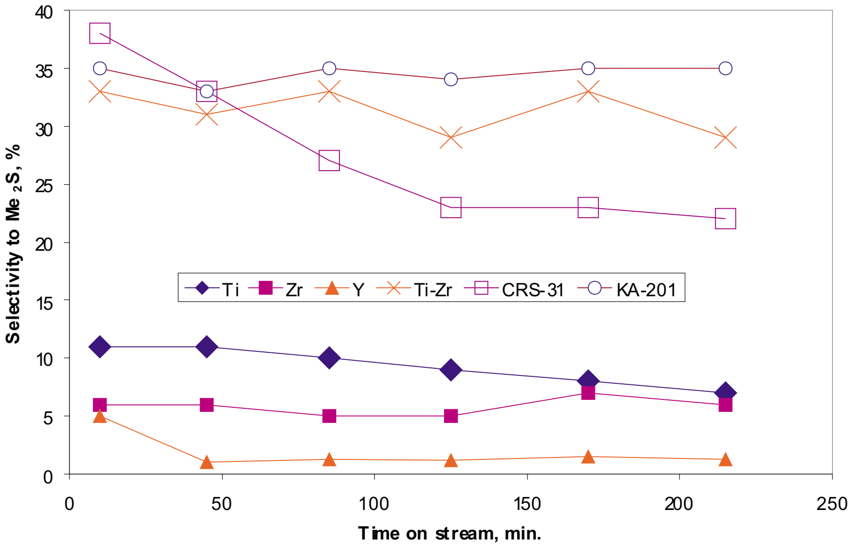

Figure 3. Selectivity to dimethyl sulfide on titania (Ti), zirconia (Zr), titania-zirconia (Ti-Zr), CRS-31 and KA-201 catalysts.

product selectivity in relevant tables are shown as average values recorded during 3 hours of reaction. As concerns the catalyst CRS-31, a decrease in selectivity to dimethyl sulfide (Fig. 3) and an increase in that to methanethiol (Fig. 4) have occurred with passing time on stream. It is worth mentioning that methanol conversion on the latter catalyst as well as on TiO_2–ZrO_2, TiO_2 and KA-201 is 100% (Fig. 2), but they differ in their selectivities (Figs. 3,4). Although total selectivity to CH_3SH and $(CH_3)_2S$ exceeds 90%, both commercial catalysts and TiO_2–ZrO_2 show considerably higher selectivity to dimethyl sulfide than other catalysts investigated (Fig. 3). Selectivities of titania and zirconia to $(CH)_2S$ are 9 and 5%, respectively, whereas that of binary oxide TiO_2–ZrO_2 is 30% (Table 1). The big difference in the selectivity pattern of the above catalysts most likely results from differences in their acid-base properties. It has been proved that dimethyl sulfide formation depends on acidity, whereas surface basicity favors the reaction path to methanethiol [1,9]. This is in good agreement both with results of our measurements of acidity of the catalysts discussed [27] and with the hypothesis on surface acidity of binary oxides put forward by Tanabe *et al.* [28] that TiO_2–ZrO_2 is more acidic than single components of the system.

Catalyst of the highest selectivity to methanethiol appeared to be yttria (Fig. 4), which belongs to basic oxides [29]. Yttria alone is, however, poorly active (Table 1), therefore, we have made an attempt at preparing catalysts of higher activity by mixing yttria with titania and/or zirconia. When yttria was added to titania, the increase in selectivity was achieved only after introducing 55 and 80 mol % Y_2O_3 and was accompanied by a reduction in methanol conversion. As a result of the latter, the yield of methanethiol was, at the best, similar to that observed on titania alone (Table 2). It is worth to add that titania

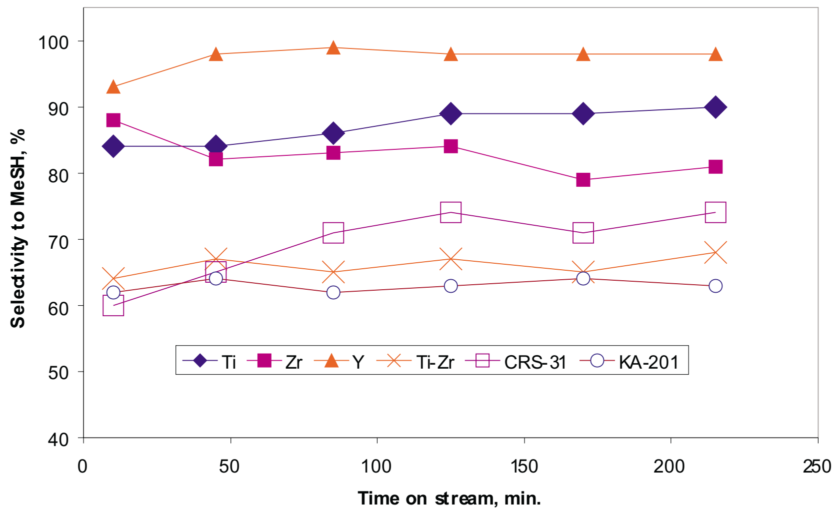

Figure 4. Selectivity to methanethiol on titania (Ti), zirconia (Zr), titania-zirconia (Ti-Zr), CRS-31 and KA-201 catalysts.

prepared in this study is characterized by higher activity than that reported in [3]. This fact can result from its considerably larger surface area (121 m^2/g) compared to that of titania catalyst (85 m^2/g) studied in the paper we refer to [3]. When a relatively small amount of yttria (8 mol %) was added to titania, selectivity to methanethiol fell down, whereas that to dimethylsulfide increased (Table 2) and this observation was in agreement with a rise in acidity we have reported elsewhere [27] for the catalysts discussed.

Table 1. Average values (based on 3 hours on stream) of conversion, selectivity and yield of products of methanol hydrosulfurization on titania, zirconia, yttria and commercial catalysts.

Catalyst	MeOH conversion	MeSH		Me_2S		Other products
	%	Selectivity %	Yield %	Selectivity %	Yield %	
Ti	100	88	88	9	9	C_1-C_4, Me_2O
Zr	53	84	45	5	3	C_2-C_4, Me_2O, Me_2S_2
Ti-Zr	100	67	67	30	30	C_1-C_4, Me_2O, Et_2S
Y	57	98	56	1	0.6	Me_2O, Me_2S_2
CRS-31	100	68	68	29	29	C_1-C_4, Me_2O, Me_2S_2
KA-201	100	63	63	34	34	C_3, Me_2O, Me_2S_2

Table 2. Average values (based on 3 hours on stream) of conversion, selectivity and yield of products of methanol hydrosulfurization on Y_2O_3-TiO_2 catalysts.

Catalyst	MeOH conversion	MeSH		Me_2S		Other products
	%	Selectivity %	Yield %	Selectivity %	Yield %	
Ti	100	88	88	9	9	C_1-C_4, Me_2O
8Y-Ti	100	64	64	35	35	C_1-C_4, Me_2O
30Y-Ti	100	86	86	14	14	C_1-C_4, Me_2O
55Y-Ti	75	92	69	6	5	C_1-C_4, Me_2O
80Y-Ti	40	97	39	1	0.4	C_1-C_4, Me_2O

Chemical mixing of zirconia and yttria (8 mol %) has also resulted in increased acidity [27], although less spectacular than that observed in the case of yttria-titania catalyst mentioned above. The catalyst 8Y-Zr has shown the highest methanol conversion in the series of yttria-zirconia catalysts and increased selectivity to $(CH_3)_2S$ (Table 3), the latter being caused by a rise in acidity. The new acid sites created by the presence of yttria can be Zr^{3+}, formation of which is promoted by Y^{3+} ions located in a close vicinity of Zr^{3+} as proved on the ground of ESR spectra of yttria-zirconia samples [30]. It is worth to add that in the series Y_2O_3–ZrO_2 the maximum concentration of the paramagnetic species of Zr^{3+} was found for the catalyst 8Y-Zr [30].

Table 3. Average values (based on 3 hours on stream) of conversion, selectivity and yield of products of methanol hydrosulfurization on Y_2O_3-ZrO_2 catalysts.

Catalyst	MeOH conversion %	MeSH Selectivity %	MeSH Yield %	Me_2S Selectivity %	Me_2S Yield %	Other products
Zr	53	84	45	5	3	C_2-C_4, Me_2O, Me_2S_2
8Y-Zr	77	85	65	10	8	C_2-C_4, Me_2O, Me_2S_2
30Y-Zr	54	87	47	6	3	C_2-C_4, Me_2O, Me_2S_2
55Y-Zr	55	91	50	4	2	C_2-C_4, Me_2O, Me_2S_2
80Y-Zr	52	94	49	0	0	C_2-C_4, Me_2O

Somewhat different selectivity pattern has been shown by ternary oxide catalysts Y_2O_3–TiO_2–ZrO_2, where selectivity to methanethiol has risen with increased contribution of yttria to the catalyst composition (Table 4). It is associated with enhancement of basic properties on addition of Y_2O_3 to TiO_2–ZrO_2 [27] and can suggest the absence of any stronger interactions between yttria and TiO_2–ZrO_2. This suggestion is supported also by a considerable decrease in methanol conversion accompanied by increase in selectivity to methanethiol, when yttria content is 55 mol % or more (Table 4).

Table 4. Average values (based on 3 hours on stream) of conversion, selectivity and yield of products of methanol hydrosulfurization on Y_2O_3-TiO_2-ZrO_2 catalysts.

Catalyst	MeOH conversion %	MeSH Selectivity %	MeSH Yield %	Me_2S Selectivity %	Me_2S Yield %	Other products
Ti-Zr	100	67	67	30	30	C_1-C_4, Me_2O, Et_2S
8Y-Ti-Zr	100	73	73	25	25	C_1-C_4, Me_2O, Et_2S
30Y-Ti-Zr	100	79	79	17	17	C_1-C_4, Me_2O, Et_2S
55Y-Ti-Zr	73	96	70	3	2	C_1-C_4, Me_2O, Et_2S
80Y-Ti-Zr	73	97	71	2	1.5	C_1-C_4, Me_2O, Et_2S

All the catalysts investigated are characterized by the predominance of sulfurizing activity, *i.e.* organic sulfur compound formation, over activity for other reactions such as methanol decomposition and possible further reactions, namely oligomerization, cyclization, *etc.* A competitive reaction, which proceeds, however, to a small extent only, is methanol dehydration as evidenced by the presence of slight quantities of dimethyl ether in reaction products. Hydrocarbons C_1-C_4 can be formed both as a result of methanol conversions and secondary reactions of sulfur compounds. However, it has to be emphasized that for most of catalysts investigated, selectivity to compounds other than those of sulfur is below 10%.

CONCLUSIONS

Oxide systems consisting of yttria and oxide of titanium group metal (titania and/or zirconia) make a good material for the development of novel catalysts for hydrosulfurization of methanol. Yttria content of 8 mol % seems to be optimal for a rise in acidity of chemically mixed oxides, which in turn, improves selectivity to dimethyl sulfide. On the other hand, at high contribution of Y_2O_3 to catalyst composition (over 55 mol %), a high selectivity to methanethiol (over 90%) can be achieved.

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