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Effect of acid–base properties on design of catalyst for methanol thiolation: A review

Effet des propriétés acido–basiques sur la conception du catalyseur pour la Thiolation au methanol: Une revue

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Abstract. Reducing the concentration and strength of Lewis acid sites together with increasing the basic properties of catalysts has been found to enhance selectivity toward the desired methanethiol product. Weak acid and strong base Lewis acid–base pairs are the key to catalyst design. A review of the history of research on catalysts shows that the main catalysts that have been studied are metal oxides and zeolites. Alumina was the most important and widely used base for a long period. It was commonly impregnated with alkali metals and tungsten. Nevertheless, newer research studies have proved that alumina can be replaced with TiO₂. Tungsten has been found to be ineffective in the design of new catalysts. Furthermore, new research studies have focused on increasing the dispersion of impregnated alkali metals together with manipulating the acid–base properties of catalysts.

Résumé. La diminution de la concentration et de la force des sites acides de Lewis en augmentant à la fois des propriétés basiques du catalyseur s'est avérée augmenter la sélectivité envers le produit désiré de méthane-thiol. Un acide faible et une base forte dans les paires acide–base de Lewis constituent les clés de la conception des catalyseurs. Une revue de l'historique des recherches sur les catalyseurs montre que les principaux catalyseurs étudiés sont les oxydes métalliques et les zéolithes. L'alumine constituait la plus importante base choisie pendant une longue période et était en général imprégnée des métaux alcalins et du tungstène. Mais les études de recherches plus récentes ont prouvé que l'alumine peut être remplacée par du TiO₂. Le tungstène s'est avéré être inefficace dans la conception de nouveaux catalyseurs. De plus, de nouvelles études de recherche se sont concentrées sur l'augmentation de la dispersion des métaux alcalins imprégnés et aussi sur la manipulation des propriétés acido–basiques du catalyseur.

* Corresponding authors.

Keywords. Methanol, Thiolation, Acid, Base, Catalyst.

Mots-clés. Méthanol, Thiolation, Acide, Base, Catalyseur.

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1. Introduction

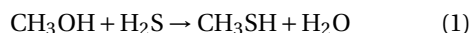
Methanethiol is an effective material in the synthesis of methionine. It is used as an intermediate in petrochemical and agricultural industries [1–12]. The industrial production of methanethiol takes place through the reaction between methanol and hydrogen sulfide. However, recent research has focused on its synthesis from syngas and hydrogen sulfide [13–15]. Although the industrial production of methanethiol has a history of about a century, research on corresponding catalysts and processes is still ongoing. K_2WO_4 /alumina is the most well-known industrial catalyst for methanol thiolation. In this reaction, adjusting acid–base properties is one of the most important parameters in the design of this catalyst. The reaction between methanol and hydrogen sulfide produces methanethiol or dimethyl sulfide, but the conversion path depends on the acid–base properties of the catalyst [16]. It is well known that the acid–base properties of catalysts are very important in methanol thiolation [13,16–26], and suitable acid–base properties can control reaction conversion and direct the selectivity of the reaction toward some desired products. The aim of this paper is to review the effects of acid–base properties on the design of methanol thiolation catalysts.

Reports of the design of this catalyst dating back to 1910 have been reviewed in this paper, and the routes for the design of future catalysts have been specified. Different catalysts including metal oxides and zeolites with different promoters, including alkali metals, are currently designed and synthesized. A general trend has been observed showing that reducing the concentration and the strength of Lewis acid sites while increasing basic properties enhances methanethiol selectivity at the cost of a lower rate of methanol conversion. New catalysts are designed to boost the dispersion of impregnated metals [5].

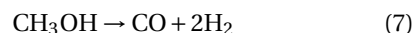
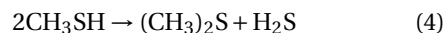
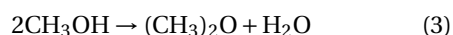
2. Methanol thiolation reaction network

Methanol thiolation is the reaction between methanol and hydrogen sulfide, where methanol

is converted into methanethiol in a fixed bed reactor and in the presence of a heterogeneous catalyst. The main reaction is as follows:



Moreover, there are some side reactions as follows [34,49]:



A reaction network has been recently developed by Pashigreva *et al.* with six reactions as shown in Scheme 1 [2].

Besides the main reaction, five side reactions are shown in Scheme 1. In this scheme, methanethiol itself is the core for four side reactions. Different side products can be produced under different process conditions (e.g. CO and H_2 are produced at high temperatures).

3. Review of catalysts

Different catalysts including thoria, metal oxides, zeolites, alumina silicates, and metal oxides promoted by alkali metals and transition metals have been manufactured and evaluated for the methanol thiolation process over the past 110 years. Table 1 reports the data on these catalysts from 35 references.

The historical trend in the type of catalysts shows that alumina was the most frequently used base material from 1958 to 2019. A review of the publica-

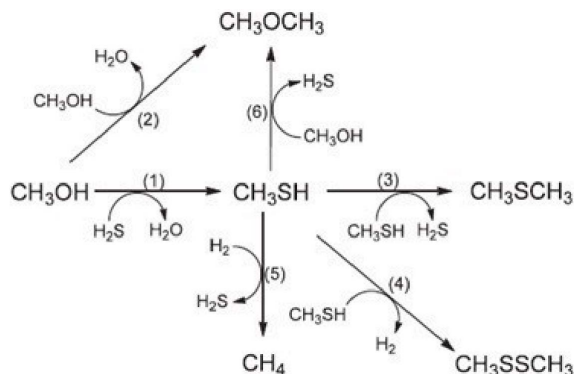
Table 1. Reviewed catalysts (1910–2019)

Ref.	Catalyst	Year
[27]	Thoria	1910
[28]	Thoria on pumice	1920
[29]	Thorium/pumice	1954
[30]	Thorium/pumice + water	1954
[31]	Activated alumina and activated gel-type alumina	1958
[32]	K ₂ WO ₄ /activated alumina	1958
[33]	Alumina + KOH/NaOH	1961
[34]	K ₂ WO ₄ /alumina	1962
[35]	Alumina	1966
[36]	KW/Al ₂ O ₃	1976
[37]	Zeolites	1985
[38]	K, W, V/SiO ₂ , Al ₂ O ₃ , AlSi	1987
[39]	Na _x W _y O _z /alumina, K ₂ WO ₄ /alumina, K ₂ WO ₄ /SiO ₂	1988
[40]	Alumina	1988
[41]	Alumina	1989
[42]	K, Na/W/Al ₂ O ₃	1989
[17]	Pure metal oxides (MgO, TiO ₂ , ZrO ₂ , CeO ₂ , Al ₂ O ₃)	1993
[22]	K ₂ CO ₃ /Al ₂ O ₃	1998
[8]	CsW/Al ₂ O ₃	1998
[43]	Na or Mo/zirconia or alumina	1998
[44]	Zeolites	1998
[9]	KW/Al ₂ O ₃	1999
[45]	Alkali/alumina, alkali/niobia, alkali/silica	2006
[25]	KW/ammonium salt/Al ₂ O ₃	2007
[10]	CsW with halide	2008
[46]	Zeolite, metal oxides	2009
[11]	KW/ammonium, phosphate, sulfide, sulfate salt/Al ₂ O ₃	2010
[12]	K _x WO _y	2012
[47]	Si/K ₂ WO ₄ /Al ₂ O ₃	2012
[48]	K ₂ WO ₄ /γ-Al ₂ O ₃	2015
[1]	K/alumina, Rb/alumina, Cs/alumina	2017
[2]	CsW/Al ₂ O ₃	2017
[3]	CsW/Al ₂ O ₃	2019
[4]	K ₂ WO ₄ /Al ₂ O ₃	2019
[5]	Cs/alumina, Cs/TiO ₂ (anatase), Cs/ZrO ₂	2019

tion dates of the papers shows that the publication rate has been higher recently, which reflects the importance of optimization for the methanol thiolation process.

4. Acid–base properties

Charge transfer through an electron transfer or a proton transfer takes place in most surface reactions.



Scheme 1. Network for the reaction of methanol with H_2S (with permission of Ref. [2]).

The ability of an oxide catalyst to donate or accept electrons/protons is related to its acid or base properties, and it can be defined by the Lewis or the Brønsted acid/base concept. According to the definition mentioned in the work of Somoraja [50], a Lewis acid site can receive a pair of electrons from the adsorbate, while a Lewis base site can transfer them to it. In addition, a Brønsted acid site can lose a proton to the adsorbate, but a Brønsted base site can accept a proton from it.

Although the first paper regarding a methanol thiolation catalyst was published in 1910, the first paper on the acid–base properties of a catalyst was released only 70 years later [38]. The main studies regarding the effect of acid–base properties on catalyst design based on the catalyst type have been organized into three categories such as zeolites, metal oxides, and supported catalysts.

4.1. Zeolites

Acid–base properties of different zeolites including HZSM-5, faujasite, SAPO-18, and AIPO-18 were studied in the reaction between methanol and hydrogen sulfide [44,46,51,52]. The results showed that acidic zeolites tend to form DMS and hydrocarbons, where reducing the acidity of zeolites increases the selectivity toward methanethiol. Comparing HZSM-5 with HNaY, NaX, and NaY shows that the activity drastically diminishes with decrease in acidity and increase in alkalinity in the following order:

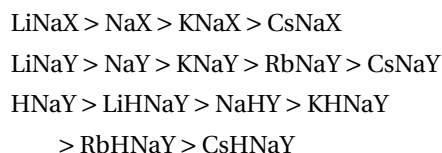


The selectivity to methanethiol is 5%–20% on HZSM-5, 60%–88% on NaX, and 69%–76% on NaY. HZSM-5

and HNaY are highly selective with respect to DMS due to strong surface acid sites. Lack of strong acid sites results in a lower activity on NaX and NaY. Zeolites are more active to methanethiol in the presence of paired acid–base sites (Na^+ and lattice oxygen) for the dissociation of H_2S [51,52].

More alkali metals impregnated in faujasite zeolites were investigated by Ziolk *et al.* [44]. Both methanethiol and DMS can form on acidic zeolites, where methanol may convert to a hydrocarbon on them. The basic property of zeolites strongly affects the yield of formation of methanethiol (Table 2).

The acidity of zeolites decreases in the following order:

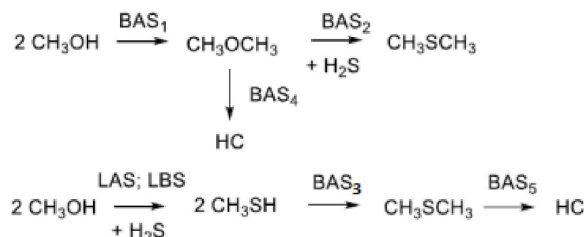


A reaction mechanism on zeolites was proposed according to Scheme 2. Methanol can be adsorbed on both Brønsted basic site and a pair of Lewis acid–base site in two different pathways. The presence of strong Brønsted acidic sites can convert the methanethiol and dimethyl ether (DME) products to DMS and hydrocarbon.

SAPO-18 and AIPO-18 were studied for the production of dimethyl sulfide and methanethiol from methanol and H_2S . The number of acid sites decreases in the following order:



AIPO-18 with the lowest number and strength of acid sites is more selective for methanethiol formation [46].



Scheme 2. Reactions of methanol on acid–base sites of zeolites. BAS: Brønsted acid sites with different strengths: $\text{BAS}_1 < \text{BAS}_2 < \text{BAS}_3 < \text{BAS}_4 < \text{BAS}_5$; LAS: Lewis acid sites; LBS: Lewis basic sites; HC: hydrocarbons (with permission of Ref. [44]).

Table 2. Activity and yield of products in the hydrosulfurization of methanol (with permission of Ref. [44])

Catalyst	LiNaY	NaY	KNaY	RbNaY	CsNaY	HNaX*	LiNaX	NaX	KNaX	CsNaX
Methanol conv. (%)	26	27	22	19	41	90	36	55	80	72
Yield (%)										
CH ₃ SH	17	20	13	12	18	2	30	50	71	65
(CH ₃) ₂ S	2	2	0.5	0.5	0	18	3	3	5	4
(CH ₃) ₂ O	6	4	7	5	21.5					
C2–C4	1	1	1.5	1	1.5					

*50% of Na exchange on NH_4^+ ; 90% of crystallinity in the dehydrated sample; this sample is active in the formation of hydrocarbons.

4.2. Metal oxides

The activity and selectivity of some metal oxides including SiO_2 , BeO_2 , MgO , ZrO_2 , ZnO , TiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\eta\text{-Al}_2\text{O}_3$, WO_3 , and V_2O_3 in the reaction between methanol and H_2S showed that WO_3 and V_2O_3 have the highest activity and selectivity to methanethiol due to their high specific surface area. They were followed by $\gamma\text{-Al}_2\text{O}_3$, $\eta\text{-Al}_2\text{O}_3$, and TiO_2 with one lower magnitude of activity. The remaining metal oxides with activity thrice less than that of WO_3 and V_2O_3 came third. The activity of metal oxides increases with decrease in their cation's ionization and electron acceptance potential as shown in Table 3 [18,53].

Al_2O_3 is the main pure metal oxide utilized for methanol thiolation reaction at all times. It has the highest activity among other pure metal oxides (Table 4). However, its weak basic sites cause reactions to form dimethyl sulfide with high selectivity. MgO shows minimal activity (about 3% as methanol conversion) but 100% selectivity for methanethiol due to very strong basic sites. According to the data from

Table 4, ZrO_2 with a yield of 69.1% for methanethiol formation at a H_2S to CH_3OH ratio of 2 is located at the top. The selectivity for dimethyl sulfide was observed to be inversely proportional to the number of basic sites. Metal oxides with very strong Lewis acid (and moderately basic) sites were reported to be suitable for the synthesis of dimethyl sulfide [17].

4.3. Supported catalysts

The principal research regarding the effect of acid–base properties of supported catalysts on the methanol thiolation reaction has been conducted during the past 30 years. The promotion of different supports has been tested including $\gamma\text{-Al}_2\text{O}_3$, SiO_2 , ZrO_2 , Nb_2O_5 , and TiO_2 by WO_3 , alkali metals and hydroxide or carbonate of alkali metals [1,2,4,5,38,42,43,45,46].

Adding WO_3 to $\gamma\text{-Al}_2\text{O}_3$ reduces the number of Lewis acid sites and basic sites, but this increases the production rate of methanethiol and lowers the production rate of dimethyl sulfide [46]. The addition of K_2WO_4 to $\gamma\text{-Al}_2\text{O}_3$ was found to cause more

Table 3. Activities and selectivities of metal oxides in the reaction of methanol with hydrogen sulfide (360 °C, H₂S/MeOH = 1.6, conversion = 50%–60%) extracted from the data in Ref. [53]

Catalyst (ionization potential, eV)	W ¹	Selec. (%) of CH ₃ SH	Yield (%) of CH ₃ SH (average)
SiO ₂ (45.13) ²	0.006	22	9 (max.)
BeO ₂ (18.21) ²	0.04	47	19 (max.)
MgO (15.03) ²	0.05	65	26 (max.)
ZrO ₂ (33.97)	0.06	85	46
ZnO (17.96)	0.10	0	0
TiO ₂ (43.24)	1.2	56	30
γ-Al ₂ O ₃ (28.44)	1.9	37	20
η-Al ₂ O ₃ (28.44)	3.2	35	19
WO ₃ (56)	32	73	40
V ₂ O ₅ (65.2)	44	85	46

¹ Reaction rate for methanethiol (mmol·m⁻²·h⁻¹).

² Conversion less than 40%.

Table 4. Activity and selectivity of catalysts (with permission of Ref. [17])

Conversion selectivity (%)	Catalyst							
	PO ₄ ³⁻ /SiO ₂	MgO	MgAl ₂ O ₄	TiO ₂ (R)	ZrO ₂	TiO ₂ (A)	CeO ₂	γ-Al ₂ O ₃
CH ₃ OH conversion (%)								
H ₂ S:CH ₃ OH = 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 ₃ SH selec. (%)								
H ₂ S:CH ₃ OH = 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) ₂ S selec. (%)								
H ₂ S:CH ₃ OH = 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 selec. (%)								
H ₂ S:CH ₃ OH = 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

reduction in the number of Lewis acid sites and basic sites. This resulted in a near-zero production yield for dimethyl sulfide, enhancing the selectivity for methanethiol. Such behavior has also been observed for SiO₂ and AlSi (Table 5). It was concluded

that acidic catalysts have higher activities, but their production rate for methanethiol and dimethyl sulfide is 50–50. Catalysts with strong Lewis acid sites have a higher tendency to produce dimethyl sulfide, and for the selective production of methanethiol, it is

Table 5. Catalysts and their properties extracted from the data in Ref. [38]

Catalyst	S_{spec} (m ² /g)	W (mmol/g·h)		Selec. (%)	Properties of L-sites (N , $\mu\text{mol/g}$) (Q , kJ/mol)	Properties of base sites	
		MM	DMS			First type X_N $XX_{(\text{PA})}$	Second type X_N $XX_{(\text{PA})}$
SiO ₂	350	0.14	0.03	30	0	0	0
7% WO ₃ -SiO ₂	290	9.7	4.6	46	-	-	-
10% K ₂ WO ₄ -SiO ₂	290	2.7	0.01	90	0	47 (910)	214 (805)
AlSi	430	0.83	4.5	6	22 (53)	80 (910)	40 (800)
7% WO ₃ -AlSi	406	68	13	56	120 (56)	0	40 (800)
10% K ₂ WO ₄ -AlSi	430	15.0	3.7	65	0	40 (915)	670 (800)
γ -Al ₂ O ₃	300	236	118	37	690 (34)	96 (900)	546 (810-840)
7% WO ₃ -Al ₂ O ₃	260	280	100	51	381 (35.5)	29 (915)	325 (800)
10% K ₂ WO ₄ -Al ₂ O ₃	260	12.1	0.05	87	214 (31.5)	137 (910-940)	425 (810)
15% K ₂ WO ₄ /Al ₂ O ₃	270	9.5	0.02	93	135 (31.5)	330 (900-925)	670 (810)
10% Na ₂ WO ₄ /Al ₂ O ₃	230	12.4	0.2	85	250 (32.5)	260 (900-930)	556 (810)

S_{spec} (m²/g, catalyst specific area); W (mmol/g·h, catalytic activity); Selec. (%), selectivity toward methanethiol); N ($\mu\text{mol/g}$, number of Lewis sites); Q (kJ/mol, strength of Lewis sites); X_N ($\mu\text{mol/g}$, number of base sites); $XX_{(\text{PA})}$ (kJ/mol, the energy of proton addition, PA stands for proton affinity).

necessary to use catalysts with strong basic sites on the surface [38].

In a similar study, some γ -Al₂O₃ based catalysts were promoted by K₂WO₄, K₂CO₃, KOH, and NaOH. K₂WO₄ led to the formation of relatively weaker Lewis acid sites and moderate basic sites, but the other three catalysts had strong Lewis acid sites and basic sites. As shown in Table 6, K₂WO₄ created more selectivity for methanethiol, but it exhibited low activity. For example, at 360 °C, the selectivity values for methanethiol were 96%, 95%, 92%, and 90%, but the methanol conversion values were 47%, 56%, 55%, and 53% for K₂WO₄, K₂CO₃, KOH, and NaOH, respectively. The other three catalysts, on the other hand, were more active and less selective. It was concluded that strong acidic and basic sites are more active but less selective for producing methanethiol [42].

The use of metals as promoters for methanol thiolation reaction has been taken into consideration for the past 20 years. The addition of Na to γ -Al₂O₃ and ZrO₂ enhances methanethiol selectivity, but it reduces catalyst activity (Tables 7 and 8). Na was loaded on γ -Al₂O₃ from 0.25% up to 4.5%. Therefore, the selectivity increased from 28% to 100%, and at the same time, methanol conversion decreased from 91% to 11%. The addition of Mo to ZrO₂ enhances the activ-

ity, yet this reduces the selectivity for methanethiol (Table 9). Moreover, Mo increases the acidity of the catalyst [43].

The addition of alkali metals to niobia leads to the formation of acid-base pairs, thereby increasing the selectivity of methanethiol and the basic sites on alumina and silica. When a support is impregnated with alkali metals, the Brønsted centers are destroyed [19], where the strength of Lewis acid sites decreases together with increase in the basic property [54]. The selectivity for methanethiol strongly depends on the nature of active sites. Table 10 reports higher methanethiol production by modified niobia, which can be attributed to the presence of acid-base pairs on its surface [45].

Although catalysts have been available for the methanol thiolation process since about 1910, the research in this area is still ongoing. Vast and comprehensive studies have been conducted on methanol thiolation since 2017 in Technische Universität München (TUM) and Institute for Integrated Catalysis by impregnating alkali metals (K, Rb, and Cs) on supports of γ -Al₂O₃ and TiO₂ [1,2,4,5]. They claim that tuning the acid-base properties of the catalyst by adjusting alkali metal properties is an approach to preparing novel catalysts.

Table 6. Catalytic activities of catalysts extracted from the data in Ref. [42]

Catalyst	T (°C)	MeOH concentration (%)	Rate (mol/g) × 10 ⁴						Selectivity toward MM (%)
			MeOH	MM	DMS	DME	CH ₄	CO ₂	
K ₂ WO ₄ /Al ₂ O ₃	360	47	46	44	0.5	1.2	0.0	0.0	96
K ₂ CO ₃ /Al ₂ O ₃	360	56	64	61	2.0	0.3	0.0	0.0	95
KOH/Al ₂ O ₃	360	55	59	54	2.4	2.1	0.0	0.0	92
NaOH/Al ₂ O ₃	360	53	58	52	2.5	2.1	0.0	0.0	90
K ₂ WO ₄ /Al ₂ O ₃	400	68	62	59	1.5	0.7	0.4	0.2	95
K ₂ CO ₃ /Al ₂ O ₃	400	75	84	76	5.3	0.0	0.8	0.7	90
KOH/Al ₂ O ₃	400	77	69	62	5.0	0.4	0.7	0.5	90
NaOH/Al ₂ O ₃	400	75	65	57	5.0	0.3	0.6	0.5	88
K ₂ WO ₄ /Al ₂ O ₃	500	89	225	175	7.0	0.0	21	9.0	78
K ₂ CO ₃ /Al ₂ O ₃	500	86	303	201	18	0.0	34	19	66
KOH/Al ₂ O ₃	500	86	256	175	19	0.0	29	18	68
NaOH/Al ₂ O ₃	500	90	313	221	22	0.0	24	23	71

Table 7. Activity and yield of product, Na on alumina (with permission of Ref. [43])

Al ₂ O ₃ modified with	CH ₃ OH conv. (%) (H ₂ S/CH ₃ OH = 1/1)	Yield (%)			
		CH ₄	(CH ₃) ₂ O	CH ₃ SH	(CH ₃) ₂ S
0% Na	99	-	-	11	88
0.2% Na	91	-	7	26	58
0.5% Na	83	-	25	45.2	12.5
1% Na	59	3	16.5	26.5	13
2.2% Na	13	-	-	13	-
4.5% Na	11	-	-	11	-

Table 8. Activity and yield of product, Na on ZrO₂ (with permission of Ref. [43])

ZrO ₂ modified with	CH ₃ OH conv. (%) (H ₂ S/CH ₃ OH = 1/1)	Yield (%)			CH ₃ OH conv. (%) (H ₂ S/CH ₃ OH = 2/1)
		(CH ₃) ₂ O	CH ₃ SH	(CH ₃) ₂ S	
0% Na	60	2	54	4	95
0.1% Na	20	Trace	20		20
0.2% Na	9	-	9		-
0.5% Na	5	-	5		5
1% Na	5	-	5		5

Alkali metals have two important roles in the final catalyst: lowering the acidic strength and creating suitable sites for the adsorption of reactants (H₂S and CH₃OH). Cs has lower electronegativity than those of Rb and K, which increases the electron den-

sity on the neighboring anions and enhances their Lewis basic strength [55–57]. Adding alkali cations to gamma-alumina blocks Lewis acid sites and prevents the formation of DME. Indeed, very strong Lewis acid sites are substituted with the weaker ones

Table 9. Activity and yield of product, Mo on ZrO₂ (with permission of Ref. [43])

ZrO ₂ modified with	CH ₃ OH conv. (%) (H ₂ S/CH ₃ OH = 1/1)	Yield (%)			
		CH ₄	(CH ₃) ₂ O	CH ₃ SH	(CH ₃) ₂ S
0% Mo	60	-	1.8	54	4.2
0.25% Mo	72	3.6	1.4	57	10
0.5% Mo	81	10.8	0.8	53	16
1% Mo	93	21.6	0.4	47	24

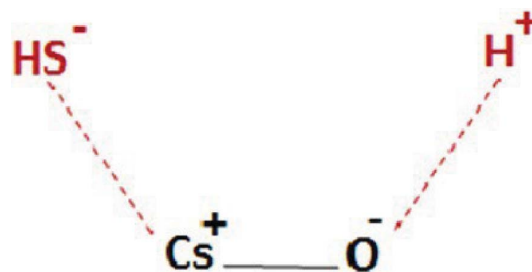
by adding alkali cations to gamma-alumina, which makes the neighboring sulfur oxyanions stronger Lewis basic sites through increasing their electric charge. As such, some acid–base pairs are formed, which help in dissociative adsorption of H₂S. H₂S is dissociated into H⁺ and SH⁻ as illustrated in Figure 1. Furthermore, SH⁻ generates nucleophilic attacks on the methoxy species, which leads to the formation of methanethiol [1].

The size and loading of cations on gamma-alumina affect the rate of formation of methanethiol. At lower loadings, the rate of methanethiol formation in Cs⁺ is less than that of Rb⁺ and K⁺ due to better dispersion of smaller cations (Rb and K). However, at higher cation loadings, Cs⁺ provides better results in the formation of methanethiol due to higher electronegativity [1] as shown in Table 11.

Due to the good performance of Cs-promoted catalysts, another attempt was made to find how the acid–base properties of the catalyst can affect the reaction route. The acid–base properties of the final catalysts can be manipulated by altering the Cs content. Catalysts (WS₂/Al₂O₃) without Cs produced DME and methanethiol, but Cs-containing catalysts (Cs-WS₂/Al₂O₃) produced methanethiol at a higher yield (Figure 2).

The addition of Cs reduces both the specific area and the acidity of the catalyst. The decrease in acidity is greater than the area reduction. The addition of Cs⁺ strongly improves the nature of the catalyst and reduces the strength and concentration of Lewis acid sites. In fact, very strong Lewis acid cation sites (Al₃⁺ and W₄⁺) are replaced with the weaker strength Lewis acid sites of Cs⁺ [2].

Cs⁺ induces very strong basic sites, which increases catalytic activity. The very strong basic sites, which associate with neighboring weak Lewis acid site alkali cations, improve the performance


Figure 1. H₂S dissociative adsorption on Cs–O.

of catalysts. The incorporation of Cs⁺ lowers the amount of adsorbed methanol but increases the rate of reaction between SH groups and the adsorbed methanol. Cs⁺ plays a key role in directing methanol conversion to methanethiol selectively. WS₂ does not have any role in the methanol thiolation reaction [4].

Cs/Al₂O₃ and CsW/Al₂O₃ reveal the same reaction rates. The binding of Cs⁺ and WS₂ is strong and makes the catalyst more stable. Two transition metal oxides, TiO₂ and ZrO₂, were examined for comparison. They were impregnated by Cs⁺ but without the addition of WS₂. TiO₂ and ZrO₂ provide Lewis acid–base pairs, while gamma-alumina has a combination of weak and strong Lewis acid sites. The highest methanethiol initial rates were observed with TiO₂. The results indicated that a methanol thiolation catalyst can be developed without WS₂. The main parameter in the design of catalysts is the existence of acid–base pairs, which provide suitable sites for the dissociative adsorption of H₂S and CH₃OH, where SH generates a nucleophilic attack on the methoxy species. Strong basic anions play the main role in the absence of strong Lewis acid sites [5].

Table 10. Conversion and selectivity of alkali modified supports in methanol thiolation reaction (with permission of Ref. [45])

	Conversion (%)	Selec. (%)			
		Me ₂ S	MeSH	Me ₂ S ₂	Me ₂ O
Nb ₂ O ₅ ·nH ₂ O	74	20	71	4	5
Li/Nb ₂ O ₅ ·nH ₂ O	14	1	93	4	2
Na/Nb ₂ O ₅ ·nH ₂ O	18	1	94	3	2
K/Nb ₂ O ₅ ·nH ₂ O	25	1	93	5	1
Rb/Nb ₂ O ₅ ·nH ₂ O	17	1	92	5	2
Cs/Nb ₂ O ₅ ·nH ₂ O	18	1	94	4	1
Nb ₂ O ₅	40	10	79	4	7
Li/Nb ₂ O ₅	18	1	92	4	3
Na/Nb ₂ O ₅	22	2	90	4	4
K/Nb ₂ O ₅	17	-	96	4	-
Rb/Nb ₂ O ₅	18	-	96	3.5	0.5
Cs/Nb ₂ O ₅	10	1	91	5	3
Al ₂ O ₃	100	63	34	2	-
Li/Al ₂ O ₃	75	30	43	2	25
Na/Al ₂ O ₃	5	-	59	-	41
K/Al ₂ O ₃	4	-	92	-	8
Rb/Al ₂ O ₃	23	6	40	-	54
Cs/Al ₂ O ₃	4	-	88	-	12

Table 11. Methanethiol rates as a function of concentration of alkali cations extracted from the data in Ref. [1]

Concentration of alkali cations (10 ³ mol/g Al ₂ O ₃)	Rate (10 ⁵ mol _{CH₃SH} /g _{cat})		
	K/Al ₂ O ₃ -H ₂ S	Rb/Al ₂ O ₃ -H ₂ S	Cs/Al ₂ O ₃ -H ₂ S
0.75	1.35	2.00	1.45
1.15	1.12	1.80	1.80
1.40	1.08	1.75	2.16
2.05	1.00	1.75	2.00

5. Conclusion

A review of historical trend in the development of methanol thiolation catalysts indicates that the primary catalysts used in the thiolation of methanol were metal oxides. The next generation of catalysts was promoted by alkali metals and tungsten. Cs was found to be the best promoter among alkali met-

als. The inefficiency of tungsten was also proved; the search for a new and more stable catalyst led to Cs-promoted TiO₂. The schematic of this trend is illustrated in Scheme 3.

As the final result, it can be concluded that the best catalyst for methanol thiolation is a catalyst with Lewis acid–base pairs in which weak acid sites are located near strong basic sites.

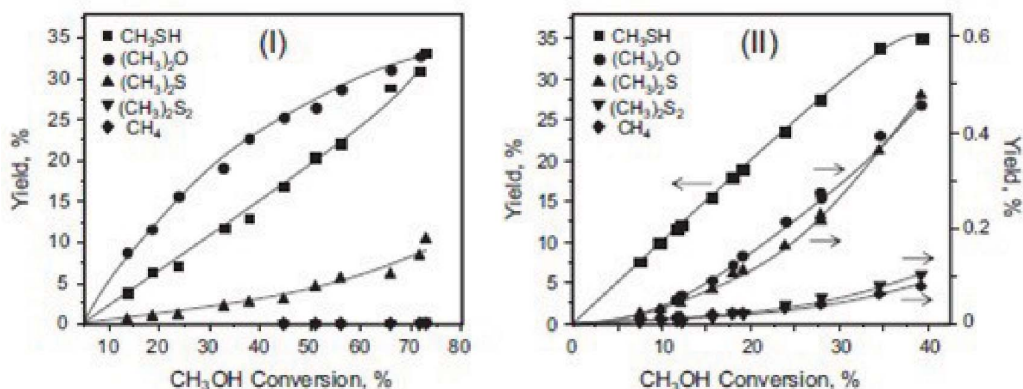


Figure 2. Product yields during the reaction between methanol and H₂S over WS₂/Al₂O₃ (I) and Cs-WS₂/Al₂O₃ (II) for varying methanol conversion (360 °C, 9 bar) (with permission of Ref. [2]).



Scheme 3. Historical trend in the development of methanol thiolation catalysts.

In general, basicity influences the yield of methanethiol. Strong basic sites help in the dissociative adsorption of H₂S, thus increasing the yield of methanethiol. The strength of neighboring acid sites affects the performance of strong basic sites. Although strong neighboring acid sites suppress the effectivity of strong base sites in methanethiol formation, the presence of weak neighboring acid sites has a synergistic effect on enhancing methanethiol production.

Conflict of interest

On behalf of all authors, the corresponding authors state that there is no conflict of interest.

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