CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Supported Tungsten Catalysts

4.1.1 XRD Results

XRD is an important tool for phase analysis such that the characteristic structure of a crystalline material can be identified. In this work, synthesized supports are pure silica HMS, aluminum-containing HMS denoted as Al-HMS, and zeolite ZSM-5. The characteristic peak of hexagonal mesoporous silica in HMS, and Al-HMS can be observed at the small angle region while zeolite ZSM-5 can be detected at the large angle range. The effect of metal loading on the structure of bared supports is also investigated using the X-ray diffractometer.

(a)   Pure Silica HMS and Al-HMS Supports

XRD patterns of mesoporous supports that are pure silica HMS and Al-HMS are shown in Figure 4.1 It indicated that all of as-synthesized materials show typical long-range order hexagonal lattice corresponding to only one characteristic peak of HMS at the (100) lattice plane. After calcination the structure of each support was remained with increasing peak intensity, resulting from the removal of template from the mesopores.
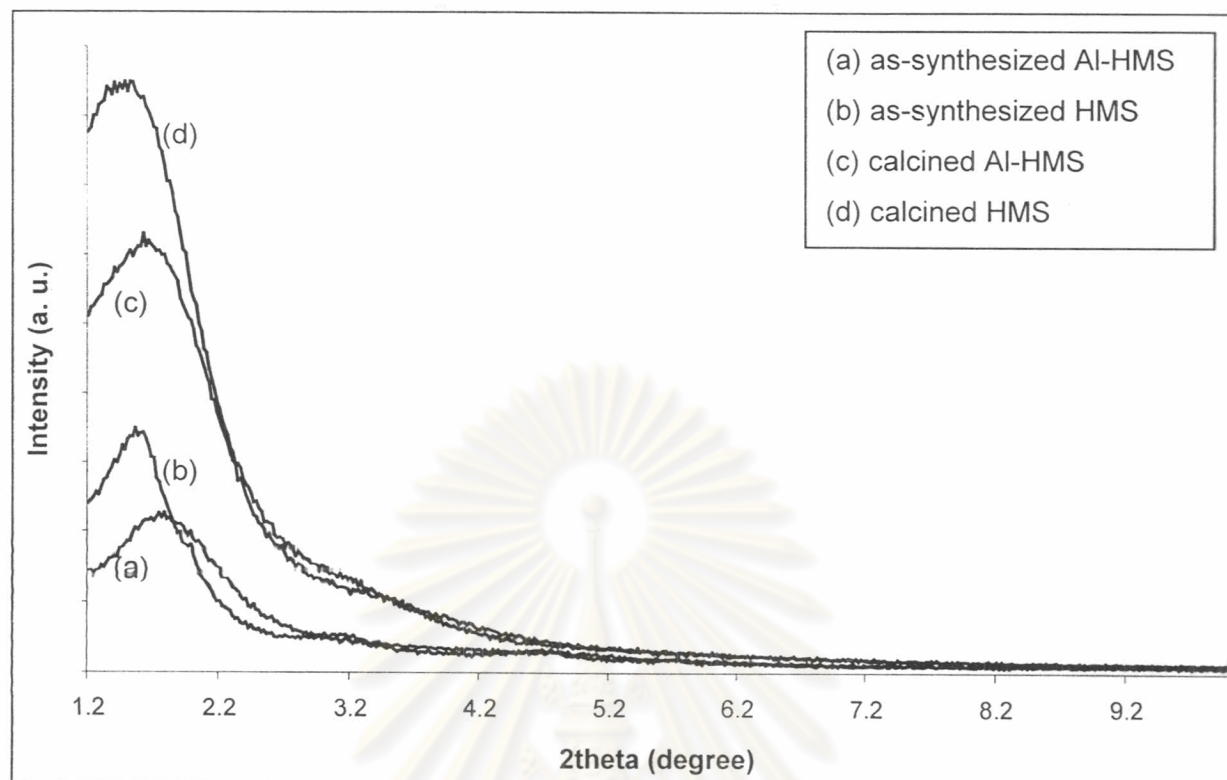
Figure 4.1 XRD patterns of as-synthesized and calcined support.

When tungsten was loaded to HMS and Al-HMS supports by incipient-wetness impregnation method, the catalysts of WO_3/HMS and WO_3/Al-HMS are obtained. The crystallinity of the loaded supports decreases which can be observed by the decrease of XRD peak intensity as shown in Figure 4.2 and 4.3. It indicates that there was an interaction between tungsten and support. The crystallinity of HMS and Al-HMS supports is an inverse function of the metal loading.
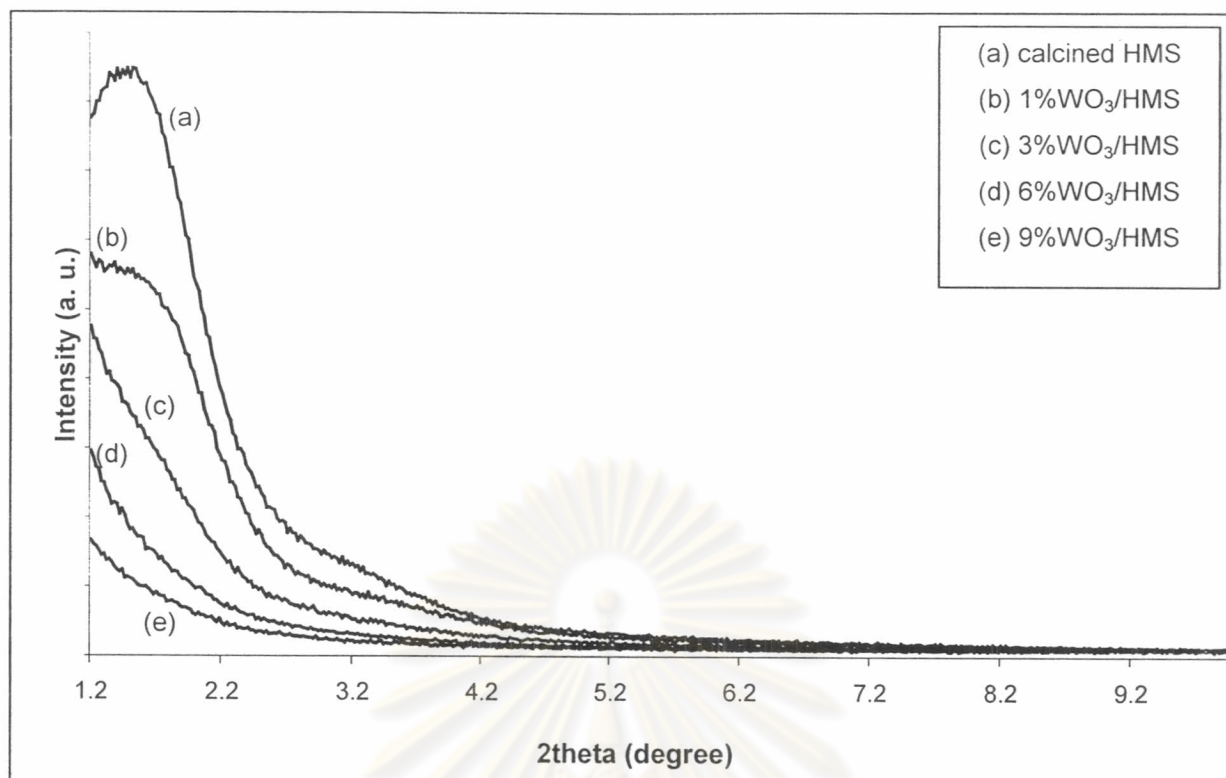
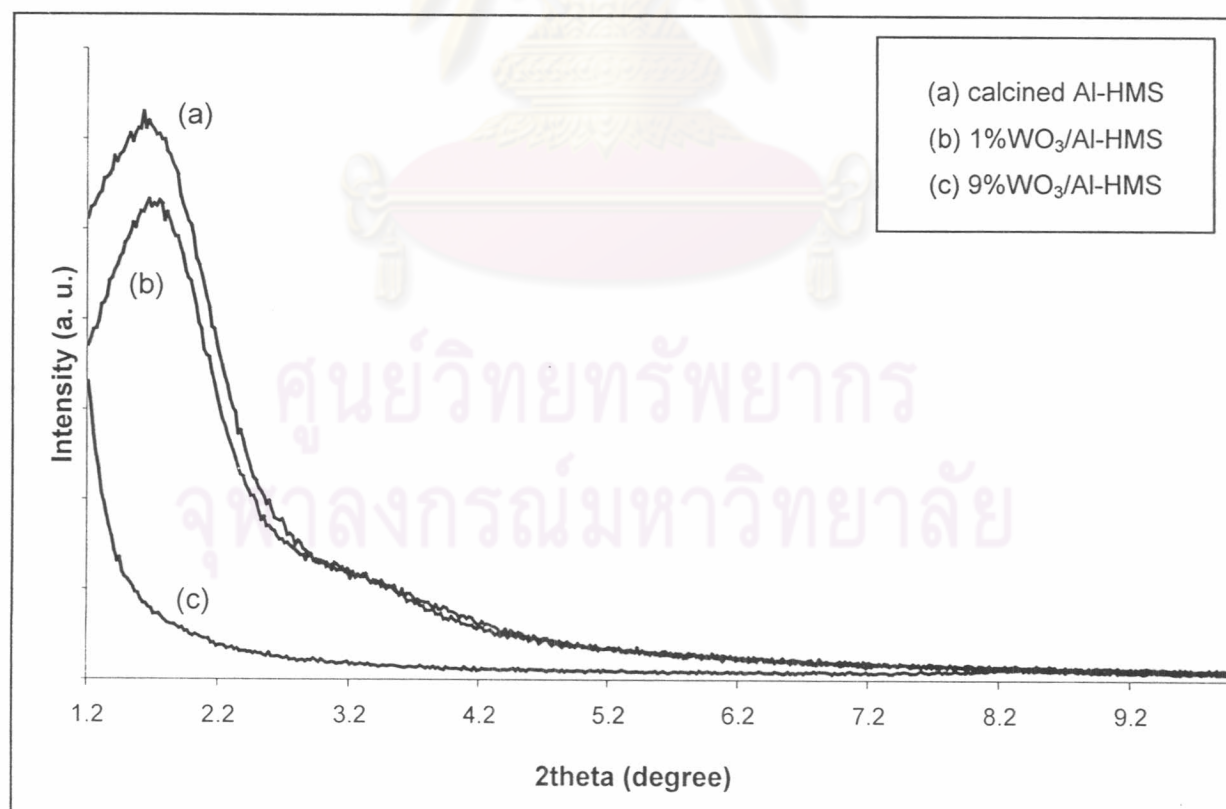**Figure 4.2**   XRD patterns of WO$_3$/HMS catalysts at various loading amounts of tungsten oxide.

Figure 4.3   XRD patterns of WO$_3$/Al-HMS catalysts at various loading amounts of tungsten oxide.

(b)   ZSM-5 Support

XRD patterns of tungsten loaded and unloaded ZSM-5 are shown in Figure 4.4. Both the as-synthesized and the template-free ZSM-5 show the characteristic pattern of MFI structure without any phase of other materials. XRD patterns of WO_3/ZSM-5 showed that the MFI structure is not affected and no tungsten oxide crystallite is observed although the metal loading reached 9%wt of WO_3.
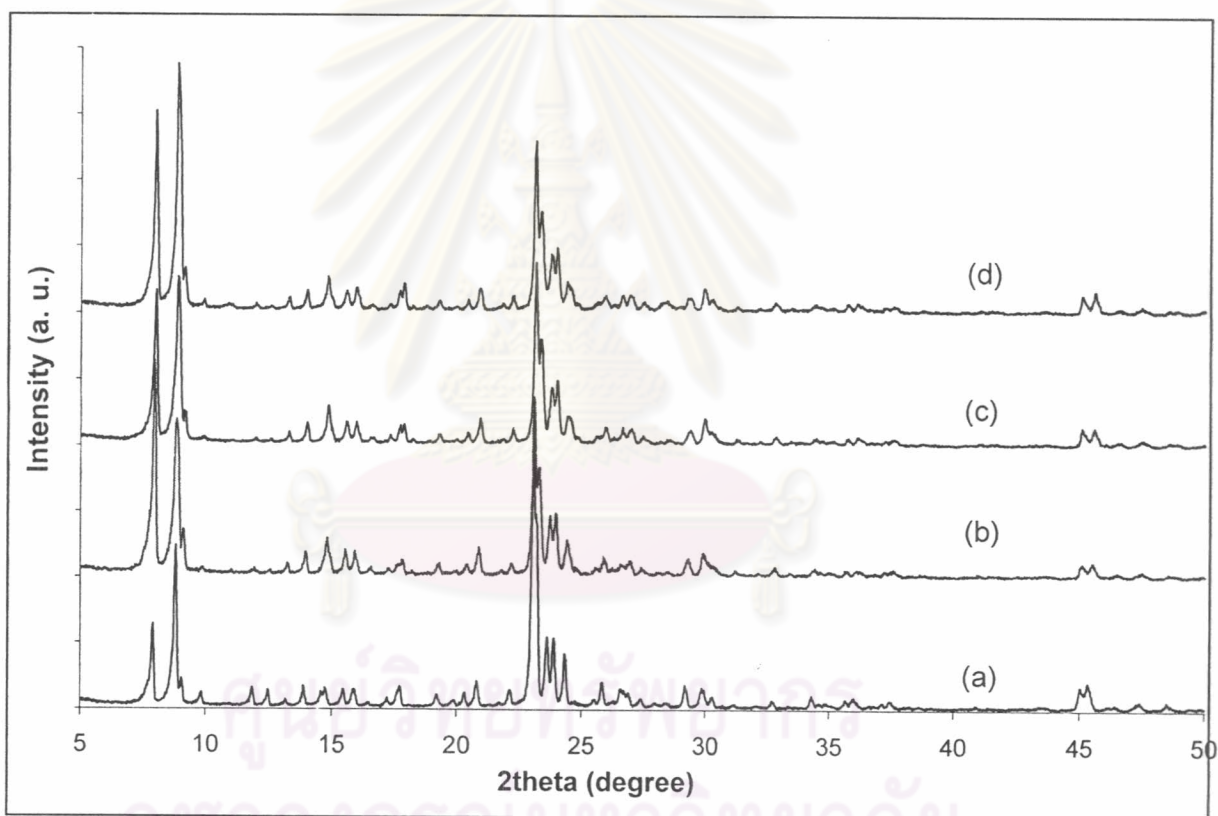

Figure 4.4   XRD patterns of as-synthesized ZSM-5 (a) calcined ZSM-5 (b), 1%WO_3/ZSM-5 (c), and 9%WO_3/ZSM-5 (d).

4.1.2 Solid-State ^{27}Al-NMR Spectra

To investigate the position of the incorporated aluminum atoms in the structure of aluminum containing support, solid-state ^{27}Al-NMR spectra can provide the information. Generally, the presence of aluminum atoms in the framework or tetrahedral position was preferable due to the fact that non-framework aluminum oxides will cause the lost of surface area in porous supports.

(a)   Al-HMS Support

The ^{27}Al-NMR spectrum of the as-synthesized Al-HMS in Figure 4.5(a) exhibits two signals at the chemical shifts of 56 and 0 ppm. The predominant peak at the chemical shift of 56 ppm typically belongs to the tetrahedral aluminum and the peak at chemical shift of 0 ppm can be assigned to octahedral non-framework aluminum. It can be concluded that aluminum atoms were incorporated into silica framework mainly in tetrahedral position and partially in octahedral position. After calcination, partial of the tetrahedral aluminum migrates to octahedral sites as shown in Figure 4.5(b), therefore a percentage amount of tetrahedral aluminum content is 41.4% of total aluminum content.

(b)   ZSM-5

^{27}Al-NMR spectra of as-synthesized and calcined ZSM-5 support are shown in Figure 4.6. There is the only one predominant peak at the chemical shift of 56 ppm which belongs to the tetrahedral aluminum atoms in the framework position. This type of aluminum retained its position after calcination.
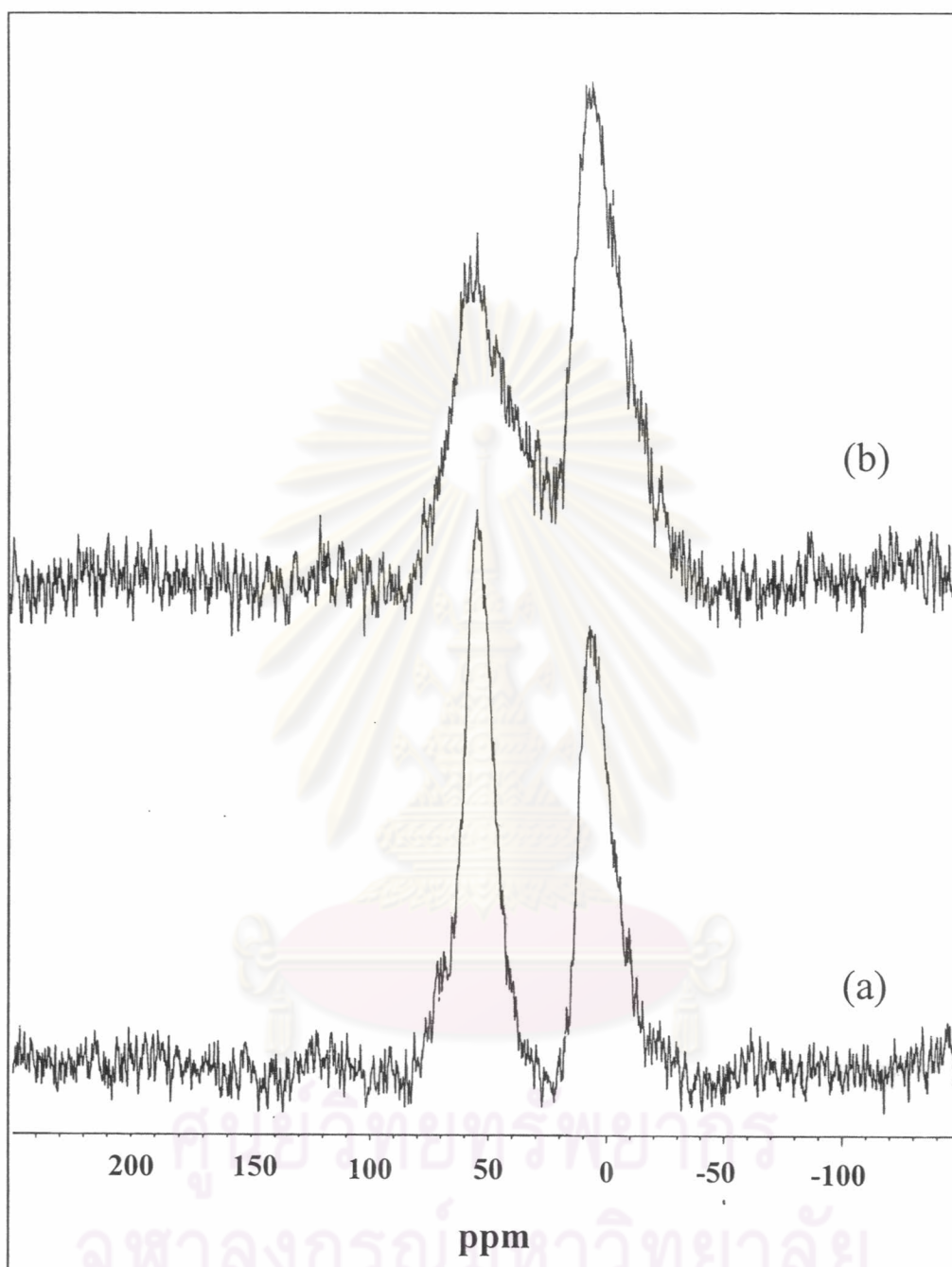
Figure 4.5 ^{27}Al-NMR spectra of as-synthesized Al-HMS (a), and calcined Al-HMS (b).
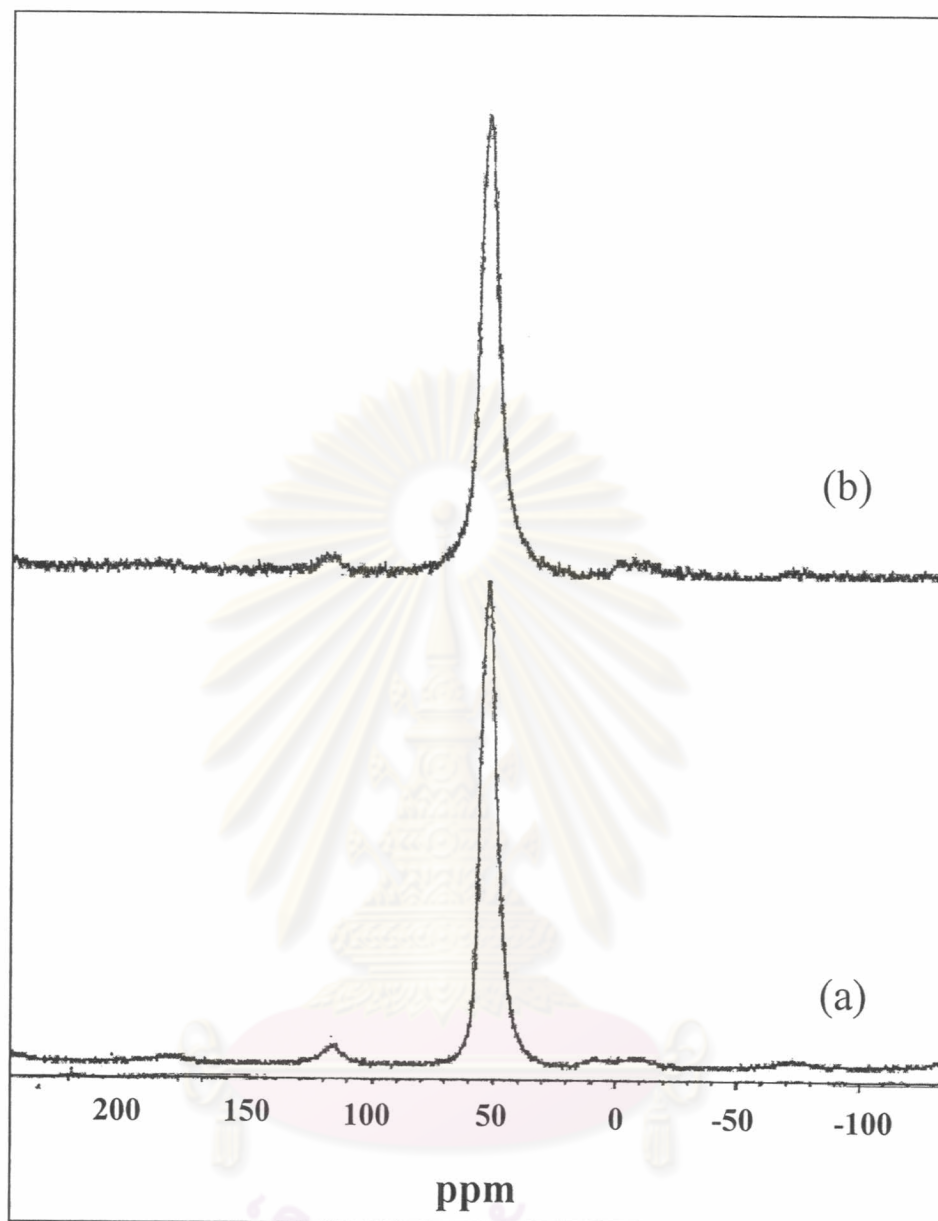
Figure 4.6 ^{27}Al-NMR spectra of as-synthesized ZSM-5(a), and calcined ZSM-5(b).

4.1.3 ICP-AES Data

The Si/Al ratio in gel for preparing Al-HMS and ZSM-5 was fixed to 40. This value in obtained products can be determined using ICP-AES analysis. From Table 4.1, the Si/Al in Al-HMS product is 43.24 while this ratio in ZSM-5 product is 37.89.

Table 4.1   Determination of Si/Al ratios in supporting materials.

Support	Si/Al in prepared gel	Si/Al in product[a]	Si/Al in product[b]
Al-HMS	40	17.68	43.24
ZSM-5	40	37.89	37.89

[a] mole silicon compared to total aluminum

[b] mole silicon compared to tetrahedral aluminum

Using the incipient wetness impregnation method, it is accepted that all tungsten in solution can be adsorbed on the supports. Therefore it is not necessary to perform the analysis of tungsten content.

4.1.4   BET Specific Surface Area

To determine the specific surface area of bared supports and supported tungsten catalysts, the BET method is applied for this purpose. The results are shown in Table 4.2.

Table 4.2   BET specific surface area of bared supports and supported tungsten catalysts at various tungsten loading amount.

Samples	The BET specific surface area (m^2/g)
Bared Al_2O_3	150.00^a
Bared HMS	706.21
Bared Al-HMS	870.50
1%WO_3/Al_2O_3	160.35
1%WO_3/SiO_2-Al_2O_3	503.66
1%WO_3/HMS	508.01
1%WO_3/Al-HMS	714.52
1%WO_3/ZSM-5	534.50^b
9%WO_3/Al_2O_3	152.60
9%WO_3/SiO_2-Al_2O_3	366.52
9%WO_3/HMS	122.14
9%WO_3/Al-HMS	170.04
9%WO_3/ZSM-5	444.20^b

[a]Value from the manufacturer

[b]Value based on Langmiur not BET calculation for micropores

According to Table 4.2. the BET specific surface areas of the bared mesoporous supports like HMS and Al-HMS were higher than those of ZSM-5 and amorphous supports. Upon loading with tungsten, the surface areas of all supports was reduced, corresponding with the XRD results. At low tungsten loading, the remaining of hexagonal structure, the surface areas of calalysts were extremely higher than those of at high tungsten loading.

4.1.5   DR-UV Spectra

In the reference spectra as shown in Figure 4.7, sodium tungstate refers to tetrahedrally monomeric tungstate species, ammonium tungstate shows characteristic of octahedrally polymeric tungstate species, and WO_3 represent the bulk tungsten oxide. Figure 4.8 and 4.9 show DR-UV spectra of various supported tungsten catalysts at $1\%WO_3$ and $9\%WO_3$ loading, respectively. By comparing the spectra of various supported tungsten catalysts with the reference spectra, it is concluded that all of samples have both characteristics of monomeric and polymeric tungstate species on the supports. The characteristic of polymeric tungstate species was obviously observed in case of high metal loading.
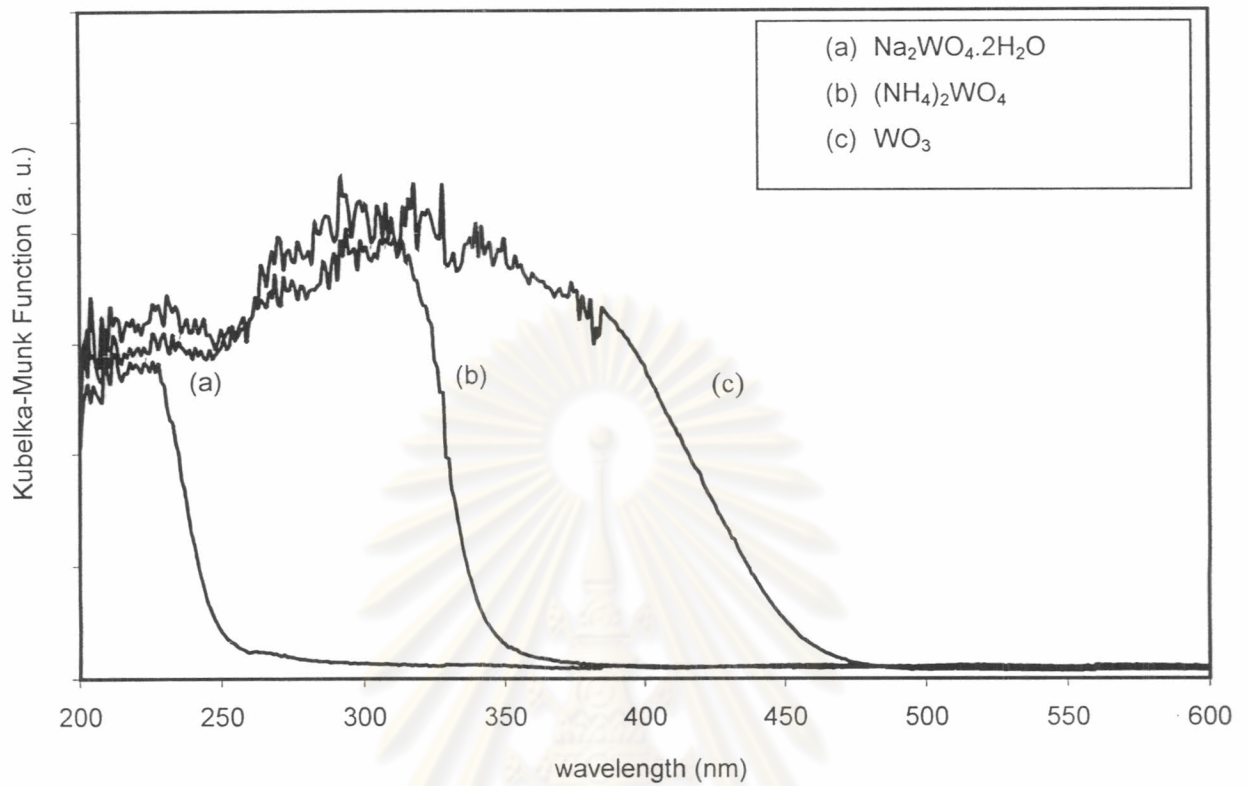
Figure 4.7   DR-UV spectra of reference tungstate species.
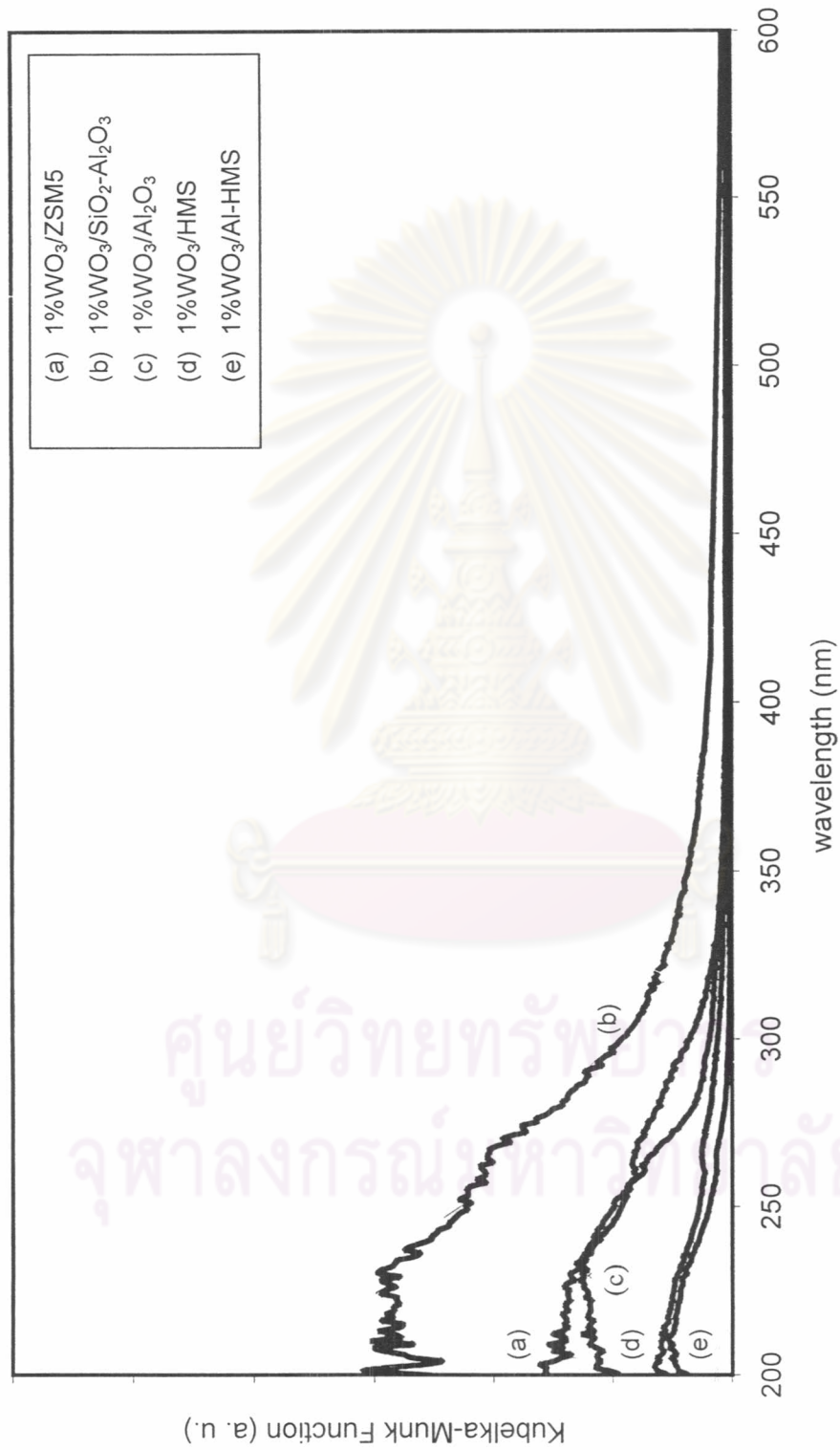
Figure 4.8 DR-UV spectra of various supported tungsten catalysts at 1%wt of WO$_3$ loading.

Legend inside figure:

(a) 1%WO$_3$/ZSM5
(b) 1%WO$_3$/SiO$_2$-Al$_2$O$_3$
(c) 1%WO$_3$/Al$_2$O$_3$
(d) 1%WO$_3$/HMS
(e) 1%WO$_3$/Al-HMS

Kubelka-Munk Function (a. u.)

wavelength (nm)
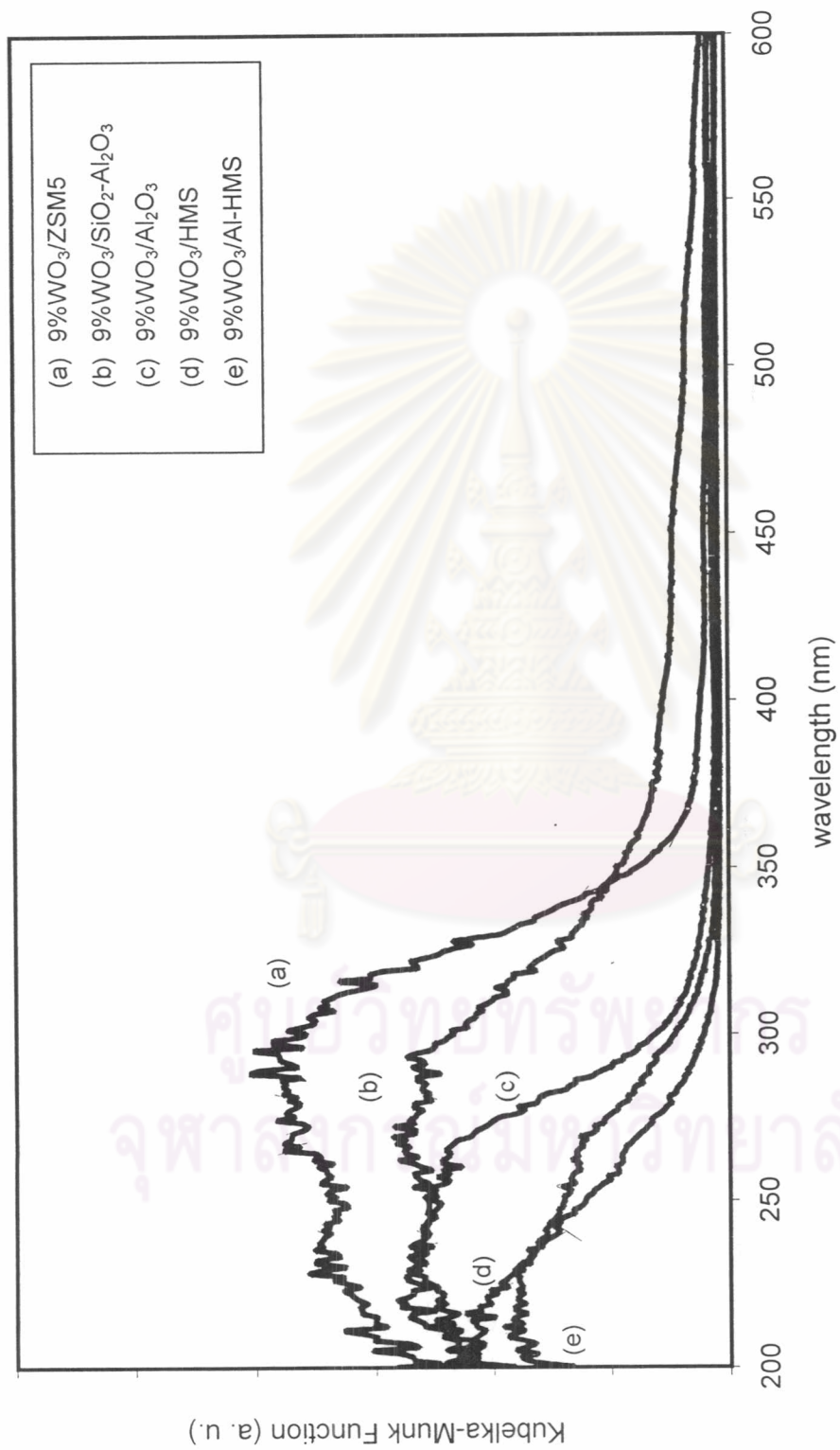
Figure 4.9 DR-UV spectra of various supported tungsten catalysts at 9%wt of WO$_3$ loading.

Legend (in chart):

(a) 9%WO$_3$/ZSM5
(b) 9%WO$_3$/SiO$_2$-Al$_2$O$_3$
(c) 9%WO$_3$/Al$_2$O$_3$
(d) 9%WO$_3$/HMS
(e) 9%WO$_3$/Al-HMS

Axes: wavelength (nm); Kubelka-Munk Function (a. u.)

4.1.6 Laser Raman Spectra

Laser Raman spectroscopy has been widely used for phase identification of metal oxides in supported metal catalysts. Table 4.3 shows Raman scattering of some tungsten oxide reference compounds. The Raman Scattering at wavenumbers about 400 cm^{-1} was assigned to W-O stretching mode. The shortest W-O bond was assigned to the highest Raman stretching mode at the wavenumbers higher than 800 cm^{-1}. The W-O bonds of intermediate length which are characteristic of bridging W-O bonds are assigned to Raman stretching mode at wavenumbers in the 600-800 cm^{-1} region.

Table 4.3 Raman shift of some tetrahedrally and octahedrally coordinated tungsten oxide reference compounds.[57]

Compound	Coordination	Raman Shifts (cm^{-1})
Na_2WO_4	tetrahedral	931, 811
$Na_2W_2O_7$	tetrahedral	940, 835
$Al_2(WO_4)_3$	tetrahedral	1060, 1030, 1002, 905, 838, 810
WO_3	octahedral	808, 719, 625, 604, 580, 520
$WO_3.H_2O$	octahedral	951, 816, 812, 639
$Na_2W_2O_7$	octahedral	957, 940, 598, 422

In Figure 4.10 shows Laser Raman spectra of supported tungsten oxide on various supports at high loading amount of tungsten. Raman shift of all supported catalysts were listed in Table 4.4.

Table 4.4   Raman shift of various supported tungsten oxide catalysts

Catalyst	Raman shift (cm^{-1})
9%WO_3/SiO_2-Al_2O_3,	967, 818, 625, 401
9%WO_3/Al_2O_3	931, 822, 633, 404
9%WO_3/HMS	949, 816, 629, 401
9%WO_3/Al-HMS	951, 820, 631, 407
9%WO_3/ZSM-5	951, 824, 635, 385
1%WO_3/HMS	968, 825, 634, 401

Raman Shift of all supported catalysts can be correlated with the tungsten oxide monohydrated phase except the band near 400 cm^{-1}. It can be due to the interaction between tungsten and support which was not found for unsupported tungstate compound references. From Raman spectrum of 1%WO_3/HMS as shown in Figure 4.11, intensity of the Raman shift around 400 cm^{-1} is higher than that of 9%WO_3/HMS. The dispersion of tungsten species in case of low loading is better than that of high loading, resulting in more pronounce of the band around 400 cm^{-1} which is very intense for bared supports. However, in case of 1%WO_3/Al-HMS, the repeatable Raman spectrum was not observed any phase of tungsten oxide.
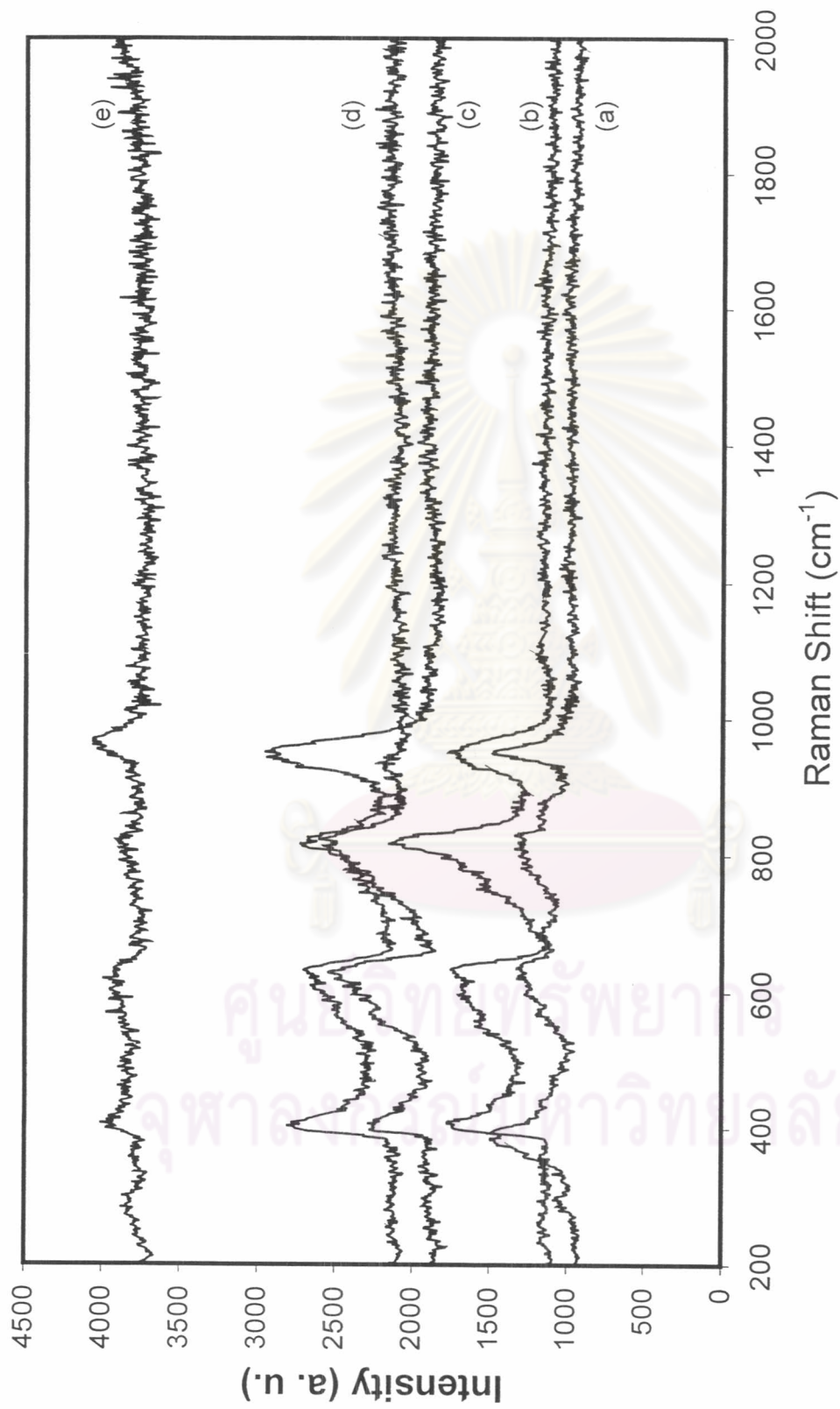
Figure 4.10 Laser Raman spectra of various supported tungsten catalyst at 9%wt of WO_3 loading.

9%WO_3/ZSM-5(a), 9%Al-HMS(b), 9%WO_3/Al$_2$O$_3$(c), 9%WO_3/HMS(d), 9%WO_3/SiO$_2$-Al$_2$O$_3$(e).
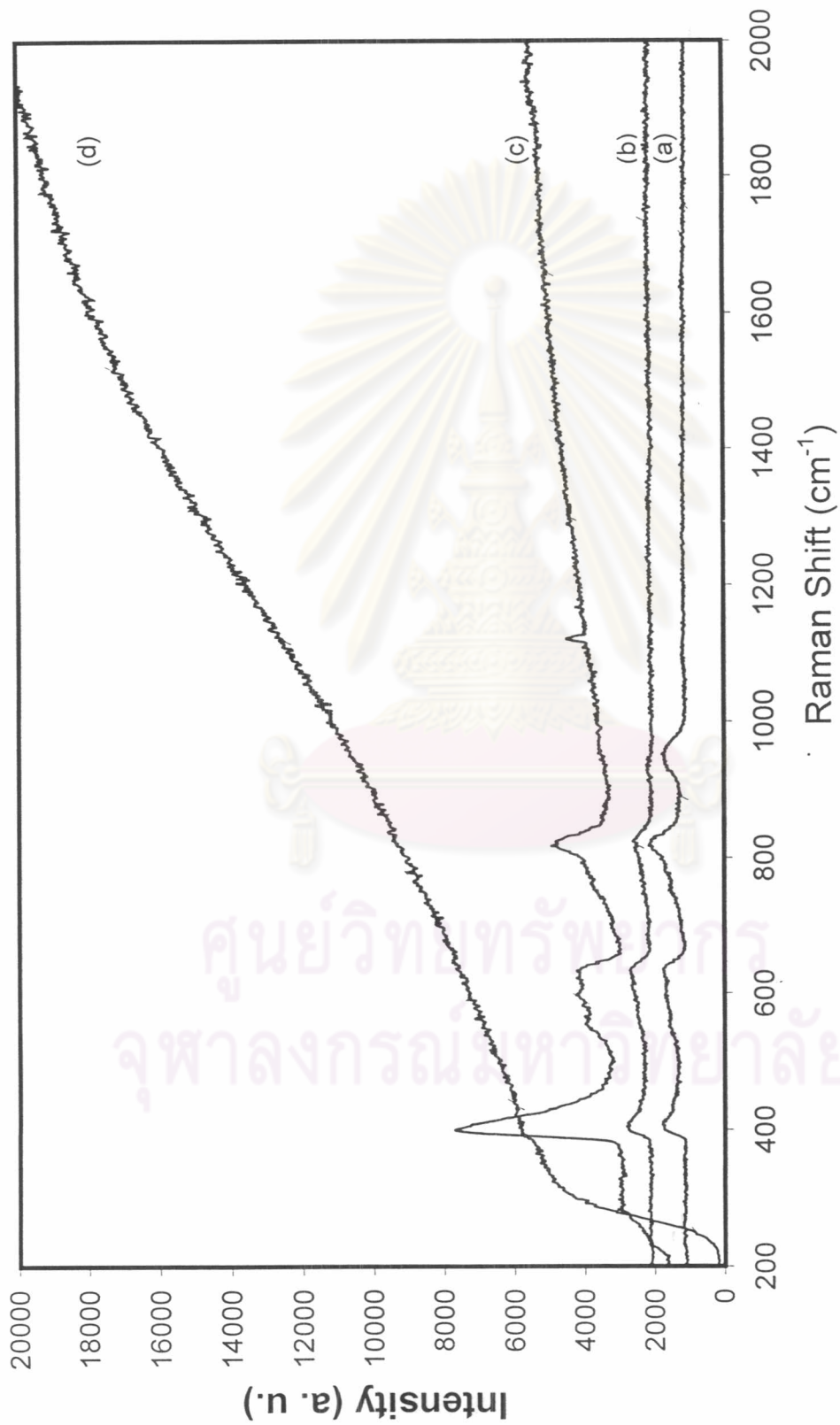
Figure 4.11 Laser Raman spectra of various supported tungsten catalysts. 9%WO$_3$/Al-HMS (a), 9%WO$_3$/HMS (b), 1%WO$_3$/HMS (c), 1%WO$_3$/Al-HMS (d).

4.2 Catalytic Activities of Various Supported Tungsten-Based Catalysts

4.2.1 Effect of Supporting Materials on Catalytic Activity of 1-Hexene Conversion

Percentage conversions of 1-hexene catalyzed by supported tungsten-based catalysts at different loading of tungsten oxide (WO_3) at the temperature of 500°C with acidity of the supported catalysts are shown in Table 4.5. At the low loading of 1%wt WO_3, the activity which was determined by 1-hexene conversion is affected by type of supports in the order of SiO_2-Al_2O_3 ~ ZSM-5 > Al-HMS > Al_2O_3 >> HMS. At the high loading of 9%wt WO_3, the activity is different and the sequence changes to SiO_2-Al_2O_3 > Al-HMS > ZSM-5> HMS >> Al_2O_3. At the temperature as high as 500°C it is known that not only metathesis but also thermal decomposition, pyrolysis and catalytic cracking of 1-hexene can take place simultaneously. These catalyst activities can be divided into three levels: the highest activity (>90% conversion), intermediate activity (30-90% conversion), and the least activity (less than 30% conversion). Al-HMS, Al-ZSM-5, and amorphous SiO_2-Al_2O_3 are strong acids while HMS is a very weak acid and Al_2O_3 is amphoteric. WO_3 is the active site for metathesis of 1-hexene while the strong acid sites in the bifunctional materials, functioning as both support and acid catalyst itself, is the cause of cracking process. It seems that cracking of 1-hexene is predominant at the low loading of WO_3 while metathesis becomes more important at high loading. At low WO_3 content 1-hexene preferably undergoes the cracking process catalyzed by strongly acidic supports. With increasing the WO_3 loading from 1 to 9%wt, the pure silica HMS supported catalyst becomes much more active for conversion of 1-hexene. This indicates that metathesis of 1-hexene is promoted by the increase in the active metathesis site, *i.e.* WO_3. Under the test condition, the appropriate catalyst support for metathesis alone is then the silica support but not the coexistence of silica and alumina. Conversion of 1-

hexene is not affected in case of using strongly acidic mesoporous aluminosilicate supports like SiO_2-Al_2O_3 and Al-HMS. This is accounted by the occurrence of cracking step prior to the metathesis step. The microporous ZSM-5 achieves some effect from the increase in WO_3 loading due to the small pore opening and that gives rise to the further reduction of the pore size, resulting in a decrease of the catalyst activity. As increasing the WO_3 loading on Al_2O_3, a sudden diminution of the catalytic activity was found and this is caused by the very low surface area along with the least acidity compared to other supports. Alumina has the least specific surface area while HMS has the largest one. A complete coverage of the cracking active site on Al_2O_3 by tungsten species is possible and prevents the alumina support from being a catalyst for cracking of 1-hexene at all. Conversion of 1-hexene over the alumina supported WO_3 catalyst at high loading is due to metathesis alone.

The yields of products obtained from the conversion of 1-hexene over various supported tungsten oxide catalysts at different loadings are also reported in Table 4.5. Only the 1% WO_3/ZSM-5 catalyst provides products in less yield of liquid than that of gas. For all other supports, the products are formed as liquid phase in a remarkably greater amount than gas phase. With increasing the loading of WO_3, the yield of gas phase reduced while the yield of liquid phase increases for all supported catalysts except for the case of Al_2O_3. The change in the latter case is in the opposite direction to other supports. This may be affected by the difference in acidity of these supports.

The coke formation is found in a little amount on each catalyst and decreases with increasing the WO_3 loading. The effect of increasing the WO_3 loading is a proof of reducing cracking activity, resulting in less amount of coke which is a common by product of cracking.

Table 4.5 Catalytic activities of various supported tungsten-based catalysts in conversion of 1-hexene at the temperature of 500°C, feed as 30.5% 1-hexene in nitrogen, GHSV of 500 h^{-1}, time on stream of 30 min.

Support (Si/Al)	Relative acidity of support	%Conversion at different % WO$_3$ loading		Yield of gas products at different % WO$_3$ loadings		%Yield of liquid products at different % WO$_3$ loadings		%Coke at different % WO$_3$ loadings	
		1%wt WO$_3$	9%wt WO$_3$	1%wt WO$_3$	9%wt WO$_3$	1%wt WO$_3$	9%wt WO$_3$	1%wt WO$_3$	9%wt WO$_3$
ZSM-5 (38)	Strongly acidic	99.40	92.07	55.36	14.85	44.03	84.90	0.61	0.25
SiO$_2$-Al$_2$O$_3$ (15)	Strongly acidic	99.42	97.35	34.21	14.91	62.56	82.43	3.23	2.66
Al-HMS (43)	Strongly acidic	.94.90	96.29	10.44	3.75	88.15	95.52	1.41	0.73
HMS	Weakly acidic	29.40	89.63	20.95	11.99	76.33	87.61	2.72	0.40
Al$_2$O$_3$	Amphoteric	70.04	18.18	18.53	29.95	81.26	69.95	0.21	0.10

Product distribution in gas phase obtained from the reaction of 1-hexene over the supported WO_3 catalysts at different loadings is shown in Figure 4.12 and 4.13, respectively. From Figure 4.12, at low loading of 1% WO_3, ethylene and propylene are mainly formed in almost equal amount for most supported catalysts except the cases of SiO_2-Al_2O_3 and Al-HMS where propylene becomes a major product.

In addition, C_3-C_5 alkanes are detected in a quite little amount for all cases except when ZSM-5 was used as the support. In the latter case C_3-C_5 alkanes are the major group of gas products. This is an evidence of the cracking process is more favored on the ZSM-5 support than metathesis under the tested reaction condition. Methane is formed in a significant amount on the catalyst supported on HMS and Al_2O_3. The results described above indicate that strongly acidic supports can diminish the methane formation which is an undesired product in industry while methane formation is favored for the catalyst supported on the pure silica HMS or Al_2O_3 alone. Butenes are detected at a low content in all cases. It is known that the common metathesis product is olefins and the common cracking product is methane. It is, indeed, rather difficult to compare the metathesis activity among these catalysts at the temperature as high as 500°C. One alterative way is to increase the metathesis active site, *i.e.* WO_3 in significant amount.
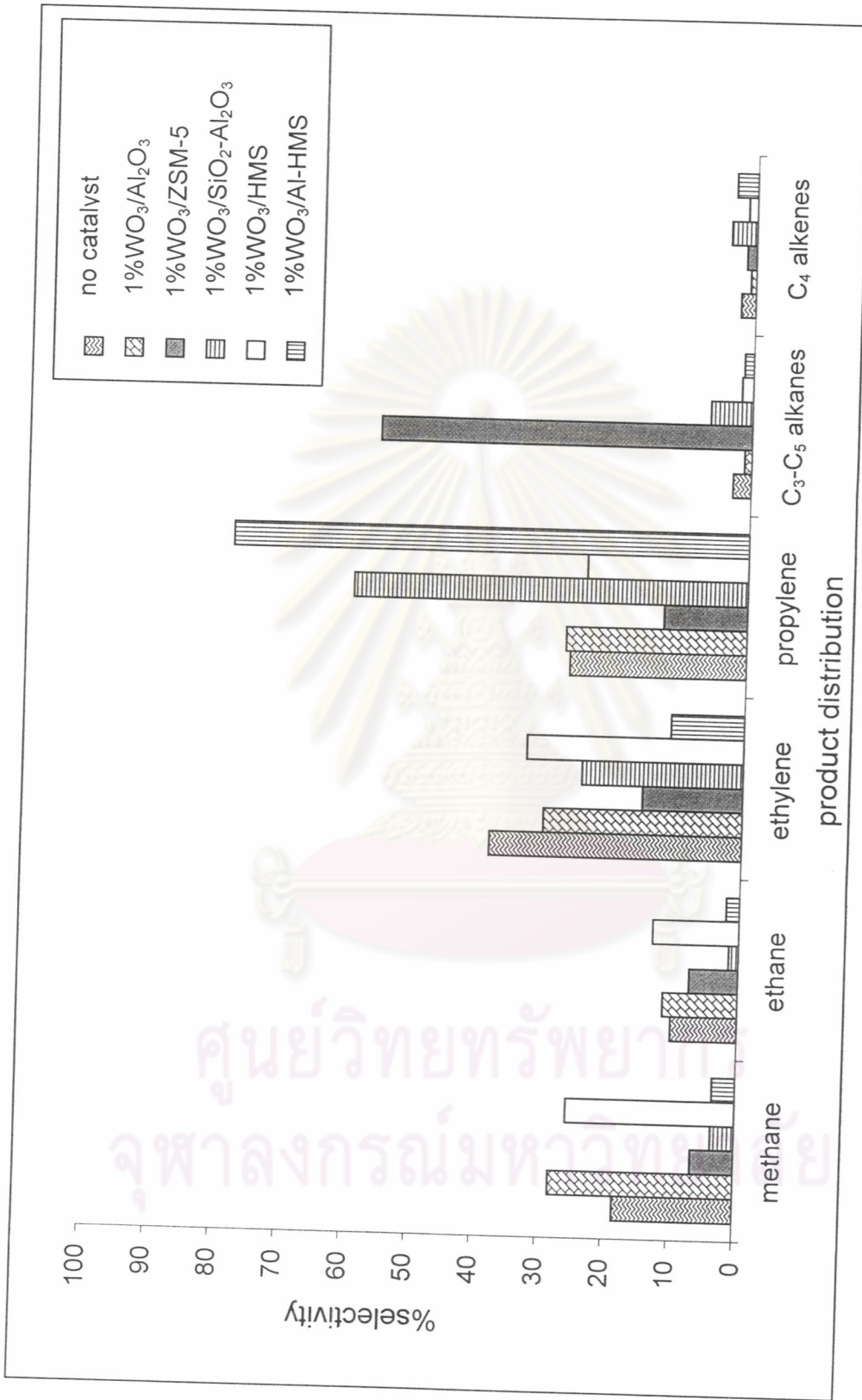
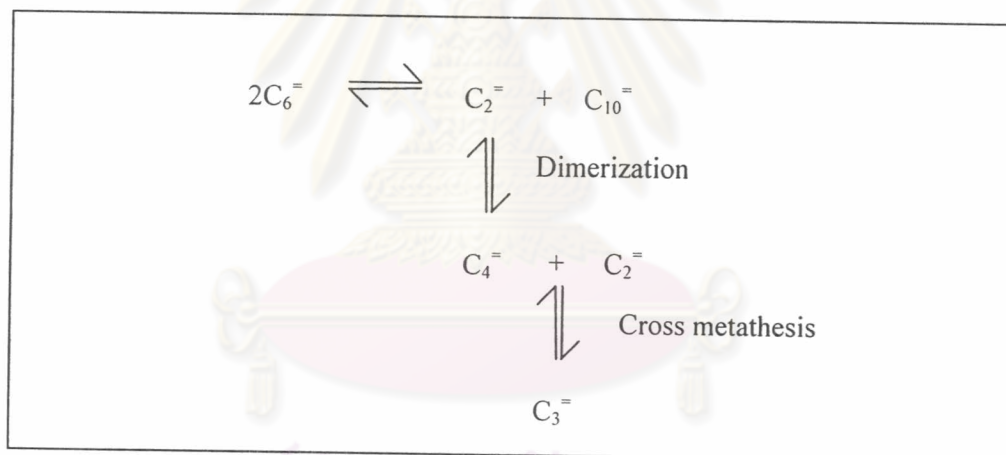**Figure 4.12** Gas product distribution of 1-hexene conversion catalyzed by various supported tungsten catalyst.

(1%wt of WO_3, GHSV = 500 h^{-1} , T = 500°C, catalyst weight = 0.35 g).

With increasing the loading of WO_3 from 1% to 9% WO_3, the selectivity to propylene considerably increases in cases of ZSM-5 and HMS supports as shown in Figure 4.3. The selectivity to ethylene drastically decreases over the WO_3 catalyst supported on HMS. The ethylene consumption is a confirmation of the metathesis activity of the WO_3 catalyst supported on HMS. This is resulted from the ethylene dimerization to form butenes followed by cross metathesis between excessive ethylene and butanes as shown in Scheme 4.1. This is in accordance with the results shown in Table 4.5 indicating the preferable metathesis at high loading of WO_3 on HMS. It is interesting that the selectivity to undesired methane is much decreased as well by increasing the WO_3 loading.

$$2C_6^= \; \rightleftharpoons \; C_2^= \; + \; C_{10}^=$$

$$\Big\updownarrow \text{ Dimerization}$$

$$C_4^= \; + \; C_2^=$$

$$\Big\updownarrow \text{ Cross metathesis}$$

$$C_3^=$$

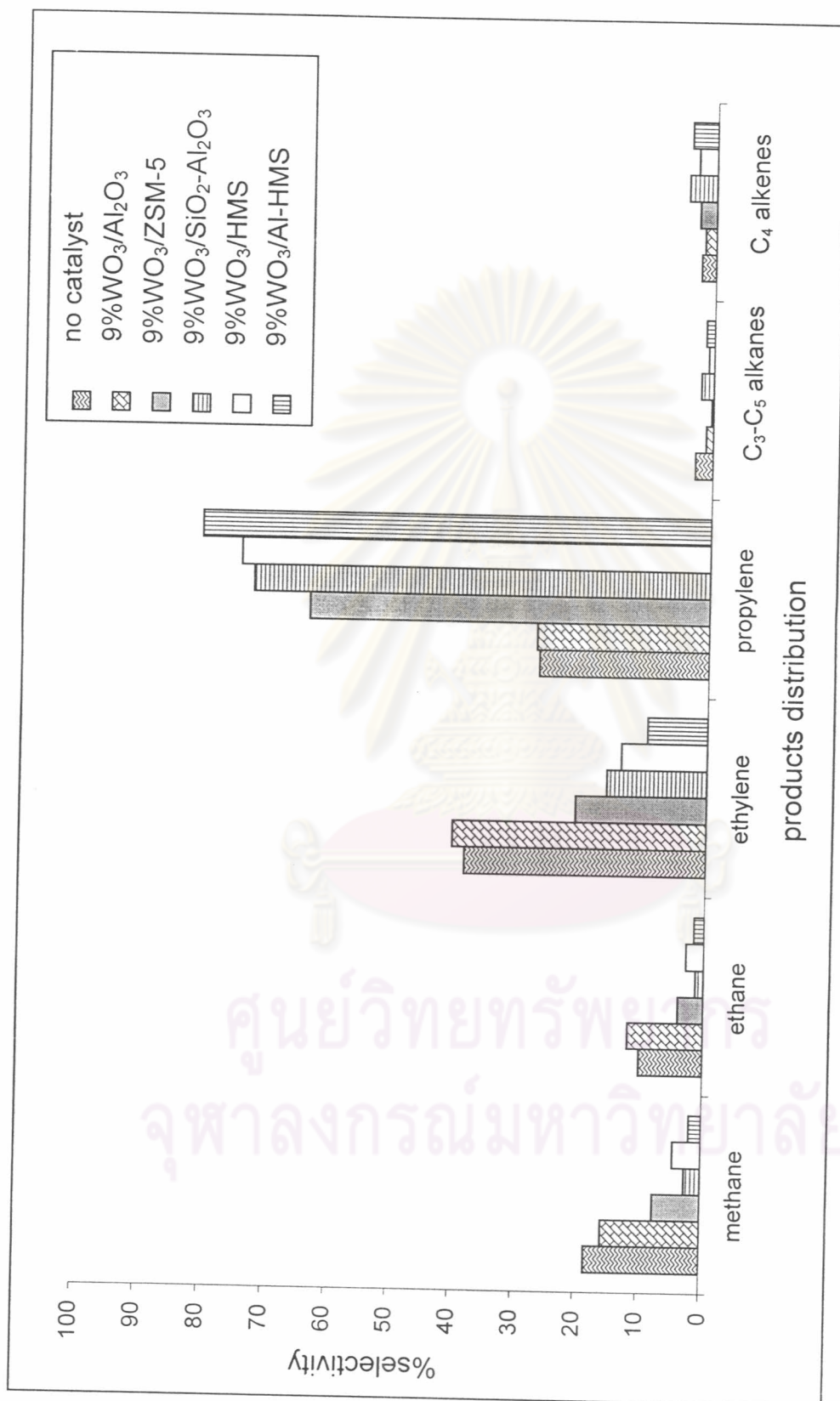**Scheme 4.1**   Production of propylene *via* cross metathesis of ethylene and butene.

Figure 4.13 Gas product distribution of 1-hexene conversion catalyzed by various supported tungsten catalyst.

(9%wt of WO_3, GHSV = 500 h^{-1} , T = 500°C, catalyst weight = 0.35 g).

4.2.2 Effect of Temperature on Catalytic Activity of 1-Hexene Conversion

Decreasing temperature is an alternate way to reduce the formation of methane and other light alkanes from cracking of the heavier alkane. The results of catalytic activities of the supported 1% WO_3/HMS catalyst at different temperatures (200-500°C) are shown in Table 4.6. By decreasing temperature from 500 to 300 and 200°C, the conversion of 1-hexene decreases from 29.40 to 12.99 and 4.85%, respectively. However, the yield of gas products is much greater and the yield of liquid product is less at low temperature than at high temperature. This is a sign of improvement of the catalytic efficiency of 1-hexene conversion. However, coke is formed up to 4% at the temperature of 200°C while it is only 1.89 and 2.82% at 300 and 500°C, respectively. Thus the amount of coke is at the minimum at the temperature of 300°C.

Table 4.6 Catalytic activities of 1%WO_3/HMS catalyst in 1-hexene conversion at various temperatures, feed of 30.5% 1-hexene in nitrogen, time on stream of 30 min.

	Reaction temperatures		
	200°C	300°C	500°C
Conversion of 1-hexene (%)	4.85	12.99	29.40
Yield of Gas products (%wt)	85.13	50.74	20.95
Yield of Liquid products (%wt)	10.74	47.37	76.33
Coke (%wt)	4.13	1.89	2.72

Considering the product distribution in gas phase obtained from using supported 1% WO_3/HMS catalyst at different temperatures as shown in Figure 4.14, a drastic increase in the selectivity to propylene is found from 24.52 to 90.40 and 98.18% as a result of decreasing the temperature from 500 to 300 and 200°C, respectively. Methane formed at the selectivity of 25.78 % at 500°C is found to be vanished upon the decrease of temperature to 300°C and 200°C as well. Therefore, it indicates that there is no competitive reaction of cracking conversion of 1-hexene at all at the temperatures of 200 and 300°C although it seems to be a major reaction over various supported tungsten based catalysts at 500°C.
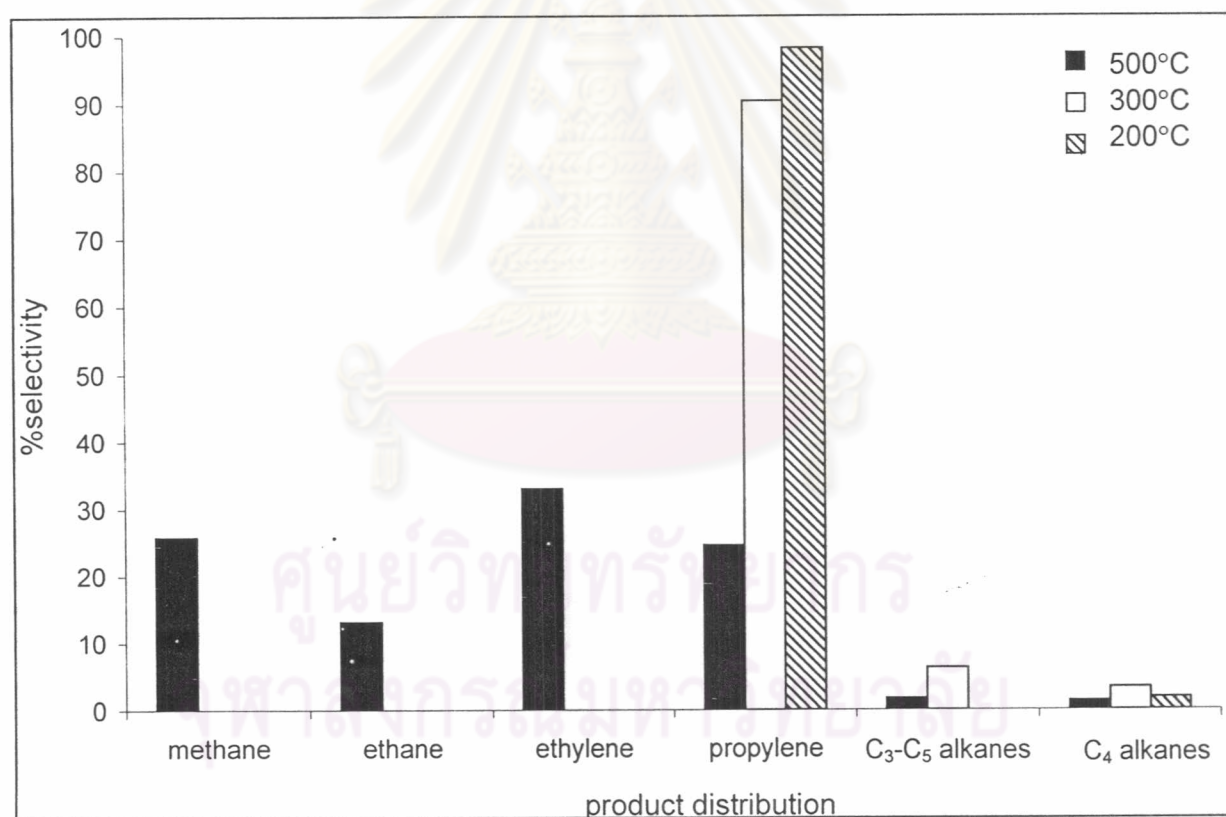

Figure 4.14 Gas product distribution in 1-hexene conversion using 1%WO_3/HMS as a catalyst at various reaction temperatures (GHSV 500h^{-1}, time on stream 30 min, catalyst weight = 0.35 g)

The temperature of 300°C is selected for comparison with other supported catalysts because of the achievement of moderate conversion of 1-hexene with very high selectivity to propylene and small coke deposited on the WO_3/HMS catalyst. The activities of various supported catalysts at 1%wt WO_3 loading in conversion of 1-hexene at the temperature of 300°C are compared in Table 4.7. It is found that the 1-hexene conversion is affected by the support and descending in the order of Al-HMS > SiO_2-Al_2O_3 > ZSM-5 > Al_2O_3 > HMS. This is close to the trend observed for the same catalysts at the temperature of 500°C. Therefore, acidity still plays an important role on the activity of the supported catalysts. The yield of gas product is also affected by the support and the increase of gas yield is found in the order of Al-HMS ~ SiO_2-Al_2O_3 < Al_2O_3 < HMS < ZSM-5. The higher yield of gas, the lower yield of liquid is observed. However, coke is formed the most on ZSM-5 (about 5%) and about 2% or less on other supports. Formation of gas is more favored than liquid in the cases of using HMS, ZSM-5 and Al_2O_3 as supports but the liquid products up to 90% yield is found for Al-HMS and SiO_2-Al_2O_3.

Table 4.7   Catalytic activity of various supported tungsten catalyst (1%wt of WO_3) in conversion of 1-hexene at 300°C, feed 30.5% of 1-hexene in nitrogen, GHSV of 500 h^{-1}, time on stream of 30 min.

Catalyst	%Conversion	%Gas product	%Liquid product	%Coke
1%WO_3/Al_2O_3	54.06	47.60	51.66	0.74
1%WO_3/SiO_2-Al_2O_3	80.88	7.64	90.13	2.23
1%WO_3/HMS	12.99	50.74	47.37	1.89
1%WO_3/Al-HMS	89.75	8.88	89.71	1.41
1%WO_3/ZSM-5	64.56	52.13	42.89	4.98

Gas product distribution from 1-hexene conversion over various supported WO_3 catalysts at the temperature of 300˚C is shown in Figure 4.15. In contrast to high temperature, the gas production distribution obtained from catalysis over Al-HMS, SiO_2-Al_2O_3 and ZSM-5 supports indicates the significant selectivity to not only propylene but also butenes and C_3-C_5 alkanes while ethylene and ethane are found in quite a few percents. HMS and Al_2O_3 exhibit in different manner from others, *i.e.* propylene is the only olefin found as the major olefin in the gas phase but ethylene and butenes are very rare. The selectivity to propylene is found as 90 and 78% over WO_3/HMS and WO_3/Al_2O_3, respectively. In spite of giving the very high selectivity to propylene, Al_2O_3 provides the maximum selectivity to methane and ethane compared to other supported catalysts. Considering both conversion and selectivity to gas products, WO_3/HMS is found to be the most effective catalyst for conversion of 1-hexene to propylene at the highest selectivity at the temperature of only 300˚C.

At the same loading of 1% WO_3 and tested at the temperature of 300˚C other catalysts can make higher conversion of 1-hexene than the WO_3/HMS catalyst but much lower selectivity to propylene resulting in producing of the mixture of propylene, C_3-C_5 alkanes and butenes. Under the more vigorous condition, *i.e.* the temperature of 500˚C, Thermal cracking process without the use of any catalyst seems to be a competitive reaction by giving very high conversion of 1-hexene and no difference in product distribution by comparing to the results obtained from using Al_2O_3 and HMS as supports. ZSM-5 is the best cracking catalyst but poor metathesis catalyst at such a condition. Only product distribution obtained from the cases of SiO_2-Al_2O_3 and Al-HMS are different from that in the absence of catalyst.
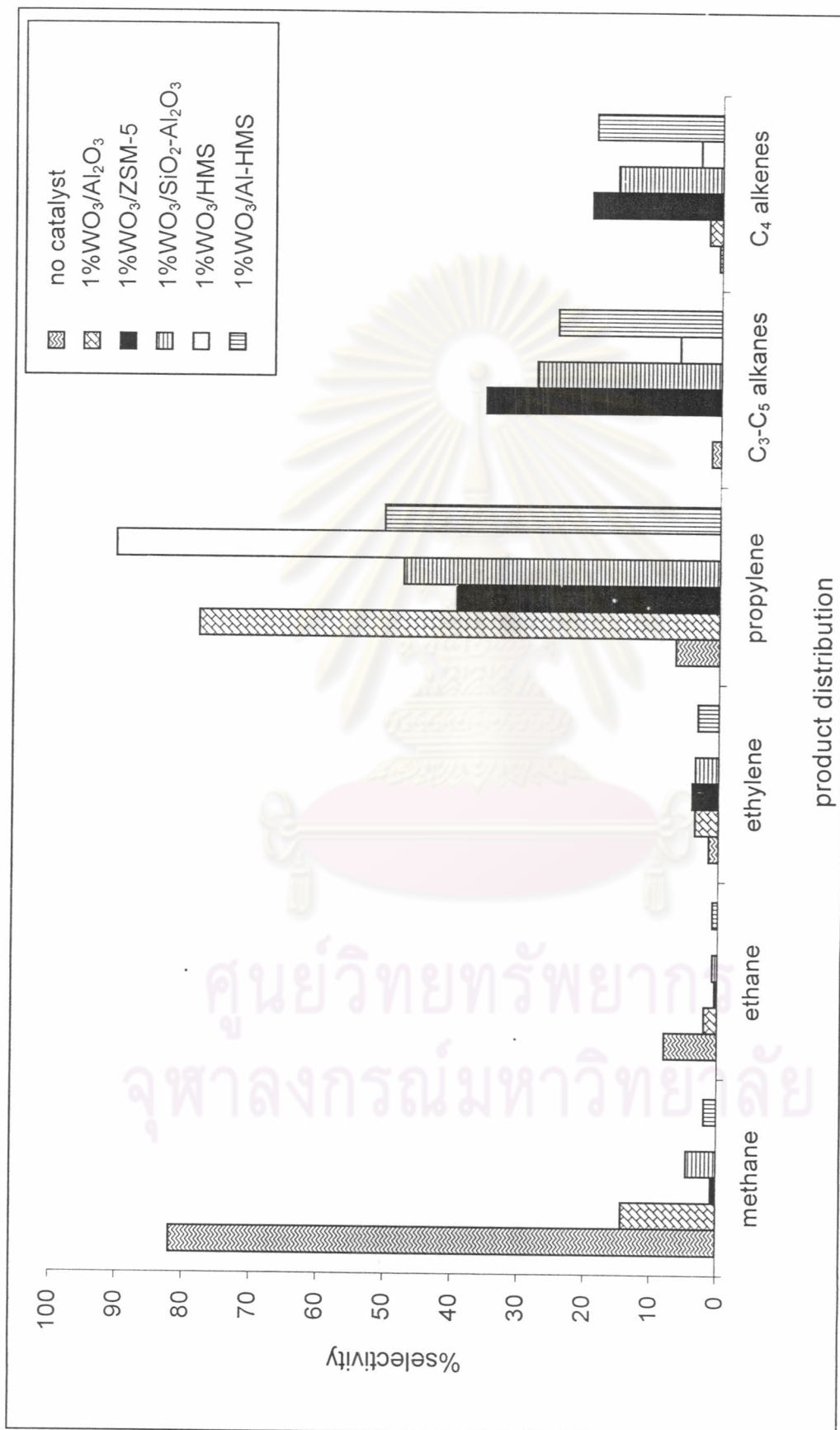
Figure 4.15 Gas product distribution of 1-hexene conversion catalyzed by various supported tungsten catalyst.

(1%wt of WO_3, GHSV = 500 h^{-1} , T = 300°C, catalyst weight = 0.35 g)

4.2.3 Effect of WO$_3$ loading on Catalytic Activity of 1-Hexene Conversion

A variation of WO$_3$ loadings (1, 3, and 6% WO$_3$) was compared to find the optimal loading in the tungsten based catalyst supported on the mesoporous HMS material on the purpose of providing the most efficiency of the catalyst in conversion of 1-hexene to light olefins, or more preferable propylene. The percentage conversions of 1-hexene over the supported WO$_3$ catalyst at different loadings at temperatures of 300 and 500°C are compared in Figure 4.16. At the temperature of 300°C, the conversion of 1-hexene increases from 12.99 to 39.60% with increasing the WO$_3$ loading from 1 to 3%, respectively. The decrease of conversion is found at the WO$_3$ loading of 6%. At the temperature of 500°C, the relation between %conversion and the WO$_3$ loading are almost parallel to that observed at 300°C. The results obtained at both temperatures are in agreement with each other that the maximum conversion of 1-hexene can be achieved at the WO$_3$ loading of 3%. The overall conversion of 1-hexene is increased upon an increase of temperature.

As shown in Table 4.8, the yield of liquid phase at the reaction temperature of 300°C increases from 47.37 to 72.43% and the yield of gas phase decreases from 50.74 to 25.89% with increasing the WO$_3$ loading from 1 to 3% but no significant difference beyond this point. Coke is formed in a small amount especially at the WO$_3$ loading of 6%. When the temperature of reaction reach to 500°C, the yield of gas products increase from 20.95 to 41.02% and the yield of liquid products decrease from 76.30 to 58.72% with increasing the loading of WO$_3$ from 1 to 3% as shown in Table 4.9.However when the loading of WO$_3$ was higher than 6%, the yield of gas phase decrease.
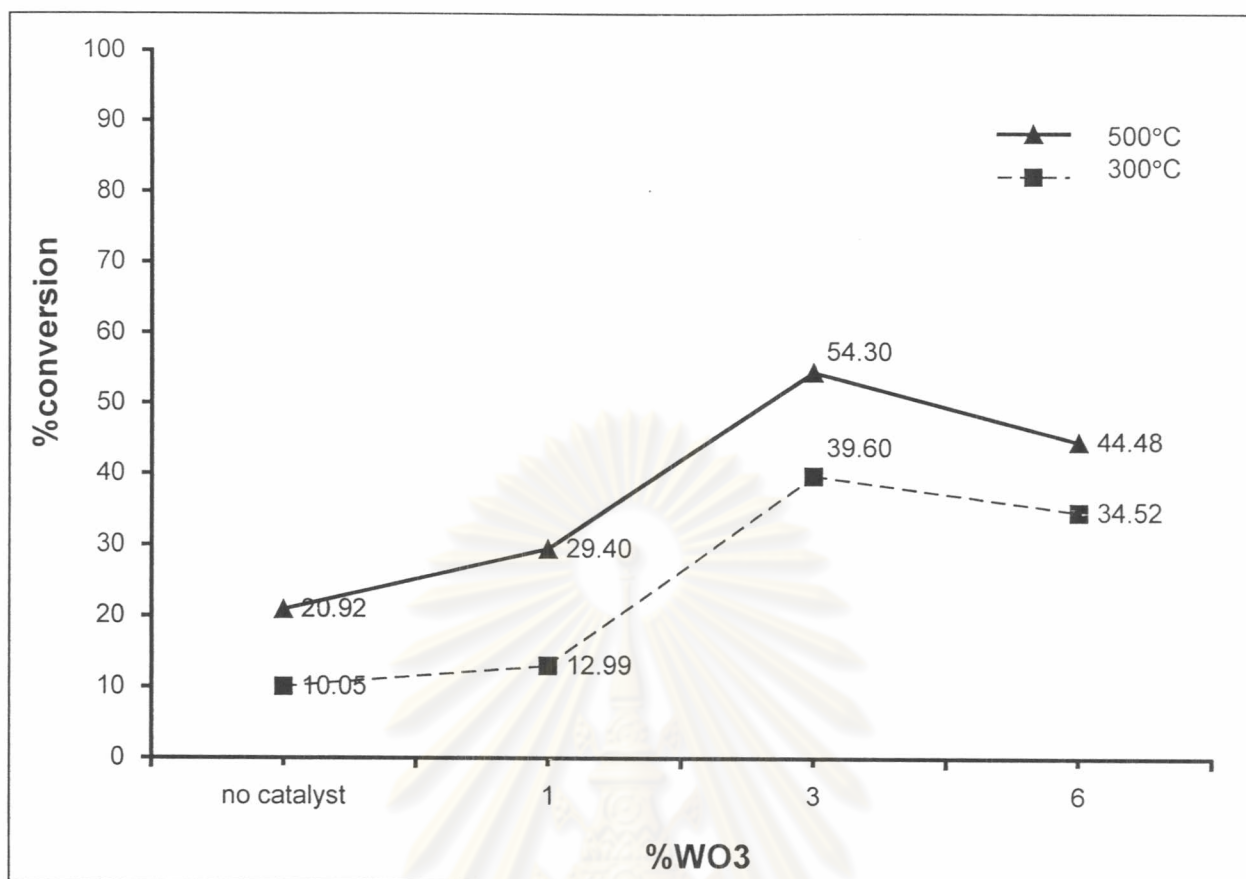
Figure 4.16   Effect of tungsten loading on activities of WO₃/HMS catalyst in 1-hexene

conversion at 300 and 500°C.

Table 4.8   Catalytic activities of various loading of WO₃ on HMS support in 1-hexene

conversion at 300°C, feed of 30.5% 1-hexene in nitrogen, time on stream

of 30 min.

	Tungsten loading (%wt)		
	1.0	3.0	6.0
Conversion of 1-hexene (%)	12.99	39.60	34.52
Yield of Gas products(%wt)	50.74	25.89	26.53
Yield of Liquid products (%wt)	47.37	72.43	72.62
Coke (%wt)	1.89	1.68	0.85

Table 4.9   Catalytic activities of various loading of WO_3 on HMS support in 1-hexene conversion at 500°C, feed of 30.5% 1-hexene in nitrogen, time on stream of 30 min.

	Tungsten loading (%wt)			
	1.0	3.0	6.0	9.0
Conversion of 1-hexene (%)	29.40	54.30	44.48	89.63
Yield of Gas product (%wt)	20.95	41.02	36.54	11.99
Yield of Liquid product (%wt)	76.33	58.72	62.02	87.61
Coke (%wt)	2.72	0.26	1.44	0.40

Product distribution of gas phase produced over the supported WO_3 catalyst at different loadings at temperatures of 300 and 500°C are shown in Figure 4.17 and 4.18, respectively. It is found that, at the reaction temperature of 300°C, the highest selectivity to propylene up to 90% is achieved from the WO_3/HMS catalyst of 1% loading while the selectivity to propylene decreases to 77% and goes up to 86% at the loading of 3 and 6% WO_3, respectively. In the absence of any catalyst, the conversion is found in some extent (Figure 4.16) with the major gas product as methane with 82% selectivity and little amounts of other C_2-C_4 hydrocarbons as shown in Figure 4.17. This confirmed that the supported tungsten-based catalysts are in charge for converting 1-hexene to propylene with the considerably high product selectivity over the WO_3/HMS catalyst. The optimal condition for conversion of 1-hexene to propylene over the WO_3/HMS catalyst is the 3% WO_3 loading, and the temperature of 300°C. In case of the high reaction temperature of 500°C, cracking is competitive reaction because methane was observed as shown in Figure 4.18. However, with increasing loading of WO_3, methane decreased.
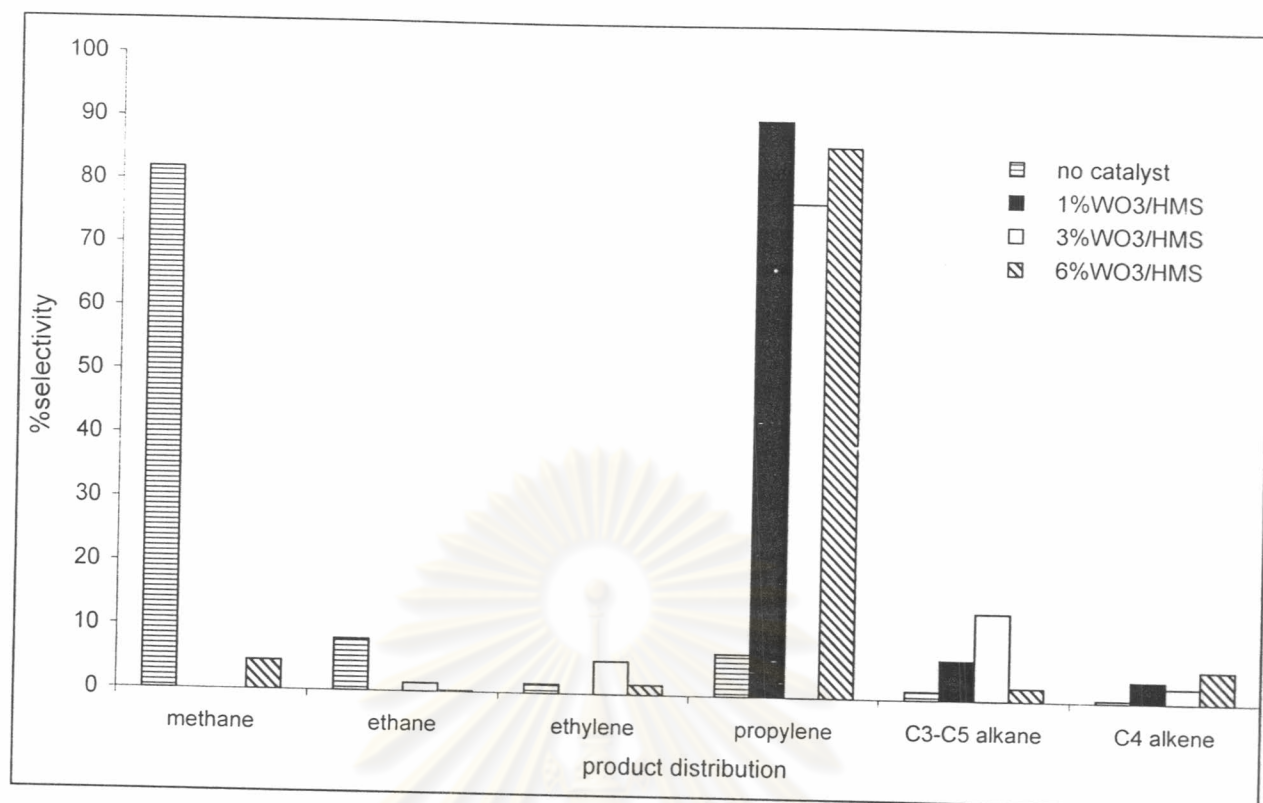
Figure 4.17 Gas product distribution in 1-hexene conversion at 300°C using
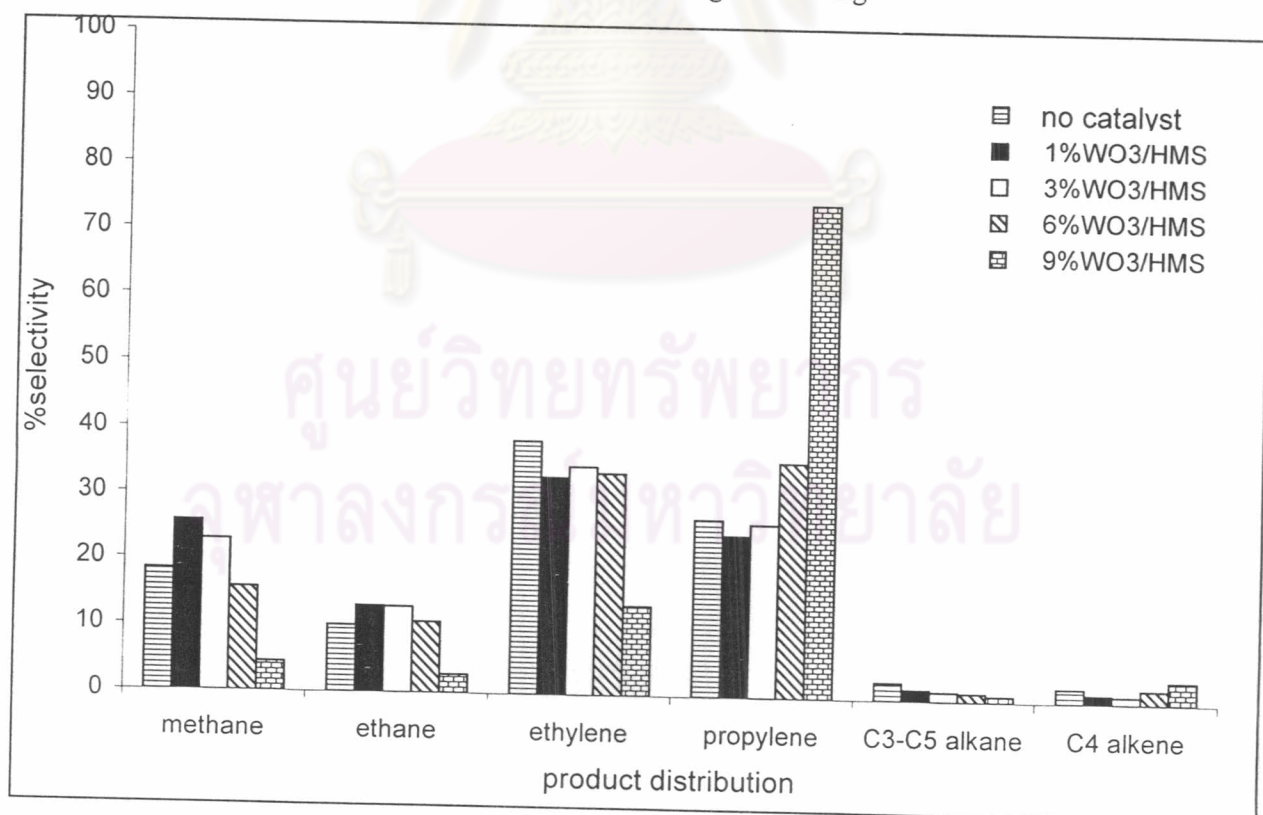
WO₃/HMS catalyst at various tungsten loading.

Figure 4.18 Gas product distribution in 1-hexene conversion at 500°C using

WO₃/HMS catalyst at various tungsten loading.