ELSEVIER

Catalysis Today 51 (1999) 25–38

CATALYSIS TODAY

Study of reactions over sulfide catalysts in $CO–CO_2–H_2–H_2O$ system

Yumin Li, Rejie Wang, Liu Chang*

Department of Catalysis Science and Technology, School of Chemical Engineering, Tianjin University, Tianjin 300072, China

Abstract

MoS_2 is a valuable sulfur tolerant catalyst widely used in hydrotreating processes and the water–gas shift reaction (WGSR). The product distribution strongly depends on the composition of the catalyst and reaction condition as well. For the sake of demonstrating the effect of promoters and carriers on the reactivity, three interrelated reactions, WGSR, methanation and methanol synthesis are taken as the models. They have the reactants CO and H_2O or H_2 in common. In fact, in the presence of MoS_2, they turn to become a system of $CO–H_2O–H_2–CO_2$. The variation of products will be shown and discussed in this paper by incorporating potassium and/or Co into the supported MoS_2 with γ-Al_2O_3 or other carriers.

Keywords: Molybdenum sulfide; Promoters; Potassium; Cobalt; Carriers; Water–gas shift; Methanation; Methanol synthesis

1. Introduction

1.1. Application of sulfide catalyst

Due to the growing shortage of low sulfur petroleum, residual oil and coal with high-sulfur content are needed more and more. The development and application of sulfur-resisting catalysts have received great attention.

Sulfide catalysts possessing many special properties are used commercially in many processes, as in desulfurization, denitrogenation, demetallization and other hydrotreatments of organic compounds. Moreover, sulfide catalysts can be used in reactions involving oxygenous compounds, as in water–gas shift reaction (WGSR), methanation, methanol and low alcohols synthesis. Besides the noble metals, only a limited number of elements in the periodic table has been used for the sulfide catalyst such as Mo and W of group VIB as the primary species in composing active sulfide catalysts and Fe, Co, Ni of group VIII as the indispensable promoters.

In the process of using sulfide catalysts and handling sulfur-containing streams, there are many drawbacks such as corrosion in equipment and instrumentation, difficulties in characterization of catalysts and analysis of sulfur contents in the system as well as the danger of poisoning.

1.2. Work done in our laboratory

Many researches have been done on sulfide catalysis in our laboratory, including hydrodesulfurization, hydrodenitrogenation, hydrodemetallization, WGSR, methanation and methanol synthesis. In the meantime, a series of catalysts has been prepared with different methods and heat treatment. The sulfidation of their oxide precursors with various sulfurizing agents accompanied with temperature programmed techniques has been carried out. Likewise, a tempera-

---

*Corresponding author.

PII: S0920-5861(99)00005-X

ture programmed technique has been applied in determining the state of active sulfur species and their reactivities with various probing media and sulfur contents in the catalysts. Deactivation of the catalysts has been investigated by simulation of that occurring in plants. Characterization of the catalysts has been performed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), chemisorption, temperature-programmed desorption (TPD), infrared spectroscopy (IR), BET, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and activity evaluation. In addition, thermic magnetic susceptibility of some catalysts has been determined with a Faraday type thermal gravimetric balance made in our laboratory.

Many of these works have been published in Chinese and foreign journals.

Here three catalytic reactions: methanation, methanol synthesis and WGSR are chosen as the examples for presentation.

1.3. Theoretical consideration

The above mentioned reactions are expressed as follows:

$$CO+3H_2 = CH_4 + H_2O, \quad \Delta H^0_{298} = -206\,\mathrm{kJ\,mol^{-1}}, \tag{1}$$

$$CO + 2H_2 = CH_3OH, \quad \Delta H^0_{298} = -97.47\,\mathrm{kJ\,mol^{-1}}, \tag{2}$$

$$CO+H_2O=CO_2 + H_2, \quad \Delta H^0_{298} = -41.17\,\mathrm{kJ\,mol^{-1}}. \tag{3}$$

From thermodynamic analysis, it is known that the $CO+H_2$ system is a really complex one. The three main type of reactions can be distinguished by (1) formation of hydrocarbons, (2) production of alcohols and (3) WGSR. Among them, methanation, methanol synthesis and WGSR are the most fundamental, important and typical ones. The first and second reactions are volume decreased, while the third one is not. All of the three reactions are exothermic and reversible. From thermodynamic calculations, it is concluded that methanol synthesis is the least favorable reaction, methanation is the most favorable one and WGSR is in between, and the equilibrium concentration of the reaction products in the CO–CO_2–H_2–H_2O system is in the following order $CH_4 > H_2O > CO_2$.

Methanation is a deep hydrogenation reaction of CO, methanol synthesis is a partial hydrogenation one and WGSR is a complete oxidation reaction involving CO being oxidized into CO_2 and water being reduced with the evolution of hydrogen.

A possible reaction path of the three reactions occurring on MoS_2-based catalysts are suggested as the following.

Deep and partial hydrogenation of CO:

$$H_2 \Leftrightarrow 2H_{ad} \tag{4}$$

$$CO \Leftrightarrow CO_{ad} \tag{5}$$

$$CO_{ad} \Leftrightarrow C_{ad} + O_{ad} \tag{6}$$

$$CO \Leftrightarrow C_{ad} + O_{ad} \tag{7}$$

$$C_{ad} \overset{+H_{ad}}{\Leftrightarrow} CH_{ad} \Leftrightarrow CH_{2ad} \overset{+H_{ad}}{\Leftrightarrow} \cdots \Leftrightarrow CH_{4ad} \Leftrightarrow CH_4 \tag{8}$$

$$CH_{ad} \overset{+CH_{ad}}{\Leftrightarrow} HC-CH_{ad} \overset{+H_{ad}}{\Leftrightarrow} C_2H_{3ad} \overset{+H_{ad}}{\Leftrightarrow} \cdots \Leftrightarrow C_2H_{6ad} \Leftrightarrow C_2H_6 \tag{9}$$

$$CH_{2ad} \overset{+C_{ad}}{\Leftrightarrow} HC-CH_{ad} \overset{+H_{ad}}{\Leftrightarrow} C_2H_{3ad} \overset{+H_{ad}}{\Leftrightarrow} \cdots \Leftrightarrow C_2H_{6ad} \Leftrightarrow C_2H_6 \tag{10}$$

$$O_{ad} \overset{+H_{ad}}{\Leftrightarrow} OH_{ad} \overset{+H_{ad}}{\Leftrightarrow} H_2O_{ad} \Leftrightarrow H_2O \tag{11}$$

$$O_{ad} \overset{+CO_{ad}}{\Leftrightarrow} CO_{2ad} \Leftrightarrow CO_2 \tag{12}$$

$$CO_{ad} \overset{+H_{ad}}{\Leftrightarrow} HCO_{ad} \overset{+H_{ad}}{\Leftrightarrow} HCOH_{ad} \overset{+H_{ad}}{\Leftrightarrow} \cdots \Leftrightarrow CH_3OH \tag{13}$$

$$HCOH_{ad} \overset{+C_{ad}}{\Leftrightarrow} HC-COH_{ad} \overset{+H_{ad}}{\Leftrightarrow} \cdots \Leftrightarrow C_2H_5OH \tag{14}$$

$$HC-COH_{ad} \overset{+C_{ad}}{\Leftrightarrow} HCCCOH_{ad} \overset{+H_{ad}}{\Leftrightarrow} \cdots \Leftrightarrow C_3H_7OH \tag{15}$$

Complete oxidation of CO by H_2O:

$$H_2O \Leftrightarrow H_2O_{ad} \Leftrightarrow O_{ad} + 2H_{ad} \Leftrightarrow O_{ad} + H_2 \tag{16}$$

$$H_2O_{ad} \Leftrightarrow H_{ad} + OH_{ad} \tag{17}$$

$$CO \Leftrightarrow CO_{ad} \overset{+O_{ad}}{\Leftrightarrow} CO_2 \tag{18}$$

$$CO_{ad} + OH_{ad} \Leftrightarrow COOH_{ad} \Leftrightarrow CO_2 + H_{ad} \overset{+H_{ad}}{\Leftrightarrow} CO_2 + H_2 \tag{19}$$

From the scheme it can be seen that the idealized and the most simple way of realizing the reactions are that methane is formed from the dissociation of CO, and followed by successive addition of H_{ad} on C_{ad}, methanol is formed from successive addition of H_{ad} on undissociated CO, as for WGSR, CO is undissociated, and H_2O is dissociated into H_2 and O_{ad} which reacts with CO_{ad} to form CO_2.

However, as far as the common active catalyst MoS_2 is concerned, CO may be dissociated or undissociated, and H_2O may be dissociated into H_2 and O_{ad} or H_{ad} and OH_{ad}. So in the practical system there may be a lot of different species present and many possible reactions may occur. As in the preparation of methane, other hydrocarbons, low alcohols and particularly, CO_2 and H_2O are formed, similar to the case of methanol synthesis. For the formation of H_2O is unavoidable, WGSR is always going along with hydrocarbon and alcohol formation resulting in the decrease of product selectivity and yield. Likewise in the WGSR, hydrocarbon and alcohol too may appear sometimes.

Under such a complex situation, the only way to modify the MoS_2 catalyst is by introducing different kind and quantity of promoters and carriers to meet the requirement for the main reaction as close as possible. That is, the working composition of catalysts definitely determines the product distribution. The following examples will display this in detail.

2. Experimental

2.1. Samples

Table 1 gives the model catalysts for WGSR [1,2]. Table 2 gives the model catalysts for methanation [3]. Table 3 gives the model catalysts for methanol synthesis [4].

2.2. Sample preparation

2.2.1. Model catalysts for WGSR

CoMoK/γ-Al_2O_3 series are prepared by successive stepwise impregnation of Al_2O_3 with the order of K_2CO_3, ammonium heptamolybdate and cobalt nitrate, after drying they are calcined at 821, 883 and 813 K for 5 h, respectively. The samples thus obtained are in oxidized form and should be sulfidized before activity evaluation.

TiO_2–Al_2O_3 supports are prepared by impregnation of γ-Al_2O_3 with $TiCl_4$ solution, then aged, dried and calcined at 773 K for 2 h.

The TiO_2–Al_2O_3 supported CoMoK samples are obtained by the successive stepwise impregnation of the corresponding solutions of Co, Mo and potassium, then dried and calcined at 673 K for 2 h.

2.2.2. Model catalysts for methanation

One group of samples is prepared by single, double and triple-step impregnation of γ-Al_2O_3 with $(NH_4)_6Mo_7O_{24}$, $Co(NO_3)_2$ and K_2CO_3 solution, respectively, then dried at 383 K for 4 h and calcined at 773 K for 8 h after each step. Another group of samples is prepared by co-impregnation of Co and Mo solution first, then followed with impregnation of potassium solution, dried at 383 K, 4 h, calcined at 573 K, 8 h, after each step. The sample prepared by co-impregnation is denoted as CoMo, while by separate impregnation denoted as Co–Mo.

2.2.3. Model catalysts for methanol synthesis

1. *Unsupported model catalysts*:
    - *Single promoter.* Alkali or alkaline earth carbonate (20 wt%) and MoS_2 (80 wt%) prepared in laboratory were mixed and ground thoroughly, pelleted and crushed into 20–40 mesh, and calcined at 643 K (2 h, N_2).
    - *Double promoter.* Ammonium molybdate and cobalt or nickel nitrate solutions were mixed with molybdenum sulfide solution, stirred for 4 h, and vacuum filtered. The precipitate was dried at 333 K, gradually heated to 723 K, kept for 3 h, and cooled down to room temperature in N_2 stream. Thus obtained substance was then mixed with K_2CO_3 and calcined again as for single promoter.
2. *Supported model catalysts.* The preparation method was the same as above, except including carriers. They were γ-Al_2O_3 from Tianjin Research Institute of Chemical Industry, a.c. (active carbon), SiO_2 (silica gel), MgO or $Mg(OH)_2$ made in laboratory. The MgO–SiO_2 double carriers were prepared by mixing and grinding SiO_2 and $Mg(OH)_2$

Table 1
Composition[a] of the water–gas shift catalysts and their reactivity

Sample[a]			Content (wt%)					CO conversion (%)[b]	
			MoO_3	CoO	K_2CO_3	Al_2O_3	TiO_2	Temperature (K)	
								613	723
High steam/CO	I	MoA	12.0			88.0		11.6	20.7
		CoA		4.5		95.5		4.45	10.0
		KA			14.5	85.5		5.87	33.2
		Co–MoA	12.0	4.5		83.5		16.4	28.6
		K–Co–MoA	12.0	4.5	14.5	69.0		45.1	78.9
	II	K(10)–Co–Mo(0.5)A	5.9	1.5	10.0	82.6		See Fig. 1	See Fig. 1
		K(0)–Co–Mo(0.5)A	5.9	1.5	0.0	92.6			
		K(10)–Co–Mo(1.0)A	8.8	4.9	10.0	86.3			
		K(0)–Co–Mo(1.0)A	8.8	4.9	0.0	86.3			
	III	K(0)–Co–Mo(1.0)A	8.8	4.9	0.0	86.3		See Fig. 2	See Fig. 2
		K(2)–Co–Mo(1.0)A	8.8	4.9	2.0	84.3			
		K(5)–Co–Mo(1.0)A	8.8	4.9	5.0	81.3			
		K(10)–Co–Mo(1.0)A	8.8	4.9	10.0	76.3			
		K(15)–Co–Mo(1.0)A	8.8	4.9	15.0	71.3			
Low steam/CO		Co–MoKT(0)A	8.0	3.0	14.0	75.0	0.0	See Fig. 3	See Fig. 3
		Co–MoKT(4)A	8.0	3.0	14.0	71.0	4.0		
		Co–MoKT(8)A	8.0	3.0	14.0	67.0	8.0		
		Co–MoKT(12)A	8.0	3.0	14.0	63.0	12.0		
		Co–MoKT(16)A	8.0	3.0	14.0	59.0	16.0		
		Co–MoKT(20)A	8.0	3.0	14.0	55.0	20.0		

[a] A=Al_2O_3, M=MoO_3, C=CoO, K=K_2CO_3, T=TiO_2, Co–Mo(0.5)=Co/Mo=0.5 (atom base), Co–Mo(1.0)=Co/Mo=1.0 (atom base).

[b] The samples were sulfided by the feed gas bubbling through CS_2 at 273 K. The feed gas composition (vol%): N_2 0.86, CO 46.2, CO_2 4.27, CH_4 0.23, H_2 48.5 and S 380 ppm, GHSV=3000 h^{-1}, temperature 553 K, atmospheric pressure, 4 h. Then, they were evaluated with steam/CO=3.0 and at 613 and 723 K.

thoroughly, followed by drying at 393 K, and calcination at 823 K in air.

2.3. Activity evaluation

2.3.1. WGSR

1. *High steam/CO*. The samples were sulfided and evaluated by the feed gas bubbling through a saturated aqueous solution of H_2S at 273 K. Feed gas composition: CO 34.48, CO_2 6.74, H_2 51.39, N_2 7.21 (vol%), $H_2O/CO=3.1$, GHSV=800 h^{-1}, at different temperatures, T=513, 613, 733, 783 K, P=atmospheric pressure (except otherwise specified).
2. *Low steam/CO*. The samples were sulfided by the feed gas saturated with CS_2 at 273 K. Feed gas composition: CO 46.2, CO_2 4.27, CH_4 0.23, H_2 48.5 (vol%), S 380 ppm, $H_2O/CO=2.2$, T=553 K, 6 h, GHSV=2200 h^{-1}, P=atmospheric pressure, then they were evaluated at T=553, 623, 673 and 723 K.

2.3.2. Methanation

The samples for methanation were sulfided by H_2 stream saturated with CS_2 at 273 K, 2 h at 673 K, then evaluated under the condition of feed gas: H_2 79.7, CO 16.8, CO_2 2.53, N_2 0.93 (vol%) containing H_2S 1600 ppm; $H_2/CO\approx4.7$, GHSV=3600 h^{-1}, at different temperatures and pressures.

2.3.3. Methanol synthesis

Reaction condition: pressure 4 MPa, temperature 536 K, space velocity 3000 h^{-1}, $H_2/CO=1.4$, 1350 ppm S in the feed gas (except otherwise specified).

Table 2
Composition and their reactivity of samples for the methanation

		Sample									
		MoA	CoA	Mo–K(5)A	Co–Mo–K(5)A	CoMo–K(0)A				CoMo–K(1)A	CoMo–K(5)A	CoMo–K(10)A
Content (wt%)	CoO		5.0		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	MoO_3	10.0		10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	K_2CO_3			5.0	5.0					1.0	5.0	10.0
	Al_2O_3	90.0	95.0	85.0	80.0	85.0	85.0	85.0	85.0	84.0	80.0	75.0
Reaction condition	P (MPa)			6.1	6.1	3.1	3.1	3.1	6.1	6.1	6.1	6.1
	T (K)			773	773	573	673	773	773	773	773	773
CO conversion (%)				16.7	30.8	1.6	12.7	30.4	57.2	58.9	53.5	39.8
Selectivity (%)	CH_4			65.2	63.5		50.6	68.7	67.0	65.4	62.5	60.5
	CO_2			34.8	36.5		49.3	31.3	33.0	34.6	37.6	39.5
Yield (%)	CH_4			10.89	19.56		6.4	20.9	38.3	38.5	33.4	24.1
	CO_2						6.26	9.52	18.9	20.4	20.1	15.7
	CH_3OH								0.25	0.38	0.82	1.18

Table 3
Reactivity of samples with different promoters or carriers for methanol synthesis

Samples		CO conversion (%)	Selectivity (%)			
			CH_4	C_2H_6	CH_3OH	C_2H_5OH
MoS_2–promotor (20 wt% carbonate) (unsupported)	None	45.9	75.2	19.2		
	K	30.8	58.3	15.7	20.9	2.3
	Na	32.4	53.8	43.8	0.89	0.83
	Ca	20.2	52.1	39.4		
	Mg	23.2	47.6	46.7	tr[a]	tr[a]
MoS_2–20 wt% K_2CO_3/carrier (supported)	γ-Al_2O_3	18.2	81.6	8.2	5.9	1.5
	SiO_2	22.0	53.4	7.0	22.1	10.5
	a.c.[b]	14.5	51.1	5.1	30.6	8.2
	MgO	12.7	65.1	2.3	29.3	3.3

[a] Trace.

[b] Activated carbon.

3. Results and discussion

3.1. WGSR

3.1.1. High steam to CO ratio

3.1.1.1. Reactivity of group 1 samples. The results in Table 1 indicate that MoS_2 alone has some catalytic activity for WGSR owing to the sulfidized species being able to react with steam, and to facilitate the charge transfer between Mo^{6+} and Mo^{4+} [5] during oxidation by H_2O and reduction by CO. The Co species has very poor activity as it is hardly sulfidized [6,7], but it has certain promoting effect as shown in CoMo sample by accelerating the oxygen and sulfur exchange during sulfidation [8] and formation of the active phase CoMoS [1,9,10]. Potassium itself gives a considerable CO conversion, because it has a very strong ability to adsorb H_2O and to start the oxidation reaction quickly. When adding it into CoMo to form a doubly promoted catalyst, its overall catalytic activity increases greatly and the stability toward H_2 increases too. It is believed to be a synergetic action. Potassium acts as an electron donor enhancing the electron density on Mo^{6+} to promote its reduction and sulfidation [5,11,12].

3.1.1.2. Reactivity of group 2 samples. Higher Co/Mo ratio (on atom base) gives higher CO conversion, both in the presence or absence of potassium under different temperatures as shown in Fig. 1. Curves in the figure show that with raising temperature, the percentage of CO conversion over the samples containing potassium increases rapidly and goes through a maximum, nearly close to the equilibrium value. This phenomenon is a typical feature of a reversible exothermic reaction with a very active catalyst. Although the activity of the samples without potassium increases also with temperature, the extent of increase is very low at a low temperature.

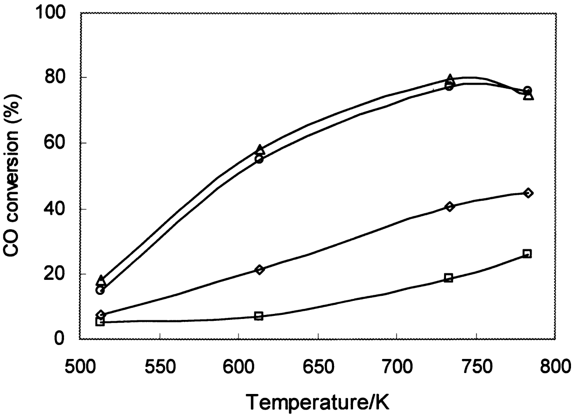

Fig. 1. Reactivity of group 2 samples for WGSR at different temperatures: (□) K(0)–Co–Mo(0.5)A, (○) K(10)–Co–Mo(0.5)A, (◇) K(0)–Co–Mo(1.0)A, and (△) K(10)–Co–Mo(1.0)A.

It implies that these samples have high activation energies.

The effect of higher Co/Mo ratio providing higher activities may be accounted for the dispersion ability of Co on Mo [13] by the formation of $CoMoO_4$ [1,14], which after reduction and sulfidation transforms into the active phase Co–Mo–S [9,10] with Co on the corner or edges of MoS_2 slabs [15]. Excess of Co will result in its isolated form [16]. When potassium is added to Co–Mo, the gap due to their different ratios is filled up markedly.

The influence of heat treatment of samples at 773 K on their reactivity varies with potassium content. When there is no potassium in the samples, the effect of heating is low, because they have been calcined under high temperature before, the change of surface structure should be little. However, the samples containing potassium, say 10.0 wt% K_2CO_3, have a comparatively large decrease in reactivity in low temperature range after heating, since potassium has a high mobility and can be taken away from the sample surface [1] by the gas stream. Particularly under high temperature steam, the loss of potassium leads to a notable loss in its remarkable promoting function, even though their reactivities are still higher than that without potassium.

3.1.1.3. Reactivity of group 3 samples. The effect of potassium content on the catalytic activity for the K–Co–Mo(1.0)A series is shown in Fig. 2. CO conversion increases with potassium loading and gradually reaches a maximum at about 10.0 wt% K_2CO_3. Such a trend of effect is similar for all the three temperatures, 613, 733 and 783 K. Therefore, the role of its action is probably the same and can be attributed to the resultant of its three main effects. Namely, the electronic function to adjust the relative charges between Mo^{6+} and Mo^{4+}; the water sorption capability to balance the ratio of surface coverage by H_2O and CO, and the dispersion ability to give a proper particle size. So potassium is really an important ingredient in the formulation of WGSR catalyst especially when operated under relatively low reaction temperature [5,11].

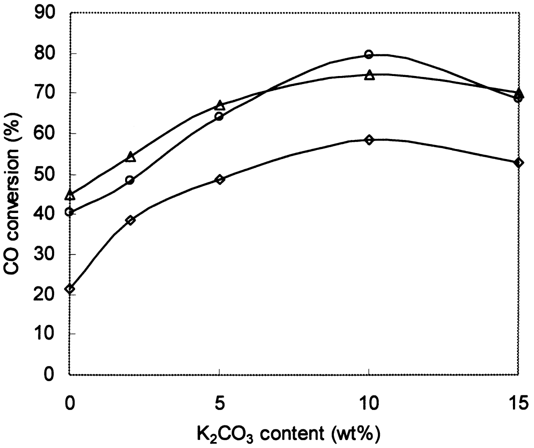

Fig. 2. Activity for WGSR of K–Co–Mo(1.0) with different potassium contents: (◇) 613; (○) 733; (△) 773 K.

Table 4
Effect of H_2O/CO^a ratio

H_2O/CO	1.5	2.6	3.1	3.7
CO conversion (%) at 573 K	38.1	69.5	71.2	68.7

[a] Sample K(10)–Co–Mo(1.0)A.

Now, it should be mentioned that all the above cited experiments were carried out under the condition of steam to CO ratio of 3.1, which is much higher than that of the stoichiometric value 1 based on the equation $H_2O+CO=CO_2+H_2$. Even under higher H_2O/CO ratio, yet at a relatively low reaction temperature, say 573 K, the CO conversion is far lesser (Table 4) than the equilibrium value. In order to enhance the conversion, one way is to raise the temperature, in our experiments, to 723–733 K giving 80.0% conversion, pretty close to its equilibrium conversion with K(10)–Co–Mo(1.0)A at H_2O/CO 3.0:1. This policy, however, leads to higher energy consumption.

3.1.2. Low steam to CO ratio catalysts

The reactivities of CoMoK samples supported on TiO_2–Al_2O_3 with different TiO_2 content under the temperature from 553 to 723 K are shown in Fig. 3. From these data it is seen that (1) with increasing TiO_2, the CO conversion falls a little at first, then rises steadily until over 15.0 wt%, then slowly. There seems to be no limitation in the amount of TiO_2. In fact in certain formulations, TiO_2 can replace γ-Al_2O_3 completely (2) the temperature curves except that at 553 K run roughly parallel, with the lower temperature curve 623 K on the top. The decrease in CO conversion for low TiO_2 (<5.0 wt%) is probably due to uneven cover-

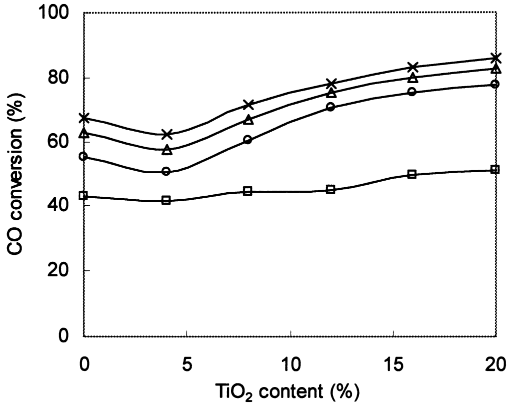

Fig. 3. Effect of TiO_2 content on the reactivity for WGSR of CoMoK/TiO_2–Al_2O_3 catalysts: (□) 553; (○) 723; (△) 673; (×) 623 K.

age on γ-Al_2O_3. The fact that reactivities rise with increasing TiO_2, shows its action with the increase in the available active Mo site. Because the number of sites is comparatively less dependent on reaction temperature, the three curves are approximately in parallel.

The relative position of these curves is explained from the thermodynamic relationship between the temperature and H_2O/CO of the WGSR. As it is an exothermic reversible reaction, if a very high activity catalyst is running under one H_2O/CO ratio, then it will provide a higher degree of conversion at relatively low reaction temperature. Here the 623 K curve lies on the top, and it is clear that the catalyst is really very active.

In practice the TiO_2-containing catalysts can be used under the conditions of even lower H_2O/CO ratios as the experiments show that, when the steam to carbon monoxide ratio in the feed is reduced from 2.2 to 1.8, the CO conversion over the catalyst with 15.0 wt% TiO_2 at 623 K falls merely from 83.3% to 80.6%, which is still much higher than that for the catalyst without TiO_2 at 623 K. Moreover, the TiO_2-containing catalysts have a higher thermal stability [2,17] than that without it, because the TiO_2 together with γ-Al_2O_3 has been calcined under 773 K, and a more stable composite carrier has already formed. Therefore, they can be operated in wider temperature and H_2O/CO ranges. It is worthy to mention that ZrO_2 has almost the same property as TiO_2 and can be used in the low steam to CO ratio catalyst [18].

TiO_2 itself is a good catalyst carrier. In addition, it has some ability of transferring electrons between the catalyst main and itself. It is sometimes called the double function carrier [19–21]. When it is incorporated with Al_2O_3, it forms an intermediate layer between Mo species and γ-Al_2O_3 [22,23]. It is known that Mo is octahedrally and tetrahedrally coordinated on γ-Al_2O_3 [11,24], but only the octahedrally coordinated species can be easily reduced and sulfidized to form the active phase, the tetrahedral one cannot [6]. As TiO_2 is added, Ti occupied the tetrahedral site on γ-Al_2O_3 and as a consequence more octahedral Mo species are formed, so the activity of the Mo phase is increased [2,24,25]. On the other hand, the interaction between Mo species and the composite carrier makes it more highly dispersed and activated as well as easily reduced and sulfidized as seen from the peaks appearing under the lower reduction temperatures in our TPR experiments. Its electronic action can adjust the Mo valences of 6+ and 4+ in a proper ratio necessary for the redox behavior of WGSR. It can react with Co to form a part of $CoTiO_3$ to enhance the promoting effect of Co [2,26]. The result is that the steam to CO ratio can be lowered to about 2, and the corresponding reaction temperature to 623 K.

3.2. Methanation

3.2.1. Reactivity of Mo–K(5)A and Co–Mo–K(5)A

Results shown in Table 2 display that the reactivity of the samples containing Co is much higher than that without it, nearly doubled, once again demonstrating the promoting effect of Co on Mo [27–29].

Referring to the reaction path of methanation, CO adsorbed on the sample must be dissociated into C_{ad} and O_{ad} first, then followed by C_{ad} hydrogenation to form CH_4. Here Co accelerates the process [3]. On the other hand, from the product distribution, except CH_4, CO_2 is also formed. Since there are two main reactions occurring in methanation: $CO+H_2\rightarrow CH_4+H_2O$ and $CO+H_2O\rightarrow CO_2+H_2$, it means that CO_2 is coming from CO directly, that is, there must be a certain amount of undissociated CO on the surface. Actually associated and dissociated CO coexist on the surface [3]. The former can be either reacted with the O_{ad} or H_2O to produce CO_2. With the same amount of potassium present in the samples, WGSR may be the predominant side reaction, as seen from Table 2 of those with and without Co, their selectivities do not differ much.

It is worthwhile to point out that the reaction is carried out at rather high pressure and temperature. High pressure benefits the volume decreasing process as in methanation, but almost does not influence in WGSR. High temperature favors CO dissociation, as required for methanation, and not for WGSR. Especially, in the methanation system the steam content is low. The reaction conditions are evidently favorable to methanation, but it ought to be said that Co–Mo–K(5)A is not a proper sample to be used as a catalyst for methanation.

3.2.2. *Reactivity of CoMo–KA samples*

3.2.2.1. Effect of temperature and pressure. The data are shown in Table 2. When the pressure is fixed at 3.1 MPa, the reactivity of the sample CoMo–K(0)A in terms of CO conversion at a low temperature, 623 K, is very poor, but it increases steadily with the temperature. However, the rate of increasing selectivity of CH_4 does not keep pace with the CO conversion, because the relative number of sites occupied by dissociated and undissociated CO changes with the competitive reaction kinetics of methanation and WGSR [30,31]. Such as under a certain particular temperature, say 673 K, in this system, the selectivity of CH_4 and CO_2 is nearly same, while at 773 K their ratio turns to about 2:1. The ratio of dissociated and undissociated CO varies with temperature and they are always in dynamic equilibrium.

At the fixed temperature 773 K with the pressure raised from 3.1 to 6.1 MPa, carbon monoxide conversion is increased greatly, but methane selectivity decreased slightly, at the same time CO_2 selectivity increased slightly. Such a result is attributed to the establishment of a new dynamic equilibrium including associated and unassociated CO under different pressures and involving the competitive reaction of methanation and WGSR. Raising pressure often leads to increase of the surface concentration of both reactants and products, and the reaction rate and yield as well.

However, in this system, the dependency of product selectivity on pressure seems less than that on temperature.

3.2.2.2. Effect of potassium content. Change in the reactivities of CoMo–KA samples with increasing potassium content is listed in Table 2. From the data it is obtained that with increasing potassium content in the sample, the selectivity of CH_4 decreases continuously and that of CO_2 increases correspondingly, but CO conversion increases a little at 1 wt% K_2CO_3, then decreases. The increase in CO conversion at first must be due to the preferential reaction of WGSR by the addition of potassium, as shown in the column of CO_2 selectivity.

Potassium is a well-known effective electronic promoter acting as an electron donor to increase the electron density in MoS_2 and to cause the adsorbed CO increasing in its bond strength to prevent too much CO dissociation.

CO-TPD results show that there is a small CO desorption peak from CoMo–K(0)A at 513 K, and a bigger one from CoMo–K(10)A at 543 K. This indicates the function of potassium. But, after treating CoMo–K(10)A in CO at 673 K, this desorption peak is sharply decreased and CO_2 is detected in the effluent gas. It means that a large portion of adsorbed CO is dissociated, at the same time the remaining part of undissociated CO reacts with the O_{ad} (from CO dissociation) to form CO_2. So, at higher temperature, even in the presence of potassium the relative selectivity of CH_4 is always higher than that of CO_2.

From the data it can also be concluded that, as the potassium content increases, the CO conversion is decreased stronger than the CO_2 is increased. The reason is that the action of potassium in promoting oxidation reaction usually is accompanied with the retardation of hydrogenation reaction, hence, potassium is generally not used as a hydrogenation promoter as in the case of CO hydrogenation to form CH_4. Yet, on the other hand, the methanol yield increases with potassium, as will be discussed in Section 3.3.

It should be noted that if the promoter Co is replaced by Ni, the selectivity of CH_4 will reach up to 98%, in the absence of potassium.

3.2.2.3. Reactivity and stability of CoMo–K(5)A. Fig. 4 shows the comparison of the reactivity of CoMo–K(5)A and Co–Mo–K(5)A in the period of 8 h, the former is much higher than the latter, and even the former decreased appreciably with time.

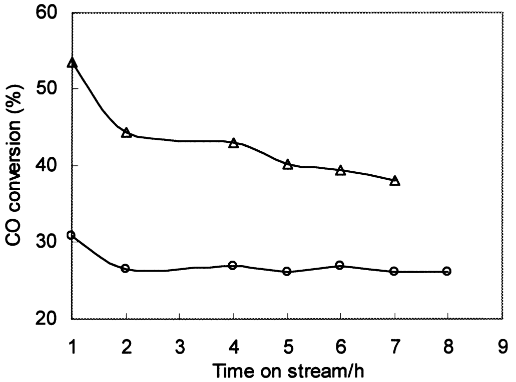

Fig. 4. Influence of preparation condition on stability at 773 K, 6.1 MPa, SV=3600 h^{-1}: (△) CoMo–K(5)A; (○) Co–Mo–K(5)A.

The XRD patterns of the oxide precursors of Co–Mo–K(5)A give the characteristic peaks of Co_3O_4 [1,3] and MoO_3 [1,3], while those of CoMo–K(5)A show only weak K_2CO_3 and Al_2O_3 peaks. After sulfiding, the former gives Co_9S_8, Co_4S_3, and MoS_2 [3], while the latter only a weak Al_2O_3 peak. From the XPS spectra of the freshly sulfided samples of the S2P peak of S^{2-}, the former gives two separate peaks, Co_9S_8 and MoS_2, while the latter only a single one.

These results lead to the following conclusion. The sample prepared by successive stepwise impregnation of Co and Mo solutions followed by calcination at 773 K, gives an uneven distribution of Co and Mo phase and a lower reactivity, while that by co-impregnation of Co and Mo mixed solution followed with a lower temperature calcination at 573 K gives a homogeneous CoMoS phase and higher reactivity. On the other hand, since the reaction temperature is 773 K, which is much higher than the calcination temperature of the co-impregnated sample, so some degree of redistribution or separation of the components is unavoidable during operation, thus being the source of instability of CoMo–K(5)A.

Fig. 5 shows the change in stability of CoMo–KA samples; with the increasing potassium the reactivity of these falls down rapidly with time on stream. XPS data show that in comparison with the standard BE (binding energy) values of $Mo3d_{5/2}$ and $Mo3d_{3/2}$ of MoS_2, those samples containing potassium after reaction have the corresponding values of Mo^{4+} shift to a lower energy side [3,5]. It means their electron densities are increased with the addition of potassium and the valency of Mo during reaction changes between $Mo^{4+\delta+}$ and $Mo^{4+\delta-}$. However, it is also observed in the XPS spectra that there is a peak shoulder at $Mo3d_{3/2}$ peak with a BE value clearly higher. It indicates that Mo^{6+} is formed from the oxidation reaction of H_2O and by the promotion effect of potassium. Moreover, the peak of S^{2-} is weakened, while that of S^{6+} is generated, both of them responding to the other source of instability and deactivation; the more potassium added, the quicker the sample deactivated.

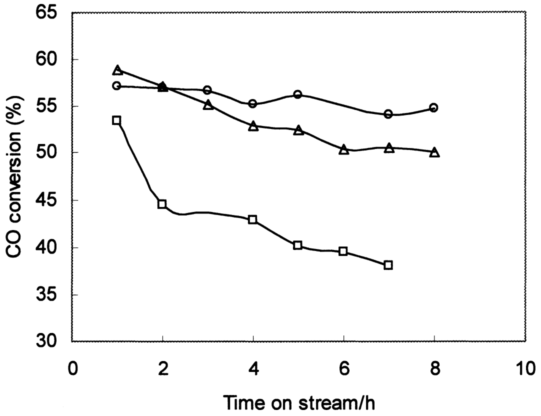

Fig. 5. Effect of potassium content on stability under methanation conditions (773 K and 6.1 MPa): (○) CoMo–K(0)A; (△) CoMo–K(1)A; (□) CoMo–K(5)A.

3.3. *Model sample for methanol synthesis*

3.3.1. *Reactivity of unsupported model catalysts*

3.3.1.1. Single promoter. The results (Table 3) show that the laboratory prepared MoS_2 itself is moderately active with a high selectivity of CH_4, some selectivity for C_2H_6, but no alcohol is formed. This means that CO is dissociatively adsorbed on the surface and hydrogenated to hydrocarbons with certain extent of chain propagation and water formation. With the carbonate promoters, the carbon monoxide conversion and CH_4 selectivity are lowered, C_2H_6 increased, while with K_2CO_3 alcohols are formed at the expense of C_2H_6. All of these promoters are basic in nature, having the property of suppressing hydrogenation, but promoting the growth of carbon chain and alcohols formation in some cases [4,32–36].

Probably, it is proper to point out that in these samples 20.0 wt% of promoters are present, much more than is reasonable for an electronic promoter, so it might be called a modifier, and of course, their basicity remains. An outstanding feature appears in K_2CO_3: the selectivity for methanol is even higher than that of C_2H_6. The observation agrees with TPR experiment, besides the common peak responsible for CH_4 formation, there is a new peak unique for methanol. The structure of the new phase is not fully clear yet, it must be a compound generated after reaction of K_2CO_3 and MoS_2, tentatively denoted as $MoS_2{\cdot}xK_2S$ ($x<1$) or Mo–S–K [33,34], in which the large potassium ion is distributed on the corner and/or edges of the MoS_2 slabs and intimately connected with an active sulfur species being able to be abstracted by hydrogen.

Fig. 6 shows that with increasing potassium content in MoS_2 samples, carbon monoxide conversion drops quickly at first, then slowly. Methane selectivity decreases continuously up to 20.0 wt% K_2CO_3, then increases. Ethane always occurs in an appreciable amount, and varies a little. Its appearance is at the expense of CH_4. Methanol selectivity changes in contrast with methane. Small amounts of ethanol are formed.

Under low potassium content, potassium mainly acts as an electronic promoter. It affects both the bonds between C and O as well as C and Mo with C–O bond weakened resulting in co-existence of associated and dissociated CO. Even in the high potassium range, such effect exists, so both hydrocarbons and alcohols are formed throughout with different selectivity.

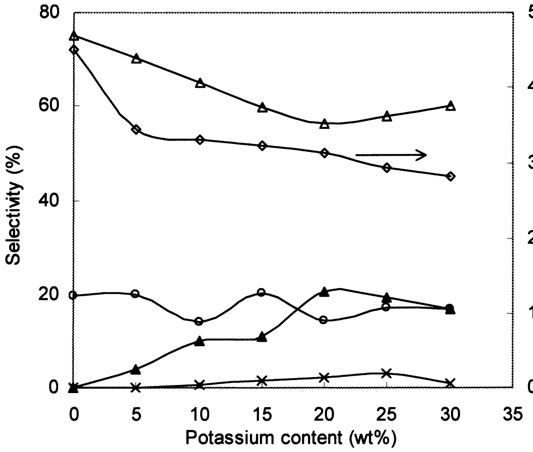

Fig. 6. Effect of potassium loading in molybdenum sulfide samples on selectivity and reactivity: (△) methane; (▲) methanol; (◇) CO conversion; (○) ethane; (×) ethanol.

In methanol formation undissociated CO is required and accompanied with a moderately activated hydrogen species. Such a requirement is preliminarily fulfilled in the present case by the structure of Mo–S–K phase, in which Mo–S is the center for CO adsorption and activation, K–S probably is for heterolytic cleavage of H_2 to form H^+ and H^-, followed by their interconnection to O and C atom, respectively. Twenty wt% K_2CO_3 is an optimum to produce a comparatively high yield of methanol with the sacrifice of some overall reactivity. Carbon chain lengthening is another function of potassium by enforcing the Mo–C linkage [37].

3.3.1.2. Double promoter. The effect of cobalt or nickel on the reactivity of Mo–S–K is that they cause an enhancement of both the CO conversion and selectivity of hydrocarbons, but the alcohols selectivity is lowered, especially with Ni. In fact, one of the main functions of Co and Ni is to promote CO dissociation and deep hydrogenation.

3.3.2. Reactivity of supported model catalysts

3.3.2.1. Single carrier. The carriers affect the reactivity and selectivity of MoS_2 with 20.0 wt% K_2CO_3 in several ways. The sequence in increasing order of reactivity is MgO<a.c.<γ-Al_2O_3<SiO_2<none (Table 3). The CH_4 selectivity increases in the order of a.c.<SiO_2<none<MgO<γ-Al_2O_3. The sequence for methanol selectivity is γ-Al_2O_3<none<SiO_2<MgO< a.c. No system favors both high CO conversion and methanol selectivity simultaneously. SiO_2 gives relatively high reactivity and not too low methanol selectivity, because it has a mild acidity that favors partial hydrogenation. MgO gives a comparatively high methanol selectivity due to its mild basicity, favoring formation of hydroxyls. Based on this idea, a proper combination of SiO_2 and MgO might furnish an optimized acidity and basicity for a high methanol selectivity and yield.

3.3.2.2. Combined carrier. The effect of changing magnesium oxide content in SiO_2–MgO combined

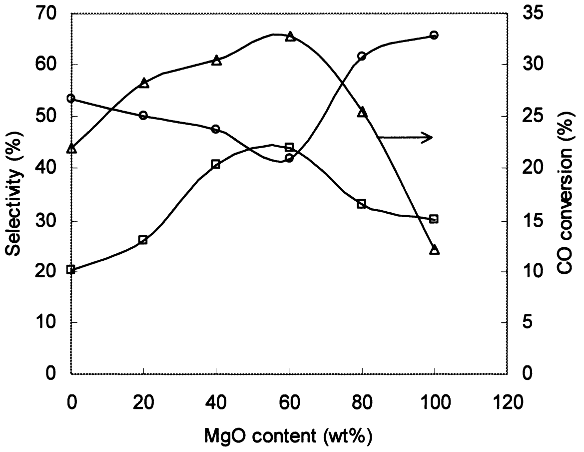

Fig. 7. Effect of MgO content in MgO–SiO$_2$ of MoS$_2$/K$_2$CO$_3$/MgO–SiO$_2$ on carbon monoxide conversion, selectivity of methane and methanol: (○) methane; (□) methanol; (△) CO conversion.

carrier on activity and selectivity is shown in Fig. 7. As MgO increases from 0 to about 60 mol%, carbon monoxide conversion goes up from 22.0% to a maximum of 32.0%, with hydrocarbon selectivity falling to a minimum of 40.0%, and alcohol rising to a maximum of 45.0%. It is remarkable that the selectivity of methanol exceeds that of CH$_4$.

Such a behavior mainly comes from the lower acid-strength and acid-site concentration of the carrier itself as well as after its interaction with MoS$_2$ and K$_2$CO$_3$, as shown in Table 5. (Peak temperature corresponds to acid-strength, adsorbed amount corresponds to number of acid-sites.)

Pure SiO$_2$ is a mild solid acid. When it is combined with some other metal oxides, its acidity may fluctuate. When MgO, a mild solid base, is incorporated in SiO$_2$, it makes SiO$_2$ more acidic at low MgO loading, whereas when more MgO is added, the acidity of SiO$_2$ decreases continuously. Meanwhile, basicity of MgO develops to form an amphoteric composite acid–base solid in a certain range of composition.

After the combined carrier MgO–SiO$_2$ (60.0 mol% MgO) is ground with the catalyst MoS$_2$–K$_2$CO$_3$ (20.0 wt% K$_2$CO$_3$) and calcined, the acidity of the final product is lowered further and conjugated weak acid–base pair are generated, necessary to stabilize both C–H bond and O–H bond in methanol synthesis. In contrast, strong acid–strong base, strong acid–weak base or weak acid–strong base pairs [38,39] do not provide such a valuable function. The sample with this combination is thus taken for further study of the effect of reaction condition on the reactive properties.

Another series of samples of MoS$_2$–20.0 wt% K$_2$CO$_3$ supported on a combined Li$_2$O–γ-Al$_2$O$_3$ carrier has also been studied. The CO conversion is very low and the methane selectivity is much higher than that of methanol. This can be attributed to the lack of proper acid–base pairs.

3.3.3. *Reactivity change with reaction conditions*

3.3.3.1. Temperature and pressure. Raising the temperature from 513 to 573 K, both the carbon monoxide conversion and hydrogenation rate is increased. The product distribution is determined by the thermodynamics as well as kinetics of the system. In the above temperature range the formation of methane and its homolog is practically irreversible, their selectivity increases with temperature, especially methane. The selectivity of methanol changes contrary to methane by the high reversibility of methanol, but that of higher alcohols increases a little. The carbon chain growth is entirely due to potassium. At 533 K, methanol yield reaches a maximum of 113.1 g/l h, at 4.1 MPa.

Raising the pressure from 4.1 to 8.1 MPa, CO conversion is increased. The selectivity of methane and methanol varies in reverse order too as in the temperature effect. At higher temperature more CO is dissociated, while at higher pressure, more CO is

Table 5
NH$_3$-TPD data of different carriers and of supported MoS$_2$/K$_2$CO$_3$

Sample	Al$_2$O$_3$	SiO$_2$	MgO–SiO$_2$	MoS$_2$/K$_2$CO$_3$/MgO–SiO$_2$
Peak temperature (K)	555	482	491	473
Adsorbed amount of NH$_3$ (mol/g cat)	1.80×10^{-6}	4.60×10^{-7}	1.67×10^{-7}	5.60×10^{-8}

undissociated. At medium temperature (533 K), the yield of methanol rises steadily up to 180 g/l h, at 8.1 MPa.

3.3.3.2. Space velocity. Raising space velocity from 800 to 3000 h^{-1}, CO conversion is decreased, the CH_3OH yield is rapidly increased from 17.6 to 113.1 g/l h, whereas methane yield is decreased.

In the whole course of reaction, the first step is associative adsorption of CO. The following step may be either to keep it undissociated and reacting with H_2 to produce methanol in a short time or transformed into the dissociated form at longer time on the surface enabling complete hydrogenation and chain growing. For partial hydrogenation of undissociated CO enough time is also needed, so CO dissociation is unavoidable. A reasonable high space velocity favors methanol formation.

3.3.3.3. H_2/CO ratio. Raising H_2/CO from 1.2 to 3.5, CO conversion and CH_4 selectivity are both increased by the mass action law, CH_3OH selectivity is decreased accordingly, so a better CH_3OH yield can be obtained somewhere between the two ratios.

After considering all of the different parameters including favorable and unfavorable effects on the methanol synthesis a compromise is made, i.e. T=533 K, P=8.1 MPa, SV=3600 h^{-1}, H_2/CO=1.4, sulfur content=1350 ppm, CO conversion=35.0%, methanol selectivity=54.0%, methanol yield=180 g/l h.

4. Summary

4.1. Fundamental features

In WGSR, methanation and methanol synthesis, the reactants and products consist of CO, H_2, H_2O, CO_2 and/or hydrocarbons and alcohols. The former four are common to the three reactions, and the later two are the products from methanation and methanol synthesis, always in competition. WGSR is the one taking place in each reaction resulting with lowering the yield of methanation and methanol synthesis by the formation of CO_2. Besides careful controlling the reaction conditions, the most effective way to lessen CO_2 content in these two reactions and increasing the yield of their main products is to design a suitable catalyst.

4.2. Active catalyst

MoS_2 is taken as the catalyst proper. It shows both the capacity of hydrogenation and oxidation in the system of CO, H_2, H_2O and CO_2. The major valency of Mo in H_2 is 4± and some Mo is present as Mo^{3+} and Mo^{5+}. In steam the major valence are Mo^{6+} and Mo^{4+}. The degree of conversion and product distribution is determined by the behavior of active phases present. Excluding the carrier, the primary and secondary active catalytic phases are Co–Mo–S–K and Mo–S–K for WGSR, CoMo–S and Co–Mo–S–K or Mo–S–K for methanation and Mo–S–K for methanol synthesis. Here, it can be seen, one active phase may be the primary phase for one reaction and at the same time the secondary phase for another reaction. Such a fact leads to many products in common. By the introduction of promoters and carriers their relative reactivities can be adjusted.

4.3. Promoters

4.3.1. Potassium

Potassium is a very important promoter used in the present system. It has many functions, e.g. basicity, H_2O absorbing ability and electron transferability as to strengthen C–O bond or C–Mo bond, to promote oxidation reaction and carbon chain growing and to retard hydrogenation reaction. Its overall effect strongly depends on the quantity applied, in the formulation, e.g., 20.0 wt% in methanol synthesis catalyst to fit for partial hydrogenation of the undissociated CO, 1.0 wt% in methanation for deep hydrogenation of the dissociated CO and 10.0 wt% in WGSR for increasing H_2O adsorption and oxidation rate.

4.3.2. Cobalt

Co is a multiple function promoter, usually used in commerce with Mo in catalytic hydrotreating process. It makes molybdenum oxide better dispersed on the carrier and isolated Mo species decreased by the reaction between Co and Mo species. Thus, it facilitates the oxide to be easily reduced and sulfided in the formation of active phases. Co also promotes the dissociation of adsorbed CO and activation of H_2 for hydrogenation.

4.4. Carrier

γ-Al_2O_3 is the most commonly used carrier for Mo species to form a uniform monolayer. It has a high surface area and a strong acidity favorable for hydrogenation reaction, as required in CO methanation, but not for partial hydrogenation in methanol synthesis and oxidation reaction in WGSR. The drawbacks come mainly from two sides. One is its high acidity, the other is its strong surface reaction with Mo species, making Mo less active. In WGSR, TiO_2 or ZrO_2 is combined with Al_2O_3 to decrease such action making Mo more active, at the same time a considerable quantity of K_2CO_3 is used to neutralize its acidity somewhat, hence a low steam/CO and low reaction temperature catalyst is obtained. In methanol synthesis an entirely new combined carrier 60.0 mol% MgO–SiO_2 was used instead of γ-Al_2O_3, in order to get a weak acid–base pair to enhance methanol selectivity.

References

[1] Z.S. Chang, Master Thesis, Tianjin University, China, 1989.
[2] L.C. Dong, Master Thesis, Tianjin University, China, 1996.
[3] D.X. Wang, Ph.D. Thesis, Tianjin University, China, 1990.
[4] Y.J. Wang, Ph.D. Thesis, Tianjin University, China, 1992.
[5] X.F. Xie, H.B. Yin, B.S. Dou, J.C. Huo, Appl. Catal. 77 (1991) 187.
[6] K.S. Chung, F.E. Massoth, J. Catal. 64 (1980) 332.
[7] S.Z. Liu, Master Thesis, Tianjin University, China, 1990.
[8] P. Arnoldy, J.L. de Booys, B. Scheffer, J.A. Moulijn, J. Catal. 96 (1985) 122.
[9] H. Topsøe, B.S. Clausen, N.Y. Topsøe, E. Pedersen, Ind. Eng. Chem. Fund. 25 (1986) 25.
[10] F. Labruyere, M. Lacroix, D. Schweich, M. Breysse, J. Catal. 176 (1997) 464.
[11] V. Kettmann, D. Balgavy, L. Sokel, J. Catal. 112 (1988) 93.
[12] D.S. Newsome, Catal. Rev.-Sci. Eng. 21 (1980) 275.
[13] R. Iwamoto, K. Inamura, T. Nozaki, A. Iino, Appl. Catal. A 163 (1997) 217.
[14] K.S. Clung, F.E. Massoth, J. Catal. 64 (1980) 320.
[15] E. Diemann, Th. Weber, A. Müller, J. Catal. 148 (1994) 288.
[16] S.M.A.M. Bouwens, J.A.R. van Veen, D.C. Koningsberger, V.H.J. de Beer, R. Prins, J. Phys. Chem. 95 (1994) 123.
[17] J. Ramirez, L. Ruiz-Ramirez, L. Cedeno, V. Harle, M. Vrinat, M. Breysse, Appl. Catal. A 93 (1993) 163.
[18] Y.F. Geng, Master Thesis, Tianjin University, China, 1998.
[19] F.J.G. Liamhas, L. Bouyssieres, A.L. Agudo, Appl. Catal. 65 (1990) 45.
[20] Z.B. Wei, Q. Xin, Acta Phys. Chim. Sinica 10 (1994) 931.
[21] Z.B. Wei, Q. Xin, X.X. Guo, P. Grange, B. Delmon, Appl. Catal. 75 (1991) 179.
[22] M.A. Stranick, M. Houalla, D.M. Hercules, J. Catal. 106 (1987) 362.
[23] S. Damyanova, A. Spojakina, K. Jiratova, Appl. Catal. A 125 (1995) 257.
[24] P. Arnoldy, M.C. Franken, B. Scheffer, J.A. Moulijn, J. Catal. 96 (1985) 381.
[25] H.C. Yao, J. Catal. 70 (1981) 332.
[26] M.A. Stranick, M. Houalla, D.M. Hercules, J. Catal. 125 (1990) 214.
[27] S.I. Kim, S.I. Woo, Appl. Catal. 74 (1991) 109.
[28] R.G. Leliveld, A.J. Van Dillen, J.W. Geus, D.C. Koningsberger, J. Catal. 165 (1997) 184.
[29] N.Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 386.
[30] H. Peggy, Y. Hou, H. Wise, J. Catal. 93 (1985) 409.
[31] M. Logan, A. Gellman, G.A. Somorjai, J. Catal. 94 (1985) 60.
[32] J.Y. Zhang, Y.J. Wang, L. Chang, Appl. Catal. A 126 (1995) L205.
[33] J.Y. Zhang, Y.J. Wang, L. Chang, Appl. Catal. A 126 (1995) L219.
[34] G.Z. Bian, Y.S. Ma, Y.L. Fu, Y.N. Xie, T.D. Hu, Acta Phys. Chim. Sinica 5 (1996) 406.
[35] Y.L. Fu, M. Jiang, G.Z. Bian, Y.Z. Yue, W. Jiang, J. Fuel Chem. Tech. (Chinese) 21 (1993) 27.
[36] W. Gao, C.F. Zhang, J.L. Pi, G. Lu, Z.B. Zhu, F. Yu, L.H. Tang, F. Liu, J. Fuel Chem. Tech. (Chinese) 21 (1993) 34.
[37] X.D. Xu, E.B.M. Doesburg, J.J.F. Scholten, Catal. Today 2 (1987) 125.
[38] K. Tanabe, T. Yamaguchi, Catal. Today 20 (1994) 185.
[39] E. Iglesia, D.G. Barton, J.A. Biscardi, M.J.L. Gines, S.L. Soled, Catal. Today 38 (1997) 339.