Chapter 2

Literature Review

One of the most important parts in energy production by fuel cell is hydrogen resource. The hydrogen could be obtained from the methanol reforming process using catalysts. The catalyst is considered as one of the important parts in methanol reforming to reduce the activation energy of reaction and enhance the reaction activity.

Literature search

There are many catalysts in methanol reforming reported in literatures. The performance of the catalysts depends on metal, promoter, support and reaction condition. Table 1 shows the catalytic system of methanol reforming as well as the catalyst performance and the reaction condition.

Abbreviation:

- Ref no. = Reference number
- SRM = steam reforming reaction
- POX = partial oxidation reaction
- OSRM = oxidative steam reforming reaction
- Temp = temperature
- cp-method = co-precipitation method
- hp-method = homogeneous precipitation method by using urea
- cpsi = cells per square inch
- CNT = carbon nano tube

Table 1 The catalytic system of methanol reforming

Ref no.	Catalyst	Reaction	Reactor	Temp (°C)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
16	$Cu/ZnO/Al_2O_3$	SRM	Micro-channel reactor	290	-	99.3	0.7	-
17	$Cu/ZnO/Al_2O_3$	OSRM	Fixed bed reactor	200	1	100	0.8	The catalysts were prepared by hp-method.
18	$ZnO\text{-}Cr_2O_3$/ $CeO_2\text{-}ZrO_2/Al_2O_3$	OSRM	Fixed bed tubular quartz reactor	280	1	100	< 1.4	The catalysts were coated on cordierite honeycomb ceramic with 400 cpsi.
19	$Cu/ZnO/Al_2O_3/Pt/Rh$	SRM	Fixed bed tubular reactor	360	-	97	< 3	- The catalysts were coated on cordierite honeycomb ceramic with 400 cpsi. - Catalyst stability at least 18 hours.
20	$Cu/ZnO/Al_2O_3$	SRM	Micro-channel reactor	340	-	98	1.3	-
21	$Pd/ZnO/Al_2O_3$	OSRM	Continuous flow reactor	350	1	100	11.5	-
22	Cu/Zn/Ce/Al oxide	OSRM	Fixed bed reactor	280	1	100	0.1	The stability of catalysts are at least 72 hours.
23	$Pd/ZnO/Al_2O_3$	OSRM	Fixed bed reactor	400	1	97	7	-

Ref no.	Catalyst	Reaction	Reactor	Temp (°C)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
24	$Pd/ZnO-Cu/ZnO/Al_2O_3$	OSRM	Micro-channel reactor	450	1	99.6	17	Pd/ZnO over $Cu/ZnO/Al_2O_3$
25	Cu/Ce	SRM	Fixed bed reactor	300	1	100	4	The performance of various promoters on CuO/CeO_2.
	Cu/Ce/Mg			300			3.5	
	Cu/Ce/Zn			300			3	
	Cu/Ce/Zr			300			2.5	
	Cu/Ce/La			300			2.5	
	Cu/Ce/Pd			280			10	
	Cu/Ce/Rh			300			14	
	Cu/Ce/Sm			300			3	
	Cu/Ce/Y			300			2	
	Cu/Ce/Ca			320			2	
	Cu/Ce/Gd			300			3	
26	Co/SiO_2	SRM	Micro-reactor	200	1	37	-	-
	Ni/SiO_2			220		53		
27	$Pd/ZnO/Al_2O_3$	SRM	Tubular packed bed reactor	250	0.84	93	2	-
28	Cu/ZnO over wafer	SRM	Micro-reactor	300	1	100	1.1	-
29	Pd-Cu/ZnO	SRM	Fixed bed tubular reactor	250	1	48	0.3	Pd over Cu/ZnO

Ref no.	Catalyst	Reaction	Reactor	Temp (°C)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
30	$Cu/ZnO/Al_2O_3$	SRM	Micro-reactor	340	-	97	2.3	-
31	$Cu/ZnO/ZrO_2/Al_2O_3$	SRM	Micro-channel reactor	260	-	92	0.1	-
32	Cu/Zn/Ce/Al oxide	SRM	Continuous flow fixed bed reactor	280	1	100	0.6	The stability of catalysts are at least 20 hours.
33	$Pd/ZnO/Al_2O_3$	OSRM	Fixed bed gas flow reactor	350	1	100	3	Finely dispersed Pd/ZnO on Al_2O_3.
34	Zn/TiO_2	SRM	Fixed bed quartz reactor	400	-	100	30	-
		OSRM					10	
35	$Cu/ZnO/Al_2O_3$	OSRM	Fixed bed flow micro-reactor	450	1	100	0.6	The catalysts were prepared via hydrotalcite using hydroxycarbonate precursor.
36	Cu/ZnO	OSRM	Stainless steel cylindrical reactor	290	-	98	1.3	The catalysts were prepared by papermaking technique.
37	Cu/Mn oxide foam	OSRM	Conventional flow in quartz tube reactor	320	1	100	6.5	-
38	$ZnO\text{-}Cr_2O_3/$ $CeO_2\text{-}ZrO_2/Al_2O_3$	SRM	Micro-channel reactor	460	-	100	2	-
39	$Cu\text{-}Cs/Al_2O_3$	SRM	Continuous flow fixed bed reactor	300	1	94	-	-

Ref no.	Catalyst	Reaction	Reactor	Temp (°C)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
40	Cu/Cr	POX	Fixed bed continuous flow quartz reactor	200	1	86.5	12.2	The performance of various promoters on Cu/Cr.
	Cu/Cr/Co					84.2	14.2	
	Cu/Cr/Ce					90.2	17.5	
	Cu/Cr/Ni					88.6	31.4	
	Cu/Cr/Mg					70	17.3	
	Cu/Cr/Zr					79.1	15.3	
	Cu/Cr/Zn					96.1	12.5	
	Cu/Cr/Fe					61.5	10.1	
	Cu/Cr/Al					77	18.1	
41	cp-Cu/ZnO	SRM	Fixed bed flow reactor	250	1	46.4	0.4	cp = co-precipitation hp = co-precipitation
	hp-Cu/ZnO					89.2	2.7	
	hp-Cu/ZnO/Al_2O_3					97.3	1	
42	Cu/ZnO	SRM	Fixed bed micro-reactor	300	1	100	3	-
43	Cu/ZnO/Al_2O_3	SRM	Fixed bed glass tube reactor	260	-	100	2	-
44	Cu/ZnO/Al_2O_3-HTN	SRM	Fixed bed tubular reactor	250	1	50	-	The catalysts were modified with hydrotalcite nitrate.

Ref no.	Catalyst	Reaction	Reactor	Temp (°C)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
45	Plate-type Pd/ZnO	SRM	Conventional flow reactor	350	1	96.9	18.2	The catalysts were coated on Al-plates.
46	Cu/Mn	OSRM	Fixed bed reactor	240	1	100	3	-
47	Cu/Zn/Y	SRM	Micro-reactor	300	1	72	0.1	-
	Cu/Zn/La					62		
48	K/Ni/Al	SRM	Fixed bed tubular reactor	400	1	85	14	The Ni/Al catalysts were promoted with K.
49	Ni/Al	SRM	Fixed bed tubular reactor	390	1	95	10	-
50	Cu/ZnO/CNT	SRM	Fixed bed tubular reactor	365	1	100	2	-
51	Cu/CeO_2	OSRM	Conventional fixed bed flow reactor	260	1	100	-	-
52	Cu/ZnO	POX	Vertical quartz tube reactor	250	-	73	-	-
	Pt/ZrO_2					93		
53	$Cu/CeO_2/Al_2O_3$	OSRM	Fixed bed reactor	280	1	100	0.19	The stability of catalysts are at least 48 hours.
54	Cu/Zn/Al/Zr-Cu	SRM	Micro-reactor	255	-	90	7	The Cu/Zn/Al/Zr catalysts were coated on various metal foams.
	Cu/Zn/Al/Zr-Cu/Zn					85	8	
	Cu/Zn/Al/Zr-Fe/Cr/Al					93	7	
	Cu/Zn/Al/Zr-Ni					83	16	

Ref no.	Catalyst	Reaction	Reactor	Temp (°C)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
55	$Cu/ZnO/Al_2O_3$	OSRM	Fixed bed reactor	350	1	100	< 1	-
56	Cu/ZnO	SRM	Fixed bed micro-reactor	300	1	100	< 1	The catalysts were prepared via a practical soft reactive grinding route based on dry oxalate-precursor.
57	Na_2CO_3-leached Al/Cu/Fe	SRM	Conventional flow reactor	300	1	-	-	H_2 production rate is 677 ml/(min·g_{catal})
	Commercial Cu based							H_2 production rate is 181 ml/(min·g_{catal})
58	Cu/ZrO_2	SRM	Fixed bed flow reactor	260	1	100	0.6	The stability of catalysts are at least 50 hours.
59	Cu/ZnO	SRM	Tubular stainless steel reactor	250	-	60	-	-
60	Mo_2C/ZrO_2	SRM	Quartz plug flow reactor	400	1	95	5	-
61	Cu/ZrO_2	SRM	Fixed bed flow reactor	250	1	-	-	H_2 production rate is 400 mol/(h·kg_{catal})
62	Au/TiO_2	POX	U-shaped quartz micro-reactor	310	1	100	0.15	-
63	Pd/CeO_2	SRM	U tube quartz reactor	400	1	-	-	Methanol consumption rate is 45 µmol/(g_{catal}·s)
	Pd/ZnO							Methanol consumption rate is 20 µmol/(g_{catal}·s)

Ref no.	Catalyst	Reaction	Reactor	Temp (ºC)	P (atm)	Methanol conversion (%)	CO (%)	Remarks
64	$Cu/CeO_2/ZrO_2$	SRM	Fixed bed flow reactor	250	1	80	-	-
65	$Cu/ZnO/Al_2O_3$	SRM	Micro-reactor	280	-	97	0.7	-

From the literatures, the catalysts could be classified into two major groups which are Cu-based and Pd-based catalyst. The various metal used in the catalysts as co-catalyst or promoter could play important role in the catalytic performance which are shown as follows.

Cu-based

Cu-based is the most popular in methanol reforming catalysts. Many literatures focused on Cu-based catalysts which are composed with various types of support and promoter. The promoters used in Cu-based catalysts could be Zn, Zr, Ce, Pt, Rh, Y, La, Ni, Mg, Pd, Sm, Ca, Gd, Mn, Cs, Cr, Co, Fe or Al. The supports used in Cu-based catalysts are Al_2O_3, CNT, wafer or cordierite honeycomb. The reaction temperature, methanol conversion and CO selectivity of the Cu-based catalysts are 473 – 723 K, 46.4 – 100 % and 0.1 – 31.4 % respectively. The performance of catalysts depends on metal content, promoter, support, reaction mechanism and reactor. The effect of dopants and preparation method of Cu-based catalysts in methanol reforming are shown as follows.

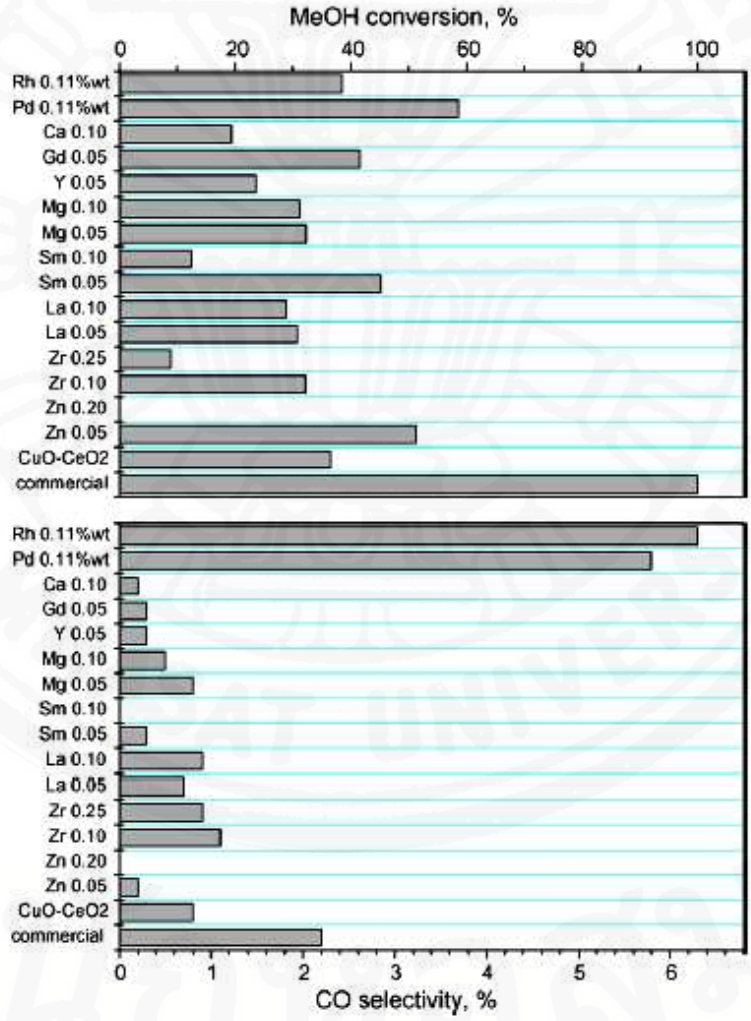


Figure 2 The performance of various promoters on Cu-based catalysts at 513 K [10]

Figure 2 shows the methanol conversion and CO selectivity of various promoters on CuO-CeO_2 catalysts. The highest methanol conversion is presented in the Pd-promoted catalyst but it also produces high CO selectivity. The second one is presented in Zn-promoted catalyst which can exhibit high methanol conversion and low CO selectivity.

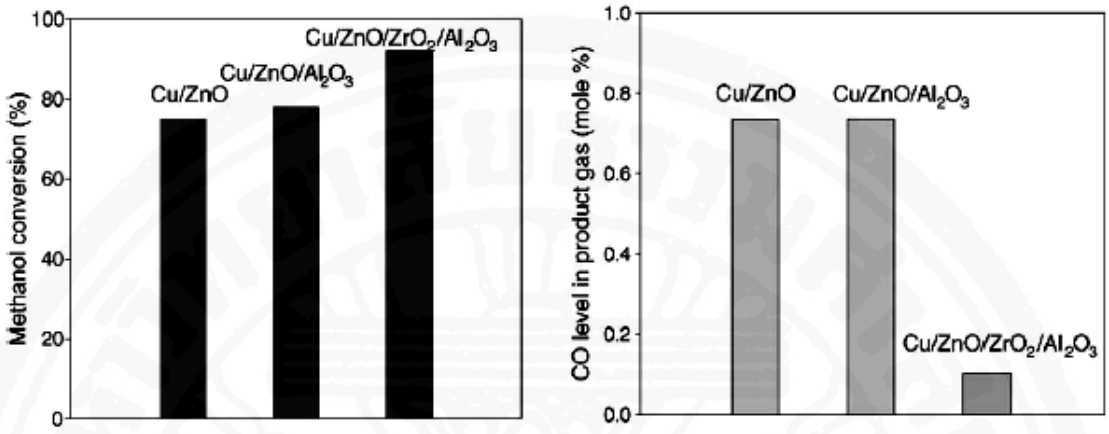


Figure 3 The performance of Zn/Zr-promoted on Cu-based catalysts at 533 K [16]

Figure 3 shows the methanol conversion and CO selectivity over Cu/ZnO, Cu/ZnO/Al_2O_3 and Cu/ZnO/ZrO_2/Al_2O_3 catalysts. The Cu/ZnO/ZrO_2/Al_2O_3 catalyst exhibits higher methanol conversion and the lowest CO selectivity.

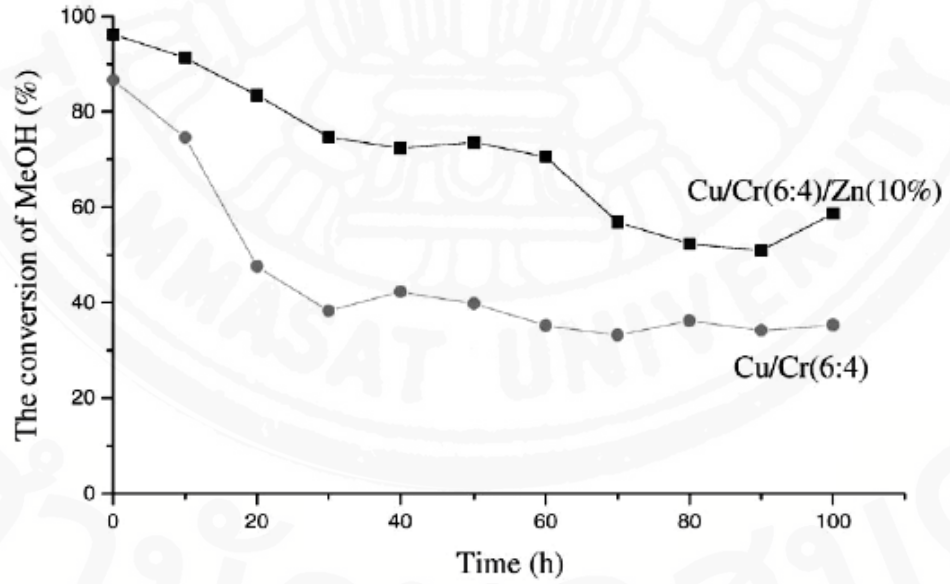


Figure 4 The performance of Zn-promoted on Cu-based catalysts at 473 K [25]

Figure 4 shows the methanol conversion over Cu/Cr and Cu/Cr/Zn catalyst. The Cu/Cr/Zn catalyst exhibits higher methanol conversion than that of the Cu/Cr catalyst. This confirms that, the methanol conversion of Cu-based catalysts could be enhanced by Zn-promoted.

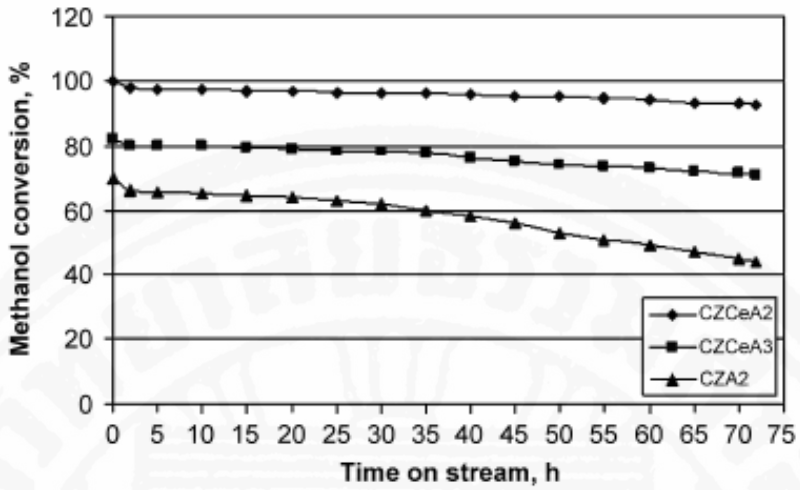


Figure 5 The catalytic stability of Ce-promoted on Cu-based catalysts prepared by precipitation method at 553 K (▲) CZA2, (♦) CZCeA2 and (■) CZCeA3 [7]

Figure 5 shows the catalytic stability of CZA2 ($Cu/Zn/Al_2O_3$: 30/20/50 wt%), CZCeA2 ($Cu/Zn/Ce/Al_2O_3$: 30/20/10/40 wt%) and CZCeA3 ($Cu/Zn/Ce/Al_2O_3$: 30/10/20/40 wt%) catalysts prepared by precipitation method. These catalysts used the metal content 50-60 wt% in precipitation method to obtain the high methanol conversion. The highest methanol conversion is presented in the $Cu/Zn/Ce/Al_2O_3$ catalyst. This figure show that the use of Ce in $Cu/Zn/Al_2O_3$ catalyst could improve the stability of catalyst which is evidenced by the slightly decrease in the activity of $Cu/Zn/Ce/Al_2O_3$ over 72 hours.

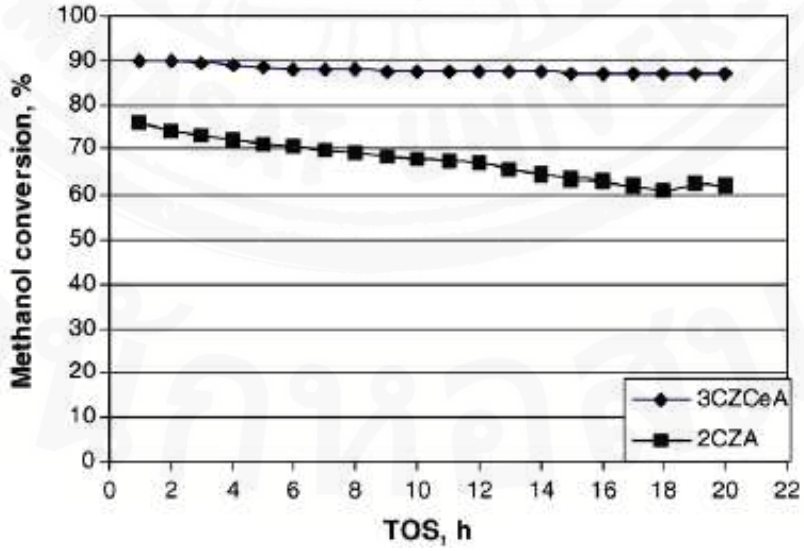


Figure 6 The catalytic stability of Ce-promoted on Cu-based catalysts prepared by impregnation method at 533 K (♦) 3CZCeA and (■) 2CZA [17]

Figure 6 shows the catalytic stability of 2CZA ($Cu/Zn/Al_2O_3$: 10/5/85 wt%) and 3CZCeA ($Cu/Zn/Ce/Al_2O_3$: 10/5/3/82 wt%) catalysts prepared by impregnation method. This figure show that the high methanol conversion could be obtained from the catalysts prepared by using the metal content 15-18 wt% in impregnation method. Therefore, the use of impregnation method in catalysts preparation can lower the metal content on the catalysts. The highest methanol conversion is still presented in the $Cu/Zn/Ce/Al_2O_3$ catalyst. This figure also show that the use of Ce in $Cu/Zn/Al_2O_3$ catalyst could improve the stability of catalyst which is evidenced by the slightly decrease in the activity of $Cu/Zn/Ce/Al_2O_3$ over 20 hours.

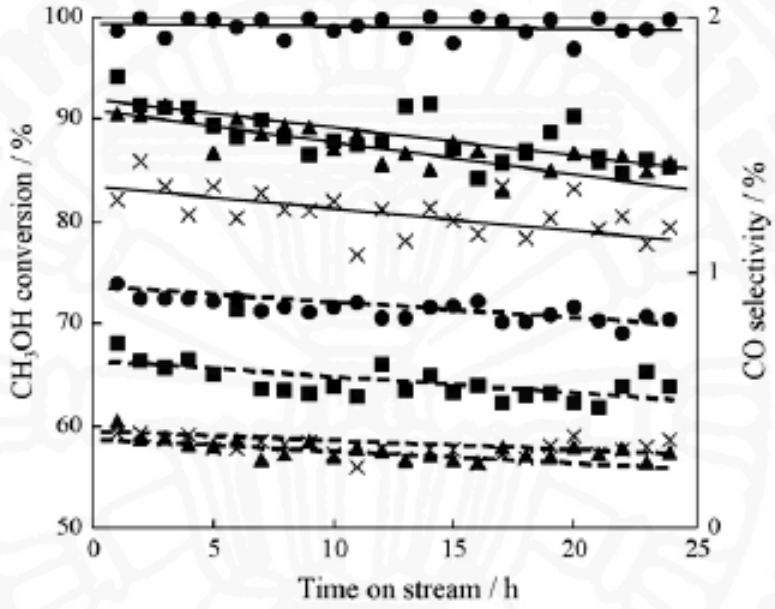
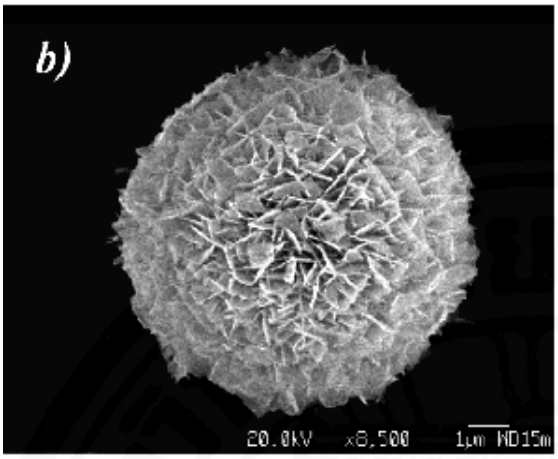


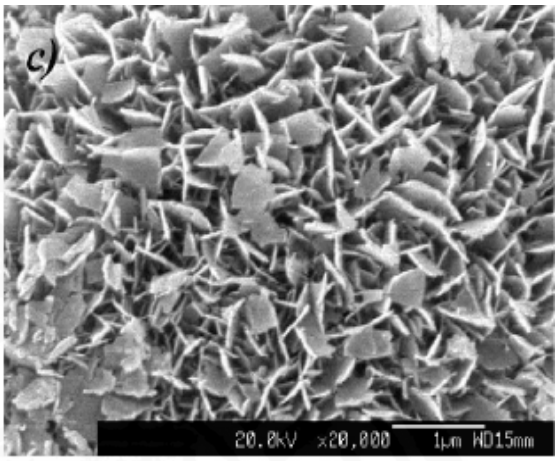
Figure 7 The performance of catalysts preparation by hp-method and cp-method at 473 K (●) hp-$Cu/ZnO/Al_2O_3$, (▲) hp-Cu/ZnO, (×) cp-Cu/ZnO and (■) commercial $Cu/ZnO/Al_2O_3$ [2]

Figure 7 shows the methanol conversion (line) and CO selectivity (dash line) over The Cu/Zn/Al and Cu/Zn catalyst prepared by homogeneous precipitation (hp-Cu/Zn/Al and hp-Cu/Zn), the Cu/Zn catalyst prepared by co-precipitation (cp-Cu/Zn) and the commercial Cu/Zn/Al catalyst. The highest methanol conversion could be obtained form the hp-Cu/Zn/Al catalyst. The hp-Cu/Zn can exhibit higher methanol conversion than that of cp-Cu/Zn catalyst. The use of urea in homogeneous precipitation of Cu/Zn-based catalysts could improve activity of the catalysts for methanol reforming reaction.

hp-Cu/Zn 8,500x



hp-Cu/Zn 20,000x



cp-Cu/Zn 5,000x

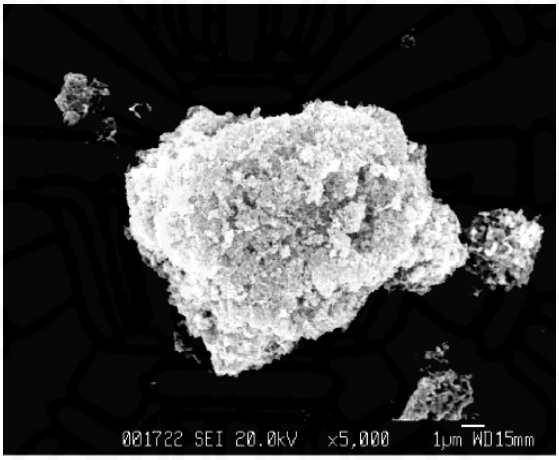


Figure 8 SEM images of catalysts prepared by hp-method and cp-method [2, 26]

Figure 8 shows SEM images over catalyst prepared by homogeneous precipitation (hp-method) and co-precipitation (cp-method). The catalyst surface of cp-Cu/Zn is quite rough while the catalyst surface of hp-Cu/Zn is composed by small pieces of metals stick together in spherical shape. Therefore, the surface area of catalysts could be enhanced by use of homogeneous precipitation in the catalyst preparation process.

Literatures have shown that the performance of catalysts can be enhanced by Zn-promoted. The catalytic stability of catalysts can be improved by Ce-promoted. The use of impregnation method in catalysts preparation could lower the metal content on the catalysts. Moreover, the surface area of catalysts plays an important role in the performance of catalysts which can be enhanced by the use of urea in the catalyst preparation process by precipitation method.

Pd-based

From literatures report, Pd has been seldom reported as an active catalyst for methanol reforming. The promoters used in Pd-based catalysts could be Zn or Ce. The supports used in Pd-based catalysts could be Al_2O_3 or Al-plate. The reaction temperature, methanol conversion and CO selectivity of Pd-based catalysts is 523 – 673 K, 93 – 100 % and 7 – 18.2 % respectively. The performance depends on metal content, promoter, support, reaction mechanism and reactor. The Pd-based catalysts could provide a comparable methanol conversion compare to the Cu-based catalysts but it require a high reaction temperature and also emits high CO. This study has not decided to use Pd-based catalysts yet but the knowledge might lead to a co-catalyst between Pd and Cu.

The effect of NH_4NO_3 in spray-pyrolysis process

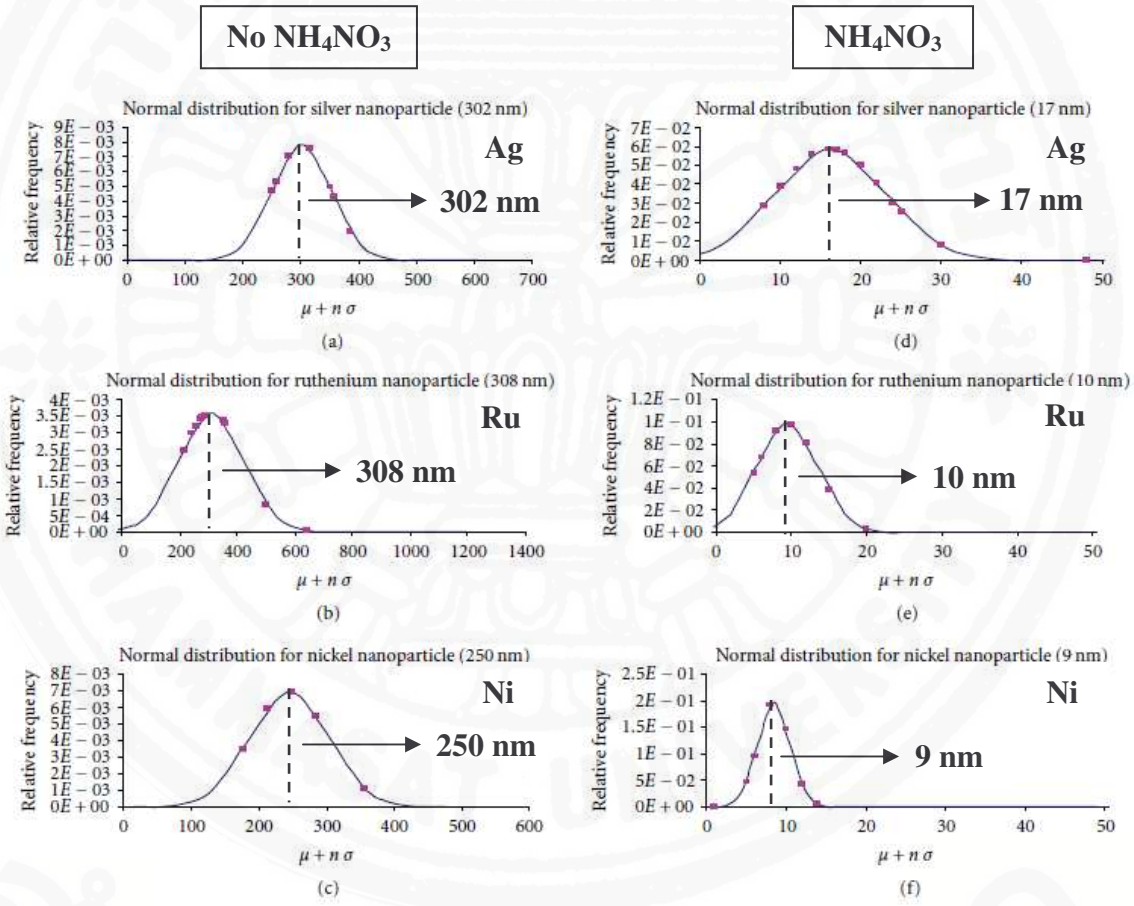


Figure 9 Particle size distribution (PSD) of nanoparticles created. Images (a), (b) and (c) present the PSDs of silver, ruthenium and nickel nanoparticles, respectively, in the absence of ammonium nitrate; while (d), (e) and (f) are PSDs of silver, ruthenium and nickel nanoparticles in the presence of ammonium nitrate, respectively [67]

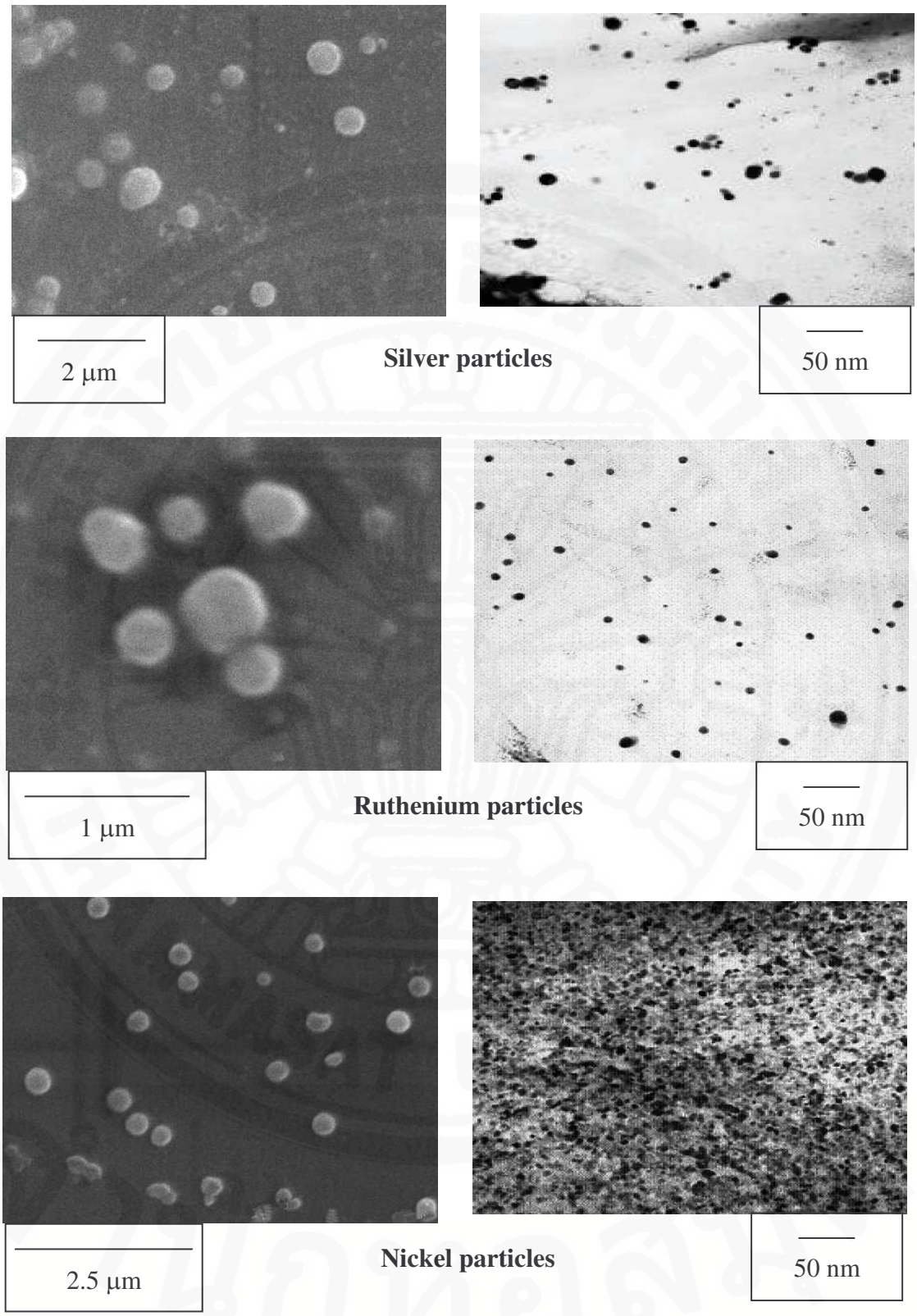


Figure 10 SEM images of Silver, Ruthenium and Nickel particles produced in the absence of NH_4NO_3 (left) and the presence of NH_4NO_3 (right) [67]

Figure 9 and 10 shows the particle size of silver, ruthenium and nickel nanoparticles from the spray-pyrolysis process. The particle size of silver, ruthenium and nickel from the spray-pyrolysis without using NH_4NO_3 are smaller than those of the spray-pyrolysis using NH_4NO_3. Therefore, the NH_4NO_3 has an ability to reduce the size of metal nanoparticles.