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Catalytic synthesis of methanethiol from hydrogen sulfide and carbon monoxide over vanadium-based catalysts

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Abstract

The direct synthesis of methanethiol, CH_3SH, from CO and H_2S was investigated using sulfided vanadium catalysts based on TiO_2 and Al_2O_3. These catalysts yield high activity and selectivity to methanethiol at an optimized temperature of 615 K. Carbonyl sulfide and hydrogen are predominant products below 615 K, whereas above this temperature methane becomes the preferred product. Methanethiol is formed by hydrogenation of COS, via surface thioformic acid and methylthiolate intermediates. Water produced in this reaction step is rapidly converted into CO_2 and H_2S by COS hydrolysis.

Titania was found to be a good catalyst for methanethiol formation. The effect of vanadium addition was to increase CO and H_2S conversion at the expense of methanethiol selectivity. High activities and selectivities to methanethiol were obtained using a sulfided vanadium catalyst supported on Al_2O_3. The TiO_2, V_2O_5/TiO_2 and V_2O_5/Al_2O_3 catalysts have been characterized by temperature programmed sulfidation (TPS). TPS profiles suggest a role of V_2O_5 in the sulfur exchange reactions taking place in the reaction network of H_2S and CO.

Keywords: Methanethiol; Carbon monoxide; Hydrogen sulfide; COS; Hydrolysis; TPS; Catalysts; Supported; Vanadium oxide; Vanadium sulfide; Titania; Alumina

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1. Introduction

Supported vanadia-based catalysts are mainly known for their activity in selective oxidation reactions [1] and the selective catalytic reduction (SCR) of NO_x with ammonia [2]. In these applications, the vanadia is usually present as a two-dimensional surface overlayer and primarily present as surface V(5+) species. The catalytic activity of supported vanadia catalysts in the sulfided state has not been extensively investigated. Research on sulfided supported vanadia catalysts is primarily related to the presence of vanadium containing porphyrins in oil, which affect the performance of hydrotreating catalysts [3]. Furthermore, vanadium sulfides are active in the decomposition of H_2S into elemental sulfur and hydrogen (at relatively high temperatures) [4]. This paper reports on another application of sulfided supported vanadia catalysts: the synthesis of methanethiol from H_2S and CO.

Methanethiol (also referred to as methyl mercaptan) is a raw material used in the synthesis of plastics and agricultural products [5]. A conventional synthesis route is thiolation (reaction of H_2S with methanol), which has been extensively investigated by Mashkina et al. [6]. An alternative synthesis route has been proposed and patented by Ratcliffe and Tromp [7], which

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comprises the reaction of CO and H_2S over TiO_2 (rutile) catalysts as well as supported vanadia/titania catalysts [8]. Although Beck et al. [9–11] published several papers on the fundamentals of the interactions of H_2O, H_2S, CO, and methanethiol with titania, the supported vanadia/titania catalyst system has not been investigated in detail. The product compositions presented in [8] are inconclusive, and little information is given on the role of vanadia in the supported catalyst. In this paper, a reaction network of the various elementary steps in the reaction between H_2S and CO over supported vanadia/titania catalysts will be presented. Furthermore, the study also makes a comparison between the catalytic performance of titania, vanadia/titania, and vanadia/alumina catalysts. Finally, various hypotheses to explain the role of the different oxide supports and active surface vanadia phases in the reaction will be discussed, based on temperature programmed sulfidation (TPS) profiles and literature data.

2. Experimental

2.1. Catalysts

Titania and supported vanadia/titania catalysts were received from Degussa. The catalysts consisted of TiO_2-P25 tablets, 1 wt.% V_2O_5 impregnated on TiO_2 and 4 wt.% V_2O_5 impregnated on TiO_2, which were subsequently crushed and sieved. Fractions of 0.3–0.833 mm (20–50 mesh) were used without further pretreatment. The BET surface area of the titania-based catalysts was $\sim 50\,m^2/g$. Thus, the surface vanadia coverage corresponded to ∼20 and ∼80% of a monolayer on the titania support for the 1 and 4% supported vanadia catalysts, respectively. A catalyst consisting of 10 wt.% V_2O_5 impregnated on alumina was received from Engelhard and was also crushed and sieved to 20–50 mesh without further pretreatment. The BET surface area of the V_2O_5/Al_2O_3 catalyst was $\sim 140\,m^2/g$, which corresponds to ∼70% monolayer surface vanadia coverage on the alumina support.

2.2. Reaction conditions

Experiments were performed in a stainless steel tube reactor (ID 8 mm) incorporated in a setup consisting of Brooks 5850E mass flow controllers (H_2S, CO, and H_2), an electronic pressure transducer, a heated transfer line, and a gas chromatograph (SRI-GC Model 8610C). CO (Praxair) was purified from nickel carbonyl with an alumina trap at 120 °C. The GC was equipped with a Valco automated gas sampling valve, a TCD detector, and a Restek RT-sulfur column (2 m, 1/8 in. diameter) for separation of H_2, CO, CH_4, CO_2, COS, methanethiol, and dimethylsulfide (DMS). The carrier gas could be switched from He to Ar, to allow for a better determination of the H_2 concentration in the product stream. Experiments were performed in mixtures of pure H_2S and CO (over the temperature range of 575–675 K and pressure range of 1–14 bar). The flow rate of the product stream was continually monitored to allow calculation of the conversion and selectivity. The product compositions were corrected for the volumetric change resulting from the reaction, assuming that the volume changed linearly as a function of residence time. The carbon, oxygen, sulfur, and hydrogen balances were usually closed within 3%. A NaOH/NaOCl aqueous solution was used to trap the sulfur species present in the product stream.

To study the effect of temperature on catalyst performance, an experiment was performed using 1 g of catalyst in a total flow of 10 ml/min of a 1:1 mixture of H_2S and CO at atmospheric pressure. The catalyst was initially exposed to the reaction mixture at room temperature, followed by a linear temperature increase with a rate of 10 K/min up to 523 K. Subsequently, the reaction temperature was varied with intervals of 25 K between 523 and 673 K, and the catalyst was reacted isothermally for 1 h at each temperature before activity and selectivity data were collected. Since the catalysts were heated in a 3-zone furnace from autoclave engineers fitted with several thermo-couples, the temperature was uniform throughout. After the highest temperature experiment was conducted, a low temperature experiment was repeated to assure that the state of the catalyst had not changed.

Other experiments were performed isothermally at 615 K, varying the H_2S and CO flow rates to study the effect of the residence time on the product distribution. To study the effect of H_2O on the reaction pathway, H_2O was added with a high pressure peristaltic pump (Rainin Rabbit HP pump) at variable injection rates.

Catalyst comparison was typically performed using 2 g of catalyst, a flow of 5 ml/min of a mixture of CO and H_2S (1:1), and a temperature of 615 K.

2.3. Temperature programmed sulfidation (TPS)

TPS Experiments were performed in an atmospheric flow reactor [3]. The sample weight varied between 50 and 150 mg. The catalyst was diluted with 100 mg of SiC, to ensure a homogeneous catalyst bed temperature, and to reduce pressure drop. The gas mixture for the sulfiding studies consisted of 3 mol% H_2S, 25 mol% H_2 and 72 mol% Ar (total flow rate 28 μmol/s) at a pressure of 1 bar. The catalyst was initially exposed to the TPS mixture at room temperature for 30 min and the temperature was subsequently increased with a heating rate of 10 K/min to 1273 K. Finally, the catalyst temperature was maintained at 1273 K for 30 min in the TPS gas mixture.

3. Results

3.1. Evaluation of reaction pathway

Fig. 1 shows the carbon containing product distribution from the reaction of H_2S with CO (1:1 feed ratio) at a pressure of 1 bar as a function of temperature over the 4 wt.% V_2O_5/TiO_2 catalyst. COS is the main product of the reaction, followed by CO_2, CS_2 and methanethiol. The methanethiol abundance shows a maximum at approximately 615 K and methane becomes a significant product above this temperature. The CO conversion increased from 15% at 575 K to 36% at 650 K and the conversion of H_2S varied from 12% at 575 K to 28% at 650 K (not shown). The optimized methanethiol yield in the present experiment amounts to 0.35 mmol h^{-1} g_{cat}^{-1}.

The evolution of carbon selectivity as a function of CO conversion is presented in Fig. 2. This plot reveals that COS is the primary product of the reaction of CO and H_2S. As the CO conversion increases, the relative contribution of COS to the amount of products decreases, whereas all the other products increase. This suggests that COS is the primary reaction product and that all the other products are due to secondary reactions from the consecutive reactions of COS. The optimized methanethiol yield at 60% CO conversion amounts to 0.4 mmol h^{-1} g_{cat}^{-1}.

The methanethiol selectivity shown in Fig. 2 was calculated using the total amount of methanethiol and twice the amount of DMS formed. Under the conditions of high CO conversion (low space velocities), approximately 50% of the methanethiol formed was

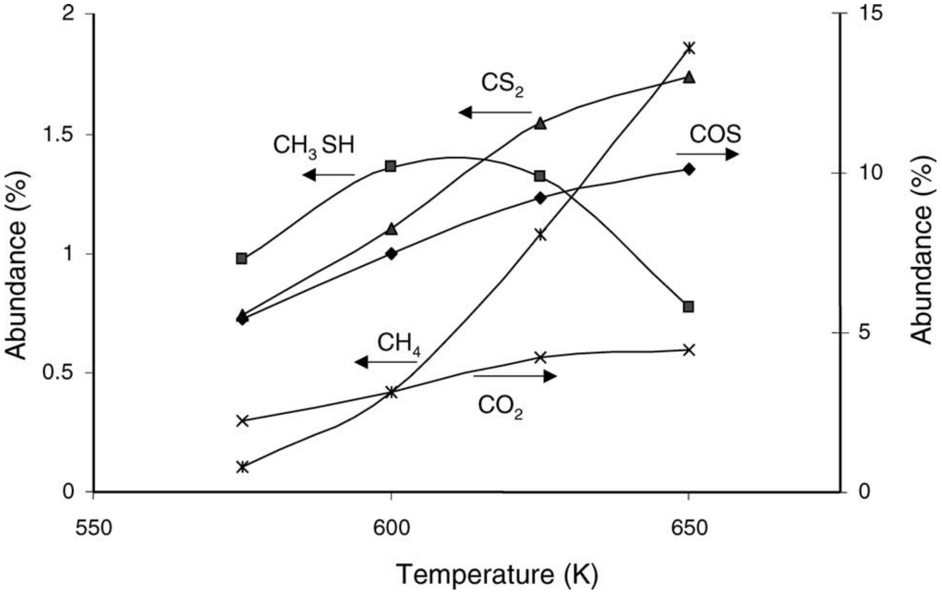

Fig. 1. Distribution of carbon containing products as a function of temperature over 1 g of a 4 wt.% V_2O_5/TiO_2 catalyst. Conditions: 1 bar; $CO:H_2S = 1:1$; total flow: 10 ml/min.

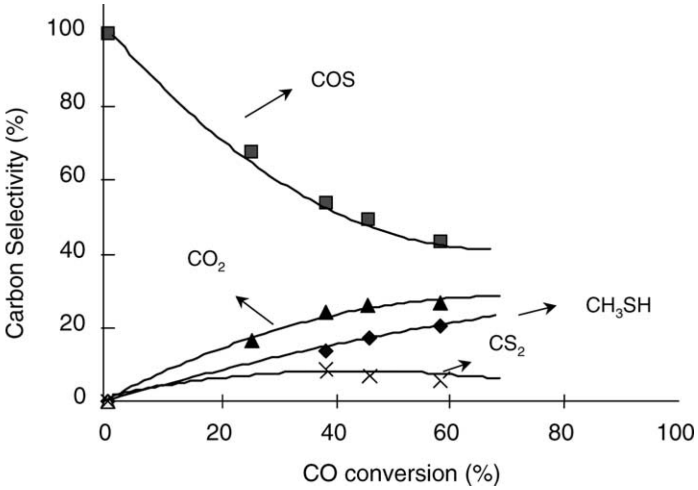

Fig. 2. Distribution of carbon containing products as a function of CO conversion at 615 K over 1 g of a 4 wt.% V_2O_5/TiO_2 catalyst. Conditions: 1 bar; $CO:H_2S = 1:1$; variable flow rate.

converted to DMS. The highest CO conversion measured at 615 K was thermodynamically limited at approximately 60% at 1 bar, and the corresponding H_2S conversion being 40%. A similar experiment was also conducted at higher pressures (not shown). The results obeyed what was expected based on thermodynamics: less quantities of COS and CS_2, and higher quantities of methanethiol were obtained at the high pressures.

The effect of water on the product composition (CO_2, COS and CH_3SH) is presented in Fig. 3. Small amounts of water only slightly affect the selectivity and activity of the catalyst. At higher water concentrations, the selectivity to methanethiol and COS decreases and eventually becomes zero. The main carbon containing product observed in the experiment with water was CO_2. Interestingly, the conversion of CO was not affected by the presence of H_2O.

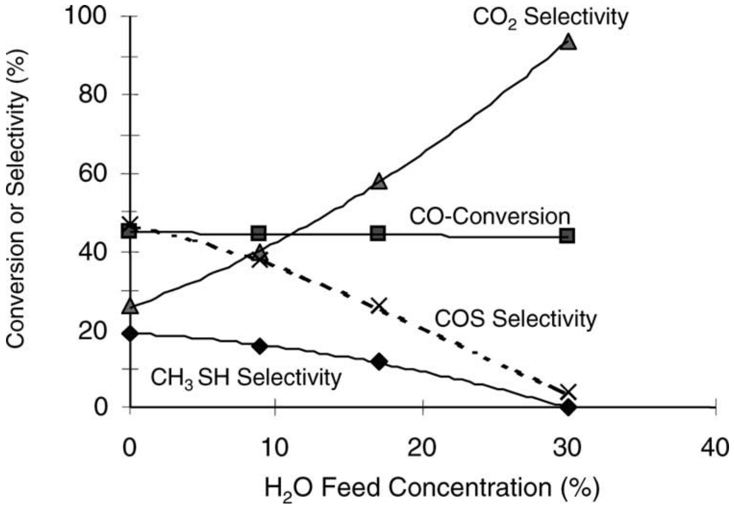

Fig. 3. Effect of water concentration on methanethiol selectivity and CO conversion at 615 K. Conditions: 4 wt.% V_2O_5/TiO_2 catalyst; 1 bar; $CO:H_2S = 1:1$.

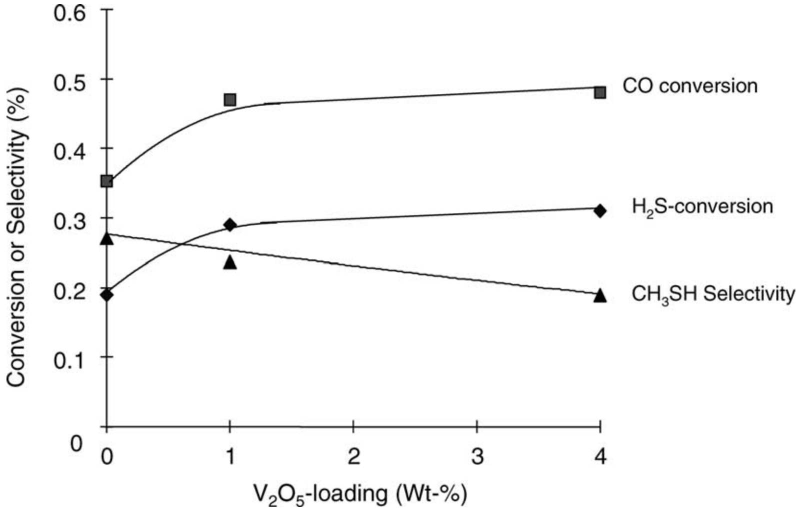

Fig. 4. Effect of vanadia content on catalyst performance at 615 K. Conditions: 2 g of catalyst; 1 bar; CO:H_2S = 1:1; total flow: 5 ml/min.

3.2. Effect of catalyst composition

The effect of the vanadia loading on the catalytic performance of the TiO_2 catalysts is shown in Fig. 4. Compared to bare TiO_2 support, the CO and H_2S conversion is significantly increased by adding 1 wt.% vanadia, while a decrease in methanethiol selectivity is observed. This is related to significantly higher concentrations of COS and CS_2 in the product stream when the vanadia containing catalyst was used. Therefore, similar yields in the order of 0.35 mmol h^{-1} g_{cat}^{-1} methanethiol are obtained. An increase of the vanadia loading from 1 to 4 wt.% does not significantly enhance the conversion (which is not thermodynamically limited under the experimental conditions).

Titania is not a prerequisite to obtain methanethiol from H_2S and CO. Fig. 5 shows that a high CO conversion was also obtained with a supported

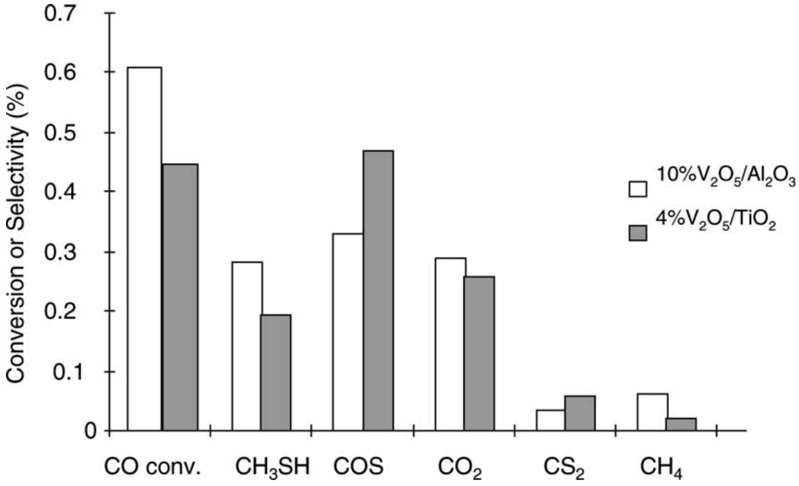

Fig. 5. Comparison of performance at 615 K of 4 wt.% V_2O_5/TiO_2 and 10 wt.% V_2O_5/Al_2O_3. Conditions: 2 g of catalyst; 1 bar; CO:H_2S = 1:1; total flow: 5 ml/min.

vanadia/alumina catalyst. A lower selectivity to COS and CS_2 was obtained with the vanadia/alumina catalyst than the vanadia/titania catalyst (4% V_2O_5/TiO_2). On the other hand, the vanadia/alumina catalyst exhibited higher selectivity towards CH_3SH, CO_2 and methane. Fig. 5 also gives a good impression of the final product ratio: the vanadia/alumina catalyst yielded an almost 1:1:1 ratio of COS:CO_2:methanethiol. In fact the vanadia/alumina catalyst is at thermodynamic equilibrium. Therefore, a direct comparison of the yields of the catalyst from this experiment is not possible. Nevertheless, the yield determined in this experiment (0.6 mmol MeSH g_{cat}^{-1} h^{-1}) is in the same order of magnitude than a sulfided K/Mo/SiO_2 catalyst, using a H_2/CO/H_2S feed [5].

It should also be mentioned here that the formation of CH_3SH from CH_3OH/H_2S is a much faster and selective reaction. Obviously, using the MeOH-route for methanethiol synthesis requires the synthesis of MeOH, which is a very inefficient process (starting from methane steam reforming). Overall, the direct synthesis from CO/H_2S appears more attractive. The difference in rates between the formation of methanethiol from MeOH/H_2S or H_2S/CO is related to the mechanism: the first reaction proceeds via methoxy surface intermediates, while COS intermediates are important in the latter reaction. This will be further discussed in a following paragraph.

3.3. Catalyst characterization

The TPS patterns of the TiO_2 containing catalysts used in this study are shown in Fig. 6. H_2S uptake is already observed at room temperature, which is typical for vanadia and molybdena containing catalysts [3,13]. The TiO_2 support itself shows very little features in the TPS profile. At the beginning of the temperature ramp, some physisorbed H_2S is desorbed (positive peak in H_2S signal), which is followed by slight H_2S uptake. Only above 625 K is sulfidation of the titania support noticeable, followed by two reduction steps at 1025 and 1195 K, as indicated by the evolution of H_2S (positive H_2S peaks) and the consumption of stoichiometric amounts of hydrogen (not shown). The vanadia containing catalysts show additional features in the TPS profiles. Here, reaction of H_2S with the catalyst can be noticed in the temperature range of 373 K up to 575–605 K (negative H_2S peaks), which is followed by H_2S production and stoichiometric hydrogen consumption (not shown) at 575 and 605 K for

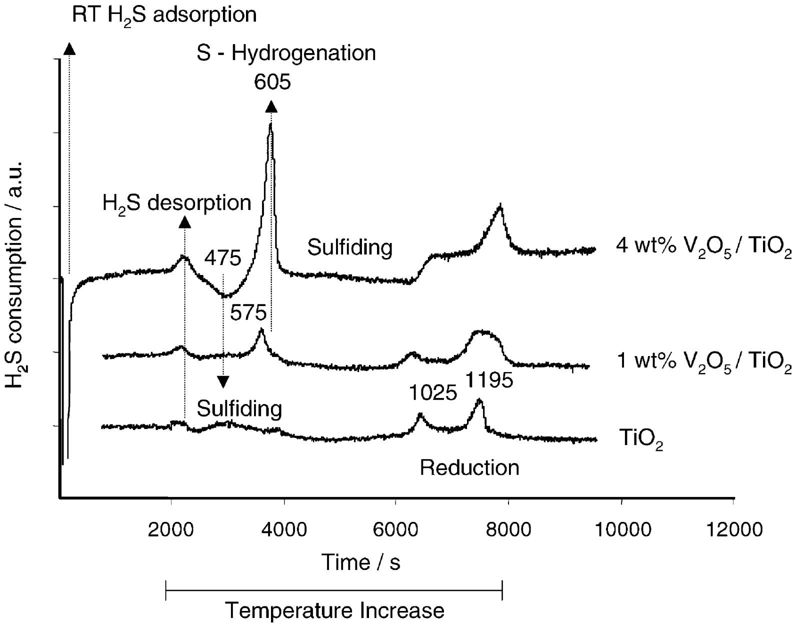

Fig. 6. TPS profiles of the TiO_2-based catalysts (the profiles are normalized to 100 mg sample).

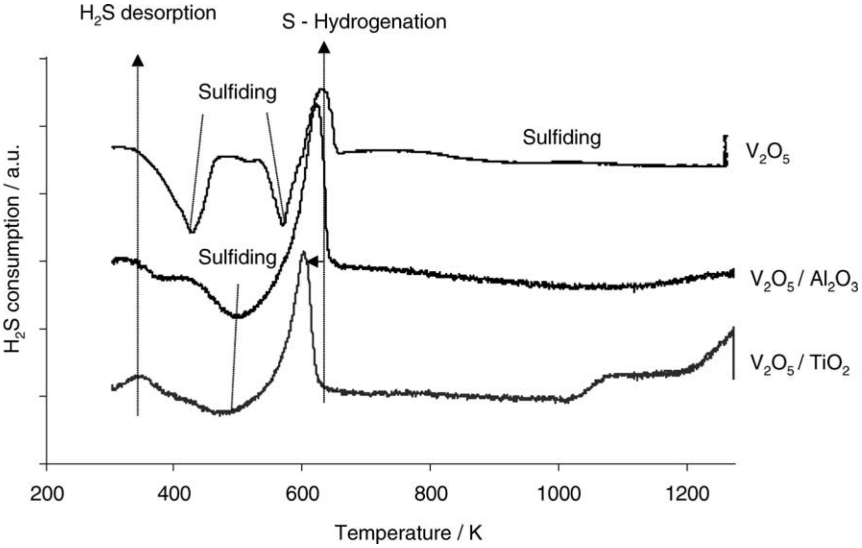

Fig. 7. TPS profiles of vanadium catalysts, compared to bulk V_2O_5 (the profiles are normalized to 100 mg sample).

the 1 and 4 wt.% V_2O_5/TiO_2 catalysts, respectively. The presence of the surface vanadia phase also induces differences in the TPS pattern at high temperatures. However, quantitative determination of the oxidation state of the sulfided phases formed is quite difficult, as elemental sulfur is also produced during the sulfidation experiment, affecting the mass balance [3].

The TPS patterns of bulk V_2O_5, the supported 4 wt.% V_2O_5/TiO_2 and 10 wt.% V_2O_5/Al_2O_3 catalysts are compared in Fig. 7. The TPS patterns of bulk V_2O_5 and 10 wt.% V_2O_5/Al_2O_3 are in good agreement with the profiles reported elsewhere [3,13]. For bulk V_2O_5 two sulfidation steps can be noticed, while these steps are apparently overlapping for the supported catalysts. The maximum rate of H_2S production (positive peaks), occurs at somewhat lower temperature (600 K) for the V_2O_5/TiO_2 catalyst than for the V_2O_5/Al_2O_3 catalyst and bulk V_2O_5.

4. Discussion

Based on the apparent product distribution observed in the various experiments (see e.g. Fig. 5), the overall reaction equation for the conversion of CO and H_2S is presented by reaction (1a):

$$3CO + 2H_2S \rightarrow CH_3SH + COS + CO_2 \quad (1a)$$

Thus, the theoretical carbon selectivity to methanethiol amounts to 33%, with the same selectivity for CO_2 (33%) and COS (33%). The expected theoretical CO conversion is 1.5 times higher than the H_2S conversion, which is confirmed by the experimental data. Barrault et al. [12] have described reactions for the conversion of CO and H_2S over a supported $K\text{-}WO_3$/alumina catalyst, assuming that water would be produced (equilibrium (1b) and reaction (1c)):

$$CO + H_2S \leftrightarrow COS + H_2 \quad (1b)$$

$$COS + 3H_2 \leftrightarrow CH_3SH + H_2O \quad (1c)$$

This reaction stoichiometry requires the addition of hydrogen to the feed since the amount produced by reaction (1b) is not sufficient for reaction (1c). Furthermore, the experimental data show that water is not present in the product stream, in agreement with thermodynamic calculations, and CO_2 is produced instead by reaction of water with CO (water gas shift, reaction (2)) or COS (reaction (3)):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$

$$COS + H_2O \leftrightarrow CO_2 + H_2S \quad (3)$$

CO_2 and CS_2 (Fig. 1) are formed by COS disproportiation (reaction (4)), which was experimentally confirmed by reaction of COS with the catalysts without other reactants (not shown):

$$2COS \rightarrow CO_2 + CS_2 \quad (4)$$

The concurrent decrease in methanethiol and increase in CH_4 concentrations above 605 K (Fig. 1), suggests that methane is formed by hydrogenation of methanethiol (reaction (5)), as suggested in [11]. Reaction (5) becomes favored over hydrogenation of COS at temperatures above 625 K:

$$CH_3SH + H_2 \rightarrow CH_4 + H_2S \quad (5)$$

The synthesis of CH_3SH from COS and H_2, reaction (1c), proceeds via a surface methylthiolate intermediate, CH_3S_{ads} [11], which also accounts for the hydrocarbon reaction products and pathways. For example, the CH_3S_{ads} surface intermediate can be directly hydrogenated to CH_3SH, and if the C–S bond is ruptured then the surface $CH_{3,ads}$ intermediate will be hydrogenated to CH_4. This is reflected in the low formation of CH_4 and the increase in CH_3SH formation until ∼615 K and the simultaneous decrease in CH_3SH and increase in CH_4 formation above this temperature. This suggests that the C–S bond in the surface CH_3S_{ads} intermediate is stable until ∼615 K on the applied catalytic surfaces and the stability of the C–S bond controls the reaction selectivity towards hydrocarbon formation. DMS, CH_3SCH_3, is formed from the condensation of two surface CH_3S_{ads} intermediates.

A reaction network for the various carbon products previously presented is shown in Fig. 8. Some comments on the relative rates of the various reactions can also be made. The rate of COS formation from CO is significantly higher than the rate of formation of CH_3SH from COS, based on the product compositions observed (see Figs. 2 and 5). The CS_2 concentration remains relatively small, suggesting that the hydrogenation reaction of COS is faster than the disproportiation reaction to CS_2. In the experiments with water added to the feed, a significant decrease in selectivity was observed (Fig. 5). At high water concentrations (20–30%), CO is completely converted to CO_2 rather than CH_3SH. This is explained by the very high rate of the COS hydrolysis reaction (reaction (3)). Barrault et al. [12] suggests that the rate of COS hydrolysis is two orders of magnitude larger than the hydrogenation reaction to CH_3SH. The conversion of CO_2 into COS

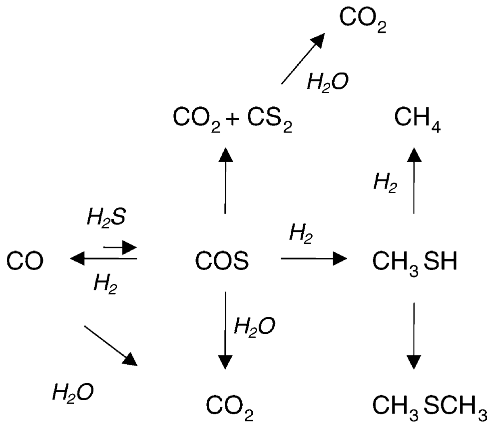

Fig. 8. Representation of the reaction network in the reaction of CO and H_2S over vanadia-based catalysts.

was not observed over the supported vanadia-based catalysts, but was identified by Barrault et al. [12] over supported K-WO_3/Al_2O_3 catalysts. Most likely, the activation of CO_2 requires the presence of potassium (or other alkali metals) in the catalyst. Unfortunately, Barrault et al. [12] did not report conversion and selectivity data for the $H_2S/H_2/CO_2$ reaction as a function of potassium content.

4.1. *Effect of catalyst composition on conversion and product selectivity*

Comparison of TPS profiles of the alumina and titania supported vanadia catalysts (Figs. 6 and 7) suggests that the support does not dramatically affect the sulfiding behavior of the surface vanadia phase in H_2S containing reaction mixtures. Below 673 K, the catalysts are only partially sulfided, since considerable H_2S uptake can be observed at higher temperatures. Only at 1273 K is the vanadia phase completely sulfided into V_2S_3 [3]. At the temperatures of interest in this study, it is generally assumed that at least four types of sulfur are present, viz. adsorbed H_2S, stoichiometric sulfur, non-stoichiometric sulfur and S–H groups [3,13]. The H_2S production noticed around 600 K for the various catalysts is attributed to the hydrogenation of non-stoichiometric sulfur, commonly referred to as excess sulfur (S_x). This excess sulfur is probably chemisorbed on coordinatively unsaturated sites, and associated with some form of vanadium oxide [13]. Recent H_2S TPSR-MS studies with 5%

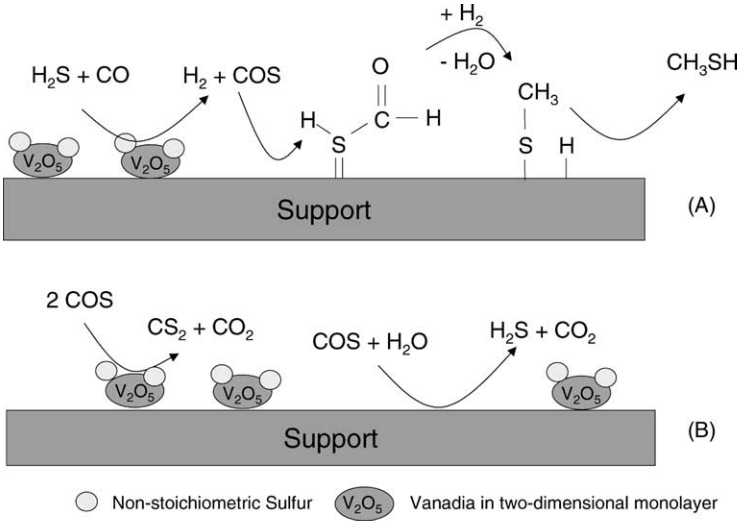

Fig. 9. Representation of the structure of the vanadia-based catalysts and the role of the components of the catalyst in the reaction network of the reaction of CO and H_2S.

V_2O_5/TiO_2, i.e. monolayer surface vanadia coverage, showed that H_2S might also be formed from recombination of H_{ads} and SH_{ads}, at ∼650 K [15]. Unfortunately, the stoichiometry of the compounds formed upon sulfidation cannot be assessed by the TPS experiments, because of the formation of excess sulfur. Some elemental sulfur was visible in the colder part of the TPS reactor. The general sulfiding mechanism of vanadia catalysts is presented in [13] and will not be further discussed here.

A schematic picture of the catalyst composition, and the role of the components in the various reaction steps is presented in Fig. 9. Fig 9A illustrates the desired pathway to CH_3SH, while the role of catalyst components in side reactions are illustrated in Fig. 9B. The thioformic acid and methylthiolate intermediates were proposed by Ratcliffe and coworkers [10], and will be discussed later. The results presented in this paper show that titania, either with or without the presence of vanadia, is a good catalyst for COS, H_2, and CH_3SH formation from a mixture of H_2S and CO. Addition of vanadia to titania enhances the activity, while the amount of vanadia appears less important for catalyst performance.

The higher activity of the supported vanadia/titania catalysts for the conversion of CO and H_2S can be correlated with the TPS profiles. Comparison of the TPS profiles shown in Figs. 6 and 7, and the product profile shown in Fig. 1, indicates a coincidence in the temperatures where hydrogenation of non-stoichiometric sulfur, and reaction of CO with H_2S occur. This suggests that the formation of non-stoichiometric sulfur (S_x) plays a role in the formation of COS and H_2 over the surface of vanadia containing catalysts:

$$H_2S \leftrightarrow H_2 + S_x \tag{6a}$$

$$CO + S_x \leftrightarrow COS \tag{6b}$$

The non-stoichiometric sulfur (associated with some form of vanadium oxide), is most likely also involved in other sulfur exchange reactions, such as in COS disproportionation. This is in agreement with TPSR-MS studies, which have shown that surface vanadia monolayers break the S–CO bond at ∼600–700 K [15] (Fig. 9B). However, in view of the decreased selectivity to CH_3SH upon introduction of vanadia to titania (Fig. 4), the partially sulfided surface vanadia phase may be only partially participating in the formation of CH_3SH. In agreement with this hypothesis, the amount of non-stoichiometric sulfur does not correlate with the small difference in activity found for the 1 and 4 wt.% vanadia/titania catalysts. This suggests that a vanadium independent step in the reaction scheme is now rate determining, which is most likely the hydrogenation of COS to methanethiol, occurring over the support.

To gain additional insight into the nature of the active surface intermediates on TiO_2 during the reduction of CO with H_2S, Ratcliffe and coworkers [10] investigated the coadsorption of H_2S and CO with temperature programmed desorption (TPD) and IR spectroscopy. Surface thioformic acid, $HSCHO_{ads}$, and methylthiol, CH_3S_{ads}, intermediates (Fig. 9A) were proposed for the formation of methanethiol. Rathcliffe and coworkers [10] propose that strongly bound CO on rutile is involved in the formation of this intermediate by reaction with adsorbed H_2S. Decomposition of additional H_2S provides hydrogen for hydrogenation of the intermediates. Although many arguments have been presented to support this mechanism, the interaction of COS with the catalyst has hardly been considered. In our opinion, adsorption of COS on the (sulfided) TiO_2 surface, followed by reaction with H_2, can also lead to the formation of the thioformic acid intermediate, as indicated in Fig. 9A. Whatever the exact route, the involvement of the support in the hydrogenation reaction to yield hydrocarbons is very likely. It should be mentioned that Rathcliffe and coworkers emphasize the specific activity of rutile TiO_2 in these reactions. From our experiments with the alumina supported catalysts, it appears that also on this support the intermediates leading to methanethiol can be formed.

The interaction of COS with the support materials used in this study has been investigated by Huisman et al. [14] in relation to the hydrolysis of COS and CS_2. Huisman presents a mechanism for hydrolysis at temperatures above 600 K, involving a consecutive surface sulfidation of the alumina or titania (by COS or CS_2 to TiS_2) and hydrolysis of the surface, the sulfidation being the rate determining step. In view of the high rates of hydrolysis reactions over TiO_2, reaction (3) most likely also occurs over the support in our experimental conditions, as illustrated in Fig. 9B. The relatively low selectivity to CS_2 observed for vanadia/alumina is likely a result of an enhanced hydrolysis of CS_2, occurring over the alumina surface [14].

Although the results in the present study and the previously discussed literature data point to a role of the support in the catalysis of H_2S with CO, at the same time it should be mentioned that in the used catalysts a large fraction (up to ∼80% for the 4 wt.% V_2O_5 catalyst) of the TiO_2 surface is covered with vanadia, and exposed surface support sites are a minority. Furthermore, recent TPRS-MS studies clearly show that the surface intermediates on titania are less reactive than the same intermediates on surface vanadia, while the surface vanadia species assist the reaction and desorption of the surface intermediates on titania [15]. Migration of surface V species and possibly the surface intermediates is suggested, and this might at least partly explain why the 1 and 4% V_2O_5/TiO_2 catalysts give comparable activity data. In future research activities, experimental conditions at relatively low CO conversion will be used to better quantify the effect of the support and vanadia loading on the catalytic activity. A further structure/activity analysis is also in progress, to verify the various mechanistic hypotheses.

5. Conclusions

In this study, the formation of CH_3SH from CO and H_2S was investigated. It was shown that the reaction occurs at moderate temperatures and pressures in the presence of titania, vanadia/titania or vanadia/alumina catalysts. The primary reaction is the formation of H_2 and COS, followed by hydrogenation of COS to CH_3SH, which is the rate determining step. The theoretical methanethiol carbon selectivity amounts to 33%, the other products being CO_2 (33%) and COS (33%). The carbon selectivity to CH_3SH is optimized at 615 K because of the stability of the C–S bond in surface methylthiolate intermediates. Higher temperatures favor complete hydrogenation of CO and COS to methane since the C–S bond of the surface intermediates is less stable at elevated temperatures.

Addition of vanadia to titania yields improvement of catalytic activity, but slightly decreases selectivity. Compared to supported vanadia/titania catalysts, the alumina supported vanadia catalysts show even higher activity, which is related to the higher surface area and vanadia content of the alumina catalyst. It is proposed that the non-stoichiometric sulfur associated with the presence of an oxidic vanadium phase is involved in the formation of COS and H_2, as well as in COS disproportionation. The hydrolysis and hydrogenation reactions most probably occur both on the exposed surface sites of the oxide support and the surface vanadia species.

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