Metal Oxides as Catalysts for the Reaction between Methanol and Hydrogen Sulfide

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The reaction between methanol and hydrogen sulfide leading to the formation of methanethiol and dimethyl sulfide has been studied using different H_2S:CH_3OH molar ratios (0.5:1, 1:1, 2:1) at 623 K on various metal oxides presenting different acidity and basicity. The correlations between activity and selectivity of catalysts and their average oxygen and cation charges as well as the strength of their acidic and basic sites, determined by adsorption of probe molecules followed by IR spectroscopy, are as follows: (i) the highest strength of basic sites and the highest negative charge on oxygen (MgO) lead to the lowest activity and the highest selectivity toward CH_3SH; (ii) the lowest strength of basic sites (medium oxygen charge) and the highest cation charge (γ-Al_2O_3) cause the highest activity and the highest selectivity toward $(CH_3)_2S$. The dimethyl sulfide selectivity is in the reverse order of the number of basic sites. IR measurements show that the reaction occurs between chemisorbed methanol (methoxy species) and SH^- species or/and H_2S molecules. Too strongly held methoxy species as on MgO and PO_4^{3-}/SiO_2 do not react with H_2S. The difference in activity and selectivity of both titania samples (anatase and rutile) is discussed.

Introduction

The catalytic reaction between methanol and hydrogen sulfide (hydrosulfurization of methanol) leads to the formation of methanethiol and dimethyl sulfide. Various metal oxides[1–8] and zeolites[8–12] were studied as catalysts. Their activity and selectivity depend on the nature of active sites: Brönsted or Lewis acid centers as well as basic sites. However, their role is not clearly established yet. In case of Na, H-FAU zeolites, it was stated that acidic hydroxyl groups play the role of active sites[9,10] but, in the absence of these centers, cations were also found to be active.[11,12] When Brönsted acid sites participate in the reaction, the process occurs via methoxylation of the zeolite surface, with subsequent reaction between methoxy groups and physically adsorbed hydrogen sulfide. Both CH_3SH and $(CH_3)_2S$ are formed. The selectivity depends on the reaction temperature, the H_2S:CH_3OH molar ratio and concentration of Brönsted acid sites.[9] Studies on the hydrosulfurization of higher alcohols (ethanol and propanol) on zeolites[13,14] showed that the increase in strength of Brönsted acid sites causes increased selectivity toward organic sulfides and also influences the competitive reaction, i.e. the transformation of alcohols to hydrocarbons.

Mashkina et al.[5,6] analyzing the activity of various oxides, mainly supported on alumina, concluded that the reaction first proceeds between methoxy groups and dissociatively adsorbed H_2S with the formation of CH_3SH on catalysts having strong acidic sites. In the next step, methanethiol transforms to dimethyl sulfide. They stated that the activity of oxide catalysts increased with concentration and strength of aprotic centers. They also postulated[5] that, in the presence of strong basic sites, both reagents dissociated and the reaction between CH_3O^- and HS^- species occurred leading to the formation of CH_3SH. Finally, they reported that the most effective catalysts in the synthesis of dimethyl sulfide were those containing pairs of acid–base centers, namely, strong Lewis acid sites and medium basic sites.[6]

The aim of the present study is to extend the work to various pure metal oxides: MgO, ZrO_2, TiO_2 rutile and anatase, CeO_2, $MgAl_2O_4$, γ-Al_2O_3, and PO_4^{3-}/SiO_2. The results on both activity and selectivity toward the $CH_3OH + H_2S$ reaction are discussed taking into account (i) the acidic and basic properties of the catalysts used and (ii) infrared measurements on the adsorption of both reactants and products on the various catalysts to access to reaction mechanisms.

To relate the catalytic properties of metal oxides to their acidity and basicity, scales are needed. Two approaches can be used, according to whether they are based on calculations of electronegativity or on experimental determinations using probe molecules.[15–17]

Lewis acidity and basicity of oxides connected with electron-accepting and electron-donating properties could be expressed by the electronegativity scale; the larger the electronegativity, the stronger the electron-accepting power. An increase in basic strength should correspond to an increase in the negative charge on the oxygen. A positive charge on the cations in metal oxides would affect their Lewis acidity. Using the Sanderson electronegativity scale and the equation for the charge calculation[18]

$$\delta_E = \frac{S_m - S_E}{2.08\sqrt{S_E}}$$

where δ_E is the average partial charge on the atom E, S_m is the average electronegativity of the molecule (metal oxide), and S_E is the electronegativity of the atom E, one can calculate an average partial charge on the atoms of the oxides used. The negative charge on the oxygen increases in the following order:

$$TiO_2 = ZrO_2 < Al_2O_3 < MgAl_2O_4 < MgO$$

The positive charge on the cations increases in the following order:

$$MgO < TiO_2 = ZrO_2 < Al_2O_3$$

The probe molecule adsorption method can give informations on both the number and the strength of active sites. The number of basic sites measured by SO_2 adsorption varies in the following order:[19]

$$TiO_2 \approx Al_2O_3 < MgAl_2O_4 < ZrO_2 < CeO_2 < MgO$$

On the basis of literature data[15,16,19–21] one can propose the following order for Lewis basicity:

$$\gamma\text{-}Al_2O_3 < MgAl_2O_4 < TiO_2\text{ anatase} < TiO_2\text{ rutile} < ZrO_2 < MgO$$

This order is not precise since it is deduced from results obtained

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TABLE I: Origin and Surface Area of the Various Metal Oxides Used

metal oxide	preparation method or origin	surface area [$m^2\ g^{-1}$]
MgO	prepared from $Mg(OH)_2$	70
ZrO_2	prepared from isopropylate	80
TiO_2-R (rutile)	Tioxide Intern. Ltd.	28
TiO_2-A (anatase)	Tioxide Intern. Ltd.	85
CeO_2	Rhone-Poulenc	100
$MgAl_2O_4$	Dow	180
γ-Al_2O_3	G.F.S.-Rhône-Poulenc	215
PO_4^{3-}/SiO_2	prepared from $(NH_4)_3PO_4$ impregnation	145

using various probe molecules. Phosphated silica and ceria are not placed in the above sequence since PO_4^{3-}/SiO_2 does not show Lewis basicity but only Brönsted acid sites. As for CeO_2, it was tested with probe molecules such as CO and SO_2[15] and showed highly basic O^{2-} sites. However, the author of the quoted paper stated that oxygen can easily be extracted and both CO and SO_2 act as reducers, ceria presenting redox properties. As regards Brönsted basicity, among the metal oxides investigated, current studies show that only zirconia, ceria, and magnesia present strong basic hydroxyls.

The order of the Lewis acid site strength can be proposed as follows:[15]

$$CeO_2 < ZrO_2 < TiO_2 < \gamma\text{-}Al_2O_3$$

Both methods lead to a similar scale of Lewis acidity but disagree somewhat for the basicity which remains a difficult property to investigate.

Experimental Section

Characteristic of Catalysts. The metal oxides were chosen due to their variety of acid–base strengths.[15–24] Their characteristics are presented in Table I. The surface area of the samples was measured by the nitrogen BET technique.

Catalytic Experiments. The continuous flow technique was used to measure the catalytic activity of metal oxides; 0.2-g samples were used. The powdered oxides were tabletted without binder, ground, sieved to the 0.5–10-mm-diameter range, and activated for 4 h in situ under a pure and dried helium flow at 673 K.

Mixtures containing H_2S (2.5, 1.25, and 0.625 vol %, depending on the desired H_2S:CH_3OH molar ratio), methanol (1.25 vol %) and helium as a carrier gas were passed through the catalyst bed and then into a gas chromatograph. The total pressure was 1 atm, and the flow rate was $2.4 \times 10^{-4}\ m^3\ h^{-1}$.

The GC analyses were performed using a SRI 8610 gas chromatograph with two detectors: a flame ionization detector (FID) and a flame photometric detector (FPD). The separation of reactants and products occurred at 338 K on a capillary column with Porapak Q. A computer analysis of the detected products was employed.

The catalytic experiments were conducted at 623 K using various H_2S:CH_3OH molar ratios: 2:1, 1:1, and 0.5:1. The catalytic activity was presented by percent of methanol conversion. The selectivity was determined as a ratio of the product yield to the methanol conversion (percent).

IR Measurements. The adsorption of H_2S and CH_3OH as well as their interaction on the various catalysts were studied using infrared spectroscopy. Before the adsorption experiments, metal oxides were activated in the 573–673 K range in a vacuum for 2 h.

Two different kinds of experiment were performed according to whether CH_3OH was adsorbed first and next H_2S was added or H_2S was first adsorbed and next CH_3OH was admitted.

FT-IR spectra were recorded with a Nicolet MX-1 spectrometer, using self-supporting pressed disks of the pure metal oxide powders. The spectra of activated catalysts were automatically subtracted.

Results

Catalytic Experiments. Previous results on zeolites were obtained from the reaction between CH_3OH and H_2S at 523 and 623 K.[9,10] Due to the lower activity of metal oxides used in this study, alumina excepted, the catalytic experiments were performed at 623 K.

According to the reactions' stoichiometry

$$CH_3OH + H_2S \rightleftarrows CH_3SH + H_2O \qquad (1)$$

$$2CH_3OH + H_2S \rightleftarrows (CH_3)_2S + 2H_2O \qquad (2)$$

one can expect that for methanethiol formation, the best H_2S:CH_3OH molar ratio should be 1:1, and for dimethyl sulfide formation, it should be 1:2 (in this paper, this ratio is denoted 0.5:1 because the same concentration of methanol in flow was maintained in all the experiments).

Tables II and III report activity and selectivity of the investigated samples for various H_2S:CH_3OH molar ratios. Usually, at the beginning of the reaction, the conversion of methanol is slightly lower than at the stationary state and in the case of CeO_2 (0.5:1) even very low.

For the sake of clarity, Figure 1A shows the activity, at the stationary state (reached after about 1 h) of the various metal oxides used, except for PO_4^{3-}/SiO_2 which was found to be inactive. The samples are ordered according to increasing activity. However, it appears that activity depends on the H_2S:CH_3OH molar ratio (Table III), being generally higher when an excess of H_2S is used, except for γ-alumina, the most active catalyst. When using the 0.5:1 molar ratio, as favorable for $(CH_3)_2S$ formation, activity is always the lowest.

The main products formed are methanethiol and dimethyl sulfide. Methane is also produced on both titania samples, ceria, zirconia and alumina. Comparison of Tables II and III shows that selectivity varies with time on stream and with the H_2S:CH_3OH molar ratio. For instance, for titania anatase, zirconia, ceria, and alumina, the selectivity toward dimethyl sulfide increases from the initial step to the stationary state using H_2S:CH_3OH molar ratio of 1:1. This could be explained invoking first the formation of CH_3SH and next, transformation to $(CH_3)_2S$, according to Mashkina et al.[5,6] However, when methane is produced in large amounts as on ceria, both selectivities to methanethiol and dimethyl sulfide increase with time on stream.

A diagram presenting the activity and selectivity of the most active samples (γ-Al_2O_3, CeO_2, TiO_2-A, and ZrO_2) is plotted in Figure 1B. It refers to results obtained at the stationary state using a H_2S:CH_3OH ratio of 1:1. Among the samples described, titania (anatase) and alumina show the highest selectivity toward dimethyl sulfide. Zirconia is a catalyst presenting a medium activity and very high selectivity toward methanethiol. The other catalysts which are quite selective toward CH_3SH but less active than ZrO_2 are TiO_2 rutile and $MgAl_2O_4$ (Table III). Ceria appears to be a very interesting catalyst since it produces the highest amount of methane and shows high selectivity toward methanethiol. The lability of CeO_2 oxygen atoms is well-known.[15] It is possible that under H_2S flow, some of these oxygen atoms are exchanged for sulfur. The sulfidation state of all samples used will be the subject of further study.

At the stationary state, the orders of activity and selectivity are those summarized in Table IV. The order of the catalyst activity (methanol conversion) does not depend on the H_2S:CH_3OH molar ratio, except for CeO_2. The presented sequences clearly show the highest activity of γ-alumina and the lowest activity of the strongest basic oxide (MgO), taking into account that PO_4^{3-}/SiO_2 is not active. Like the selectivities, they strongly

TABLE II: Activity and Selectivity of Catalysts at the Initial Step of the Reaction

conversion, selectivity, %	catalyst							
	PO_4^{3-}/SiO_2	MgO	$MgAl_2O_4$	TiO_2(R)	ZrO_2	TiO_2(A)	CeO_2	γ-Al_2O_3
CH_3OH conversion, %								
$H_2S:CH_3OH$ = 2:1	0	2	39	30	70	94	60	97
1:1	0	2	14	27	30	54	64	90
0.5:1	1	2	12	10	15	35	4	33
CH_3SH select., %								
$H_2S:CH_3OH$ = 2:1	0	100	84	96	99	52	76	50
1:1	0	100	93	91	99	53	41	4
0.5:1	0	100	100	81	96	27	0	0
$(CH_3)_2S$ select., %								
$H_2S:CH_3OH$ = 2:1	0	0	16	2	1	47	0	50
1:1	0	0	0	2	1	40	2	95
0.5:1	0	0	0	0	0	60	0	86
CH_4 select., %								
$H_2S:CH_3OH$	0	0	0	2	0	1	24	0
1:1	0	0	0	7	0	7	57	1
0.5:1	0	0	0	19	4	13	100	14

TABLE III: Activity and Selectivity of Catalysts at the Stationary State of the Reaction

conversion, selectivity, %	catalyst							
	PO_4^{3-}/SiO_2	MgO	$MgAl_2O_4$	TiO_2(R)	ZrO_2	TiO_2(A)	CeO_2	γ-Al_2O_3
CH_3OH conversion, %								
$H_2S:CH_3OH$ = 2:1	0	2	32	45	72	91	68	99
1:1	0	3	15	25	34	52	59	99
0.5:1	1	2	14	15	16	32	42	43
CH_3SH select., %								
$H_2S:CH_3OH$ = 2:1	0	100	91	95	96	57	80	46
1:1	0	100	87	91	90	36	50	15
0.5:1	0	100	96	85	100	31	36	2
$(CH_3)_2S$ select., %								
$H_2S:CH_3OH$ = 2:1	0	0	8	3	3	41	1	53
1:1	0	0	1	1	9	57	7	84
0.5:1	0	0	4	3	0	52	1	93
CH_4 select., %								
$H_2S:CH_3OH$ = 2:1	0	0	0	2	1	2	19	0
1:1	0	0	0	8	1	7	43	1
0.5:1	0	0	0	12	0	17	63	5

depend on the $H_2S:CH_3OH$ molar ratio, γ-Al_2O_3 always being most selective toward dimethyl sulfide.

Infrared Measurements. Infrared spectroscopy was applied to study the reaction between methanol and hydrogen sulfide. It is known from the literature[25-30] that in the case of most used samples, the methoxy groups are formed from methanol chemisorption. However, the stability of these chemisorbed species in the hydrosulfurization process conditions is not known.

Figure 2 shows the IR spectra, for various metal oxides, after methanol adsorption at room temperature followed by evacuation at room temperature (spectra 2a), 473 K (2b), and 573 K (2c).

From the intensity variation of the CH stretching bands with the evacuation temperature presented in Figure 2 and in paper[29] for MgO it is possible to determine the thermal stability of methanol chemisorbed species:

$$MgO > ZrO_2 > TiO_2\text{-R} > \gamma\text{-}Al_2O_3 > TiO_2\text{-A}$$

Methoxy groups are also formed on PO_4^{3-}/SiO_2 and their thermal stability is as on magnesia.

IR spectroscopy is able to differentiate species resulting from adsorption of methanol, methanethiol, and dimethyl sulfide as shown for instance on ZrO_2 (Figure 3). The wavenumbers of characteristic bands for the last two adsorbed compounds are reported in Table V allowing one to distinguish them from adsorbed methanol. The best region to distinguish between chemisorbed $(CH_3)_2S$ and CH_3SH is the 1050–900-cm^{-1} range.

The interaction between methanol and hydrogen sulfide on zirconia is presented in Figure 4. Adsorption of methanol at 623 K followed by evacuation at the same temperature leads to the formation of two types of methoxy group characterized by ν(CO) bands at 1152 (type I) and 1044 cm^{-1} (type II).[25] Admission of hydrogen sulfide at room temperature does not change the wavenumber of the ν(CO) methoxy bands but only slightly influences their intensity (Figure 4b). Heating at 623 K leads to the disappearance of bands due to the methoxy groups and formation of new IR bands (Figure 4c). Most of them can be assigned to the organic sulfur compounds, CH_3SH and $(CH_3)_2S$, on the basis of the results presented in Table V. A shoulder at about 960 and a band at 2845 cm^{-1} characterize the formation of methanethiol. Bands at 980, 1032, 1435 and ca. 2980 cm^{-1} are assigned to adsorbed dimethyl sulfide. These results show that methoxy groups formed upon methanol chemisorption react at 623 K with H_2S toward methanethiol and dimethyl sulfide. The bands at 1372, 1386, and 1583 cm^{-1} observed in Figure 4c most probably originate from formate species which can be formed during the transformation of methanol.[31]

Formate species were also formed on alumina after reaction between chemisorbed methanol and hydrogen sulfide at 623 K. They were accompanied by bands originating from methanethiol and dimethyl sulfide. The reverse sequence, i.e., first adsorption of H_2S and next that of CH_3OH, led to the formation, at 623 K, not only of formate species and sulfur organic compounds but also of methane, characterized by bands at 3017 and 1306 cm^{-1} disappearing after evacuation at room temperature.

On anatase, no formate species were formed but, in addition to those due to organic sulfur compounds, a band was noted at 1620 cm^{-1}, due to the formation of water, the other reaction product.

IR measurements carried out on PO_4^{3-}/SiO_2 and MgO confirmed the results obtained in the dynamic system, indicating that neither sample is active in the hydrosulfurization of methanol. Figure 5 presents the spectra for PO_4^{3-}/SiO_2. After activation of the catalyst, two ν(OH) bands are observed at 3740 and 3663 cm^{-1}, due to SiOH and POH groups, respectively. The adsorption

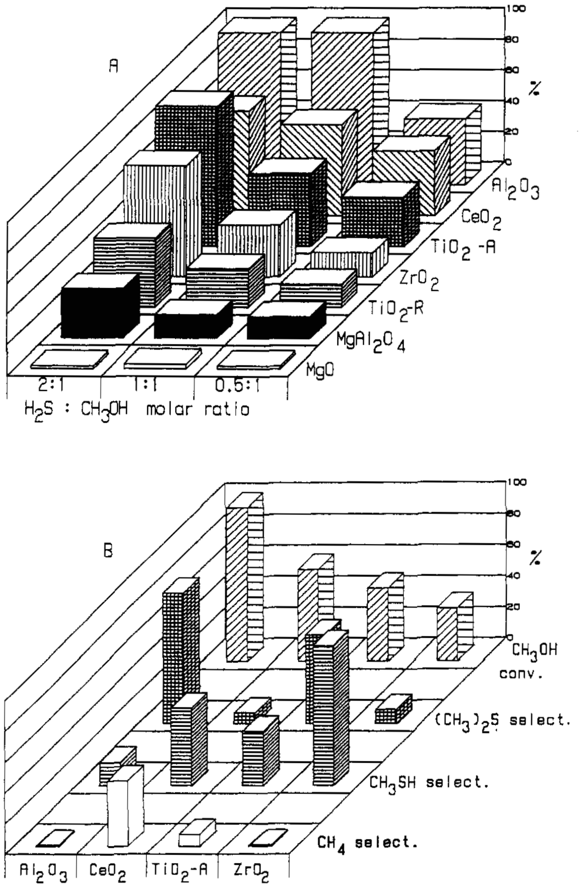

Figure 1. (A) Methanol conversion at the stationary state of the $CH_3OH + H_2S$ reaction, using various reactant molar ratios. (B) Activity and selectivity of metal oxides at the stationary state of the reaction; H_2S:CH_3OH = 1:1.

TABLE IV: Sequences of the Activities and Selectivities at the Stationary State of the Reaction

CH_3OH conversion	
$H_2S:CH_3OH = 2:1$	γ-Al_2O_3 > TiO_2(A) > ZrO_2 > CeO_2 > TiO_2(R) > $MgAl_2O_4$ > MgO
1:1	γ-Al_2O_3 > CeO_2 > TiO_2(A) > ZrO_2 > TiO_2(R) > $MgAl_2O_4$ > MgO
0.5:1	γ-Al_2O_3 > CeO_2 > TiO_2(A) > ZrO_2 > TiO_2(R) > $MgAl_2O_4$ > MgO
CH_3SH selectivity	
$H_2S:CH_3OH = 2:1$	MgO > ZrO_2 > TiO_2(R) > $MgAl_2O_4$ > CeO_2 > TiO_2(A) > γ-Al_2O_3
1:1	MgO > TiO_2(R) > ZrO_2 > $MgAl_2O_4$ > CeO_2 > TiO_2(A) > γ-Al_2O_3
0.5:1	MgO > ZrO_2 > $MgAl_2O_4$ > TiO_2(R) > CeO_2 > TiO_2(A) > γ-Al_2O_3
$(CH_3)_2S$ selectivity	
$H_2S:CH_3OH = 2:1$	γ-Al_2O_3 > TiO_2(A) > $MgAl_2O_4$ > TiO_2(R) = ZrO_2 = CeO_2 > MgO = 0
1:1	γ-Al_2O_3 > TiO_2(A) > CeO_2 > ZrO_2 > $MgAl_2O_4$ = TiO_2(R) > MgO = 0
0.5:1	γ-Al_2O_3 > TiO_2(A) > $MgAl_2O_4$ > TiO_2(R) > CeO_2 > ZrO_2 = MgO = 0

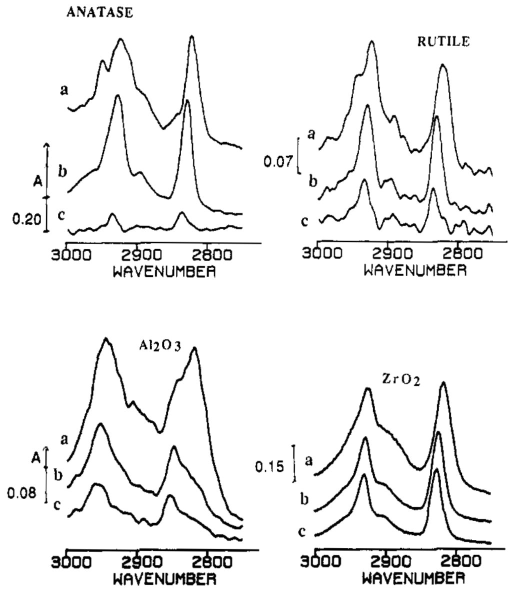

Figure 2. Infrared spectra of methanol adsorbed species after evacuation: (a) at room temperature, (b) at 473 K, and (c) at 573 K on TiO_2 anatase and rutile, alumina, and zirconia.

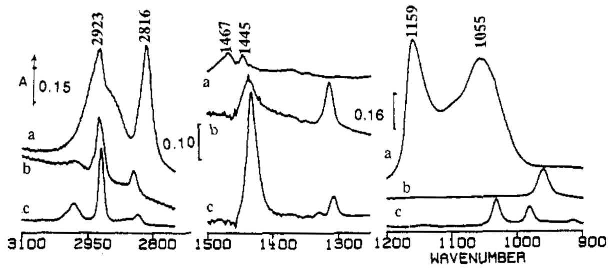

Figure 3. Comparison of IR spectra of the adsorbed species given by (a) CH_3OH, (b) CH_3SH, and (c) $(CH_3)_2S$ at room temperature on ZrO_2.

TABLE V: Wavenumbers of Some Characteristic Bands for CH_3SH and $(CH_3)_2S$ Adsorbed on ZrO_2 Allowing Distinction of Organic Sulfur Compounds from Methanol Adsorbed Species

compound	CH str [cm^{-1}]	CH bend [cm^{-1}]
CH_3SH	2990	1420
	2846	1307
		960
$(CH_3)_2S$	2983	1432
	2834	1329
		1308
		1032
		980
		913

of methanol at room temperature leads to a decrease of their intensity and to the formation of methoxy species. Admission of H_2S followed by heating at 623 K does not show any new band originating from reaction products. The slight decrease in ν-(CH_3) bands intensity was also observed after heating the sample without H_2S and could be due to a partial desorption of methoxy species during heating.

Discussion

To relate the catalytic activity and selectivity of metal oxides to their acidic–basic properties, we first use the Sanderson scale. The charge on the oxygen atom for most samples investigated is plotted in Figure 6 along with the activity and selectivity results in the reaction between methanol and hydrogen sulfide (H_2S:CH_3OH = 1:1). For other molar ratios, the plots present the same tendency. The medium oxygen charge, the highest activity and selectivity toward dimethyl sulfide are observed. Simultaneously, the lowest selectivity to CH_3SH is noted on the sample with medium oxygen charge. The samples on the left- and right-hand sides of alumina, i.e., the solids presenting low and high oxygen charge, are less active and selective toward $(CH_3)_2S$ but more selective toward CH_3SH.

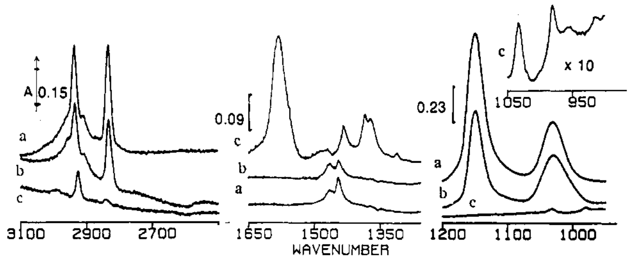

Figure 4. Infrared spectra of adsorbed species on ZrO_2 (a) after CH_3OH addition and evacuation at 623 K, (b) then admission of H_2S at room temperature, and (c) then heating at 623 K.

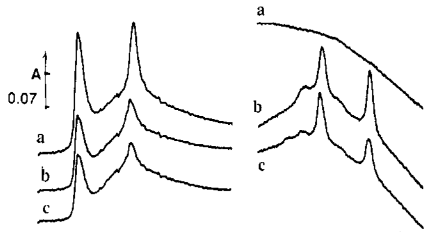

Figure 5. Infrared spectra of PO_4^{3-}/SiO_2 (a) after treatment at 673 K, (b) after CH_3OH admission and evacuation at room temperature, and (c) then evacuation at 623 K.

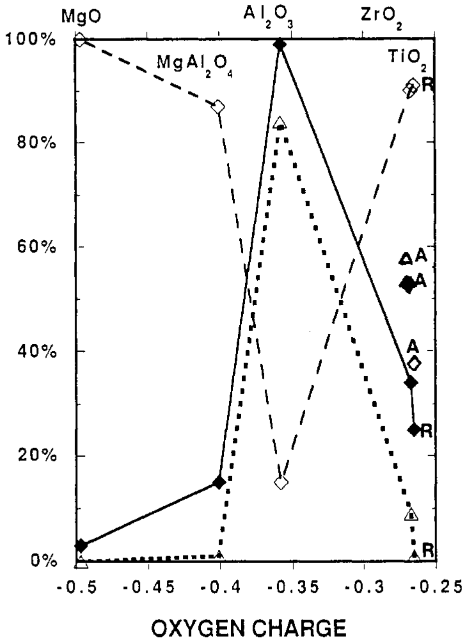

Figure 6. Activity and selectivity in methanol hydrosulfurization (H_2S: CH_3OH = 1:1) as a function of calculated oxygen charge for various metal oxides: (—) CH_3OH conversion, (- - -) CH_3SH selectivity, (· · ·) $(CH_3)_2S$ selectivity. A, anatase, R, rutile.

For the same samples, the relation between average partial charge on cations and activity and selectivity in the hydrosulfurization process is presented in Figure 7. One can see that the activity and selectivity toward $(CH_3)_2S$ increase with cation charge. The reverse is observed for selectivity toward CH_3SH. Since the spinel $MgAl_2O_4$ contains two cations presenting quite different charges, it is not considered in the plot.

The results presented in Figures 6 and 7 confirm the conclusions of Mashkina et al.[6] who have found, for other catalysts, that the most effective metal oxides for dimethyl sulfide synthesis are those that present strong Lewis acid sites and medium basic sites.

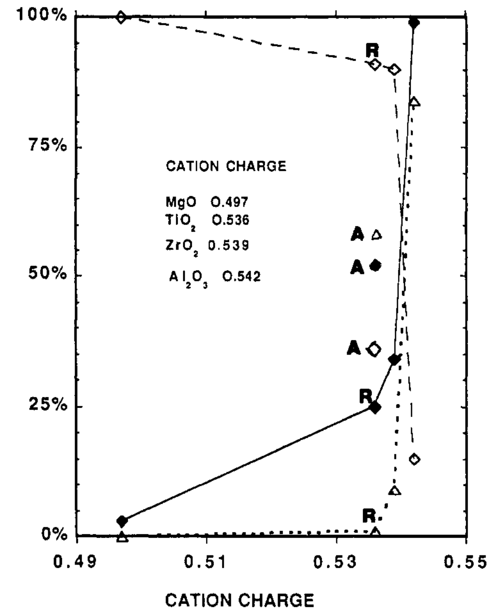

Figure 7. Activity and selectivity in methanol hydrosulfurization (H_2S: CH_3OH = 1:1) as a function of calculated cation charge for various metal oxides: (—) CH_3OH conversion, (- - -) CH_3SH selectivity, (· · ·) $(CH_3)_2S$ selectivity. A, anatase; R, rutile.

The presented plots (Figures 6 and 7) are based on theoretical calculations of cation and oxygen charges. One should note that the two titania samples, which have the same chemical composition, i.e., the same calculated oxygen and cation charges, present a different activity and selectivity, showing that other factors play an important role. Therefore the discussion should be extended to considerations based on experimental measurements of surface acidity and basicity.

The order given for the number of basic sites measured by SO_2 adsorption[19]

$$TiO_2 \approx Al_2O_3 < MgAl_2O_4 < ZrO_2 < CeO_2 < MgO$$

is in good agreement with the reverse order of the dimethyl sulfide selectivity (Table IV), in particular for a H_2S:CH_3OH molar ratio of 2:1: the rarer the basic sites, the higher the selectivity to dimethyl sulfide.

The strength of active sites for Lewis acidity and basicity, measured with probe molecules[15–17,19–21] and mentioned in the Introduction, can be compared to results on the hydrosulfurization process summarized as sequences of activity and selectivity (Table IV): (i) the highest basicity of metal oxides (MgO) leads to the lowest activity and the highest selectivity to methanethiol; (ii) the lowest strength of basic sites (γ-Al_2O_3) implies the highest activity and the highest selectivity to dimethyl sulfide. The activity and selectivity of other samples do not bear a simple relationship to their basicity or acidity. This can be explained, taking into account the fact that they have pairs of Lewis acid and base centers which are involved in the reaction between methanol and hydrogen sulfide, as concluded by Mashkina et al.[1–8] Indeed, the adsorption of both methanol and hydrogen sulfide requires oxygen and cation sites acting as Lewis base and acid centers.[25–29]

Our results confirm that methanol has to be chemisorbed in the form of methoxy groups to react with hydrogen sulfide. It is well-known that methoxy species formation requires pairs of acidic–basic centers.[25–29] On basic catalysts, the first step of the formation of methoxy species is methanol interaction with O^{2-} sites leading to H-bonded species; on acidic oxides, the first step is the formation of coordinated methanol species.[15] However, the formation of methoxy species is not the only factor to consider since such species are formed on MgO and phosphated silica, both oxides being inactive toward the hydrosulfurization process (Table II and III). The strength of methanol chemisorption has also to be taken into account; if the methoxy species are too strongly held, they do not react with H_2S (Figures 2 and 5).

The question about the active form of adsorbed H_2S is still open. Mashkina et al.[4] proposed a mechanism involving methoxy and HS^- species, but in a recent paper, using NMR,[8] they also suggest that H_2S molecules can react with methoxy groups.

Literature results show that H_2S adsorption on MgO leads to the exchange of a few surface oxygens by sulfur[32] according to the reaction

$$H_2S + O_{surf}^{2-} \rightarrow H_2O + S_{surf}^{2-}$$

The stability of methoxy species and the lack of HS^- formation explain the very weak activity of magnesia. The same reasons can be invoked in the case of phosphated silica. By contrast, HS^- is one of the chemisorbed forms of H_2S on alumina.[33-35] This species is stable at high temperature,[35] whereas methoxy groups are not too strongly held, thus explaining the highest activity of this oxide. Among the other metal oxides, it has been reported that H_2S chemisorption on anatase does not lead to HS^- species up to 623 K.[36,37] In such a case, the hydrosulfurization reaction would occur between methoxy species and H_2S molecules. Good activity is observed nevertheless (Figure 1).

The last point to be discussed is the difference in activity and selectivity between the two titania samples. Anatase and rutile present different surface properties as shown for instance by methanol adsorption:[30] on rutile, dissociative adsorption occurs at room temperature, whereas on anatase, coordinated species are first formed giving rise, after heating, to methoxy groups. Differences have also been noted on H_2S adsorption since, on rutile, an additional irreversibly adsorbed species have been reported.[36] This difference in behavior has been related to structural effects.[30,36]

For this reason, correlations of catalytic activity to surface properties determined by probe molecules appear more appropriate that those obtained by Sanderson's calculations of electronegativity.

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