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Dual effects of supported W catalysts for dehydroaromatization of methane in the absence of oxygen

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The screening of a series of W-based catalysts on different supports i.e. HZSM-5, Hβ, USY and Al_2O_3 for the dehydroaromatization of methane (DHAM) revealed that HZSM-5 emerged as the best support. Next, the performance of W/HZSM-5 and W-H_2SO_4/HZSM-5 catalysts for the DHAM reaction was compared to study the effect of acidic treatment in the impregnation method. The results showed that the optimum activity of W-H_2SO_4/HZSM-5 catalyst exceeded that of W/HZSM-5 catalyst. Finally, the influence of Si/Al ratio in the W-H_2SO_4/HZSM-5 catalyst was studied and the catalyst with Si/Al ratio = 30 was found to be the most promising for the DHAM reaction. The remarkable activity of the catalyst is attributed to the presence of dual effects: suitable content of octahedral polymeric and tetrahedral monomeric tungstate species accompanied by proper amount and strength of acid sites in the catalyst.

KEY WORDS: dehydroaromatization; methane; W-based catalysts; tungstate species.

1. Introduction

Dehydroaromatization of methane (DHAM) to aromatics have received considerable attentions [1–18] in the study of catalytic reactions. The most common catalysts reported to be promising for DHAM are HZSM-5-supported Mo and also W catalysts [2–18]. Some of the characteristics of an active DHAM catalyst include a highly dispersed active metal species on the surface and also a proper amount of acidity for the support [1–12]. Mo-based catalysts supported on HZSM-5 have been used for catalytic reaction of DHAM in the absence of oxygen. By using *in situ* FT-IR pyridine technique, the acid sites of Mo/HZSM-5 and the interaction between Mo species and HZSM-5 were investigated [2]. By combining FT-IR study with catalytic evaluation, it was concluded that Mo/HZSM-5, which had a 60% remaining number of original Brönsted acid sites exhibited a good catalytic performance. In addition, Naccache *et al.* [3] reported that the formation of Mo_2C species in Mo/HZSM-5 under methane stream was responsible for the formation of aromatics. The reaction mechanism for the production of aromatics proceeded *via* the formation of acetylene from methane on Mo_2C and the acetylene subsequently oligomerized into aromatics. ^{27}Al and ^{29}Si MAS NMR were employed to investigate the interaction between Mo species and HZSM-5 [13]. The results revealed that strong interaction occurred between the metal species and HZSM-5 on Mo/HZSM-5 with relatively higher amount of Mo species and caused the framework aluminum to be extracted into the extra framework. As a consequence, the catalytic activity dropped dramatically.

Recently, many authors reported that the activity and stability of a HZSM-5-supported W catalyst for DHAM increased at a relatively high temperature [4–7,14]. Improved active and heat-resisting catalysts for DHAM have also been developed by the incorporation of Zn (or Mn, La, Zr) into W/HZSM-5 [4–6]. The present work studies the dehydroaromatization of methane over a series of 3 wt% W-based catalysts prepared with different supports, under different preparation conditions and several Si/Al ratios. The relationship between the nature of tungsten species and the acidic sites of the catalysts with the catalytic activity is reported.

2. Experimental

2.1. Catalyst preparation

A series of 3% W-based catalysts with different supports were prepared by aqueous impregnation of support materials (HZSM-5; Hβ; USY; Al_2O_3) with ammonium meta tungsten ($(NH_4)_6W_{12}O_{40}{\cdot}H_2O$) solution, followed by drying at 393 K for 2 h and calcining at 773 K for 5 h. Another set of a series of 3% W-H_2SO_4/HZSM-5 catalysts with different Si/Al ratios were prepared by impregnating HZSM-5 with ($(NH_4)_6W_{12}O_{40}{\cdot}H_2O$) and H_2SO_4 solution (pH = 2–3)

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followed by drying and calcining at the same previous conditions. All the catalysts were pressed, crushed, and sieved to a size of 30–60 mesh.

2.2. Catalyst characterization

The BET surface area and the pore volume of the samples were obtained by means of nitrogen adsorption detemined at 77 K in a Thermo Finnigan surface area analyzer. The acidity of the catalysts was measured by means of TPD-ammonia using a Micromeritics TPD/TPR/O analyzer. The samples were pretreated in flowing nitrogen at 15 K/min up to 873 K and then cooled to 383 K. Next, the samples were saturated with pure ammonia followed by flushing the physically adsorbed ammonia in helium stream at 373 K for 1 h. Finally, the sample was heated up to 873 K in a heating rate of 15 K/min. The recorded spectra represent the number and strength of the catalyst acidity. The nature of W species on the catalysts was determined by means of UV diffuse reflectance spectra. UV DRS spectra were performed on a Perkin-Elmer Lamda-900 spectrometer. The scanning wavelength range was 198–500 nm and the scan speed was 120 nm/min.

2.3. Catalyst evaluation

The catalyst test was conducted in a micro fixed-bed quartz reactor with internal diameter of 9 mm and length of 300 mm under atmospheric condition. In each run, the catalyst charge was 1 g. Prior to the catalytic testing, the catalysts were pretreated in nitrogen stream for 1 h at 823 K. Feed gas containing CH_4 + 10% N_2 was passed through over the catalyst bed at GHSV of 1800 ml/(g.h). Nitrogen was used as an internal standard for calculating the methane conversion and selectivity of the reaction products. Some experiments were carried out at the GHSV between 1800–9000 ml/(g.h) over 3%W-H_2SO_4/HZSM-5 catalysts with different Si/Al ratios. The reaction products were analyzed by a Hewlett-Packard 5890 on-line GC equipped with TCD using Porapak Q, molecular sieve 5A, UCW 982, and DC 200 columns.

3. Results and discussion

3.1. Catalytic performance of supported W catalysts

Figure 1(a)–(c) show the methane conversion and product selectivity as a function of time on stream over W/USY, W/Al_2O_3, W/Hβ, W/HZSM-5 and W-H_2SO_4/HZSM-5 catalysts. It can be seen that methane conversion decrease gradually with increasing time on stream over all the catalysts. Without considering the acidified effect of W supported on HZSM-5 catalyst, the data on conversion reveal that W/HZSM-5 catalyst, prepared using a neutral solution in the impregnation method, is the most active. The effect of preparation condition using H_2SO_4 solution with pH = 2–4 for the impregnation method was studied by comparing the activities of W/HZSM-5 and W-H_2SO_4/HZSM-5. The result shows that W-H_2SO_4/HZSM-5 gives higher methane conversion than W/HZSM-5 catalyst at the initial time on stream (within 100 min) and exhibits a maximum value of 9.59% at 973 K and GHSV = 1800 ml/(g.h.), but decreases very rapidly beyond that. The rapid deactivation observed for W-H_2SO_4/HZSM-5 catalyst after reaching its maximum conversion at temperature of 1073 K, pressure of 0.1 MPa, and GHSV of 1500 ml/(g.h.), respectively is similar to the work reported by Zeng *et al.* [4]. Figure 1(b) exhibits the corresponding aromatics selectivity for DHAM over 3% W-based catalysts with different supports. Obviously, the aromatics selectivity over all the catalysts decreases steadily with time on stream after reaching maximum. Over the whole time on stream, it can be seen that W-H_2SO_4/HZSM-5 displays the highest aromatics selectivity having maximum at 99.5% whereas the lowest aromatics selectivity on stream is observed over W/Al_2O_3 catalyst.

In addition to aromatics, the products also contain C_2 hydrocarbons, but to a lesser extent. The selectivity of C_2-hydrocarbons (C_2H_4 and C_2H_6) over the 3 wt.%-loading W catalysts with various supports is given in figure 1(c). As can be seen, considerable amount of C_2 is produced over W/Al_2O_3 catalyst compared with other W supported catalysts. Between the W/HZSM-5 and W-H_2SO_4/HZSM-5 catalysts, the C_2-hydrocarbons selectivity is higher over the latter than that the former. Meanwhile, the selectivity of C_2-hydrocarbons over W/Hβ and W/USY catalysts are lower than that over the W-H_2SO_4/HZSM-5 and W/Al_2O_3 catalysts.

Next, the effect of Si/Al ratio in the acidified W-based catalyst using HZSM-5 as a support was determined. Several W-H_2SO_4//HZSM-5 catalysts with different Si/Al ratios were prepared by the impregnation method in acidic solution with pH 2–3. The variation of methane conversion over 3 wt.% W-H_2SO_4/HZSM-5 with different Si/Al ratios is presented in figure 2(a). The results indicate that methane conversion is dependent on the Si/Al ratio of the HZSM-5 support. The higher is the Si/Al ratio, the lower the methane conversion will be. A methane conversion over 3 wt.% W-H_2SO_4/HZSM-5 catalyst with Si/Al = 30 approaches a maximum at 22.08%, and further increases in the Si/Al ratio leads to a decline in the methane conversion. Meanwhile, the selectivity of aromatics over 3 wt.% W-H_2SO_4/HZSM-5 with different Si/Al ratios is presented in figure 2(b). A maximum in the aromatics selectivity of 97.49% is achieved over the 3% W-H_2SO_4/HZSM-5 (Si/Al ratio = 30) catalyst. On the other hand, the C_2 selectivity over 3% W-H_2SO_4/HZSM-5 with various Si/Al ratios increase with an increase in the time on stream, as seen in figure 2(c). A gradual but significant increment

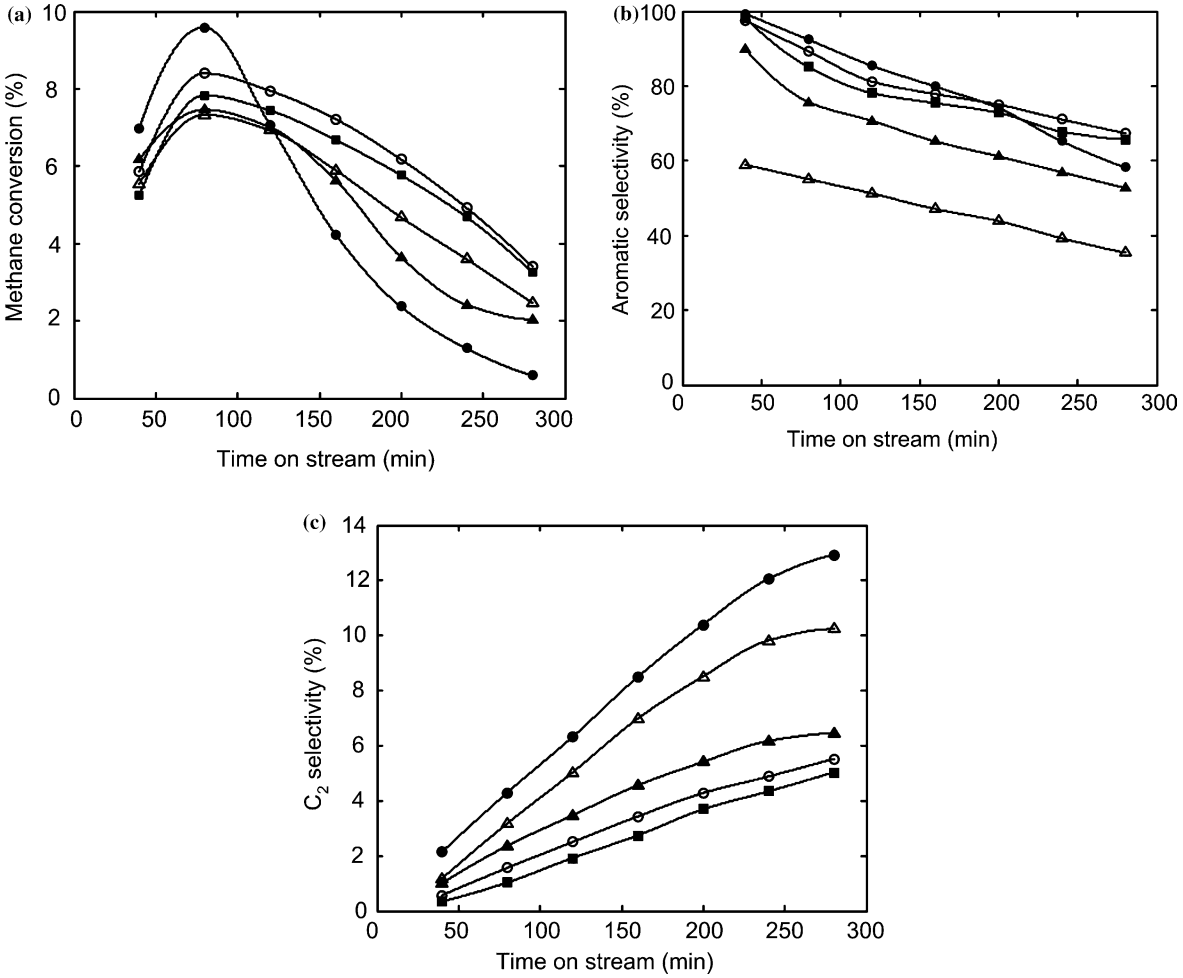

Figure 1. Methane conversion and product selectivities over the 3 wt.%-loading W catalysts with various supports for DHAM at 973 K, GHSV = 1800 ml/(g.h) , Feed Gas = CH_4 + 10% N_2, 1 atm. Catalysts: (●)W-H_2SO_4/HZSM-5(Si/Al = 30);(○)W/HZSM5 (Si/Al = 30); (■)W/Hβ(Si/Al = 25); (▲)W/USY(Si/Al = 5.1); (△)W/Al_2O_3.

in the on-stream C_2 selectivity from 2.69% to 12.19% was observed over the 3% W-H_2SO_4/HZSM-5 catalyst with Si/Al = 30.

Further investigation was carried out to study the effect of GHSV on the catalytic activity over W-H_2SO_4/HZSM-5 catalysts with different Si/Al ratios. The results are presented in figure 3(a)–(c) for the dependence of GHSV on methane conversion, aromatic selectivity and C_2-hydrocarbons, respectively. The influence of GHSV on the catalysts activity for non-oxidative DHAM reaction has been studied in various ranges of the GHSV [6,18]. In the present work, GHSV in the range of 1800–9000 ml/(g.h) was applied. The results show that methane conversion and aromatic selectivity decrease significantly, while C_2 hydrocarbons selectivity increases obviously with increasing GHSV. As can be seen in figure 3, the decreasing activity with time on stream over all the 3% W-H_2SO_4/HZSM-5 catalysts with different Si/Al ratios exhibits a similar trend indicating that large GHSV is unfavorable to methane conversion and formation of aromatics product. A similar observation has been confirmed previously [6]. Furthermore, from figure 3 it can also be seen the rapid decline in methane conversion and selectivity of aromatics over 3% W-H_2SO_4/HZSM- 5 catalyst with Si/Al = 30, while, a gradual decrease over both the catalysts with Si/Al = 50 and 80 are observed. The trend could be attributed to coke formation. In addition, study on the effect of adding O_2 into methane feed gas for DHAM reaction over 3W-H_2SO_4/HZSM-5 (Si/Al = 30) catalyst was performed to enhance the catalyst activity. The results in figure 4 shows that the activity of catalyst is improved significantly after introducing 2% O_2 in methane feed. It has been reported by several authors [1,6,8,17,19] that the addition of a suitable amount of oxidants such as CO, CO_2 and O_2 into methane feed resulted in remarkable enhancement in the catalyst activity and stability due to suppression of coke deposited in the catalyst. In the oxidative condition, the aromatics and C_2-hydrocarbons products accompanied by COx (CO and CO_2) as side-products were detected, whilst in the non-oxidative condition, the aromatic and

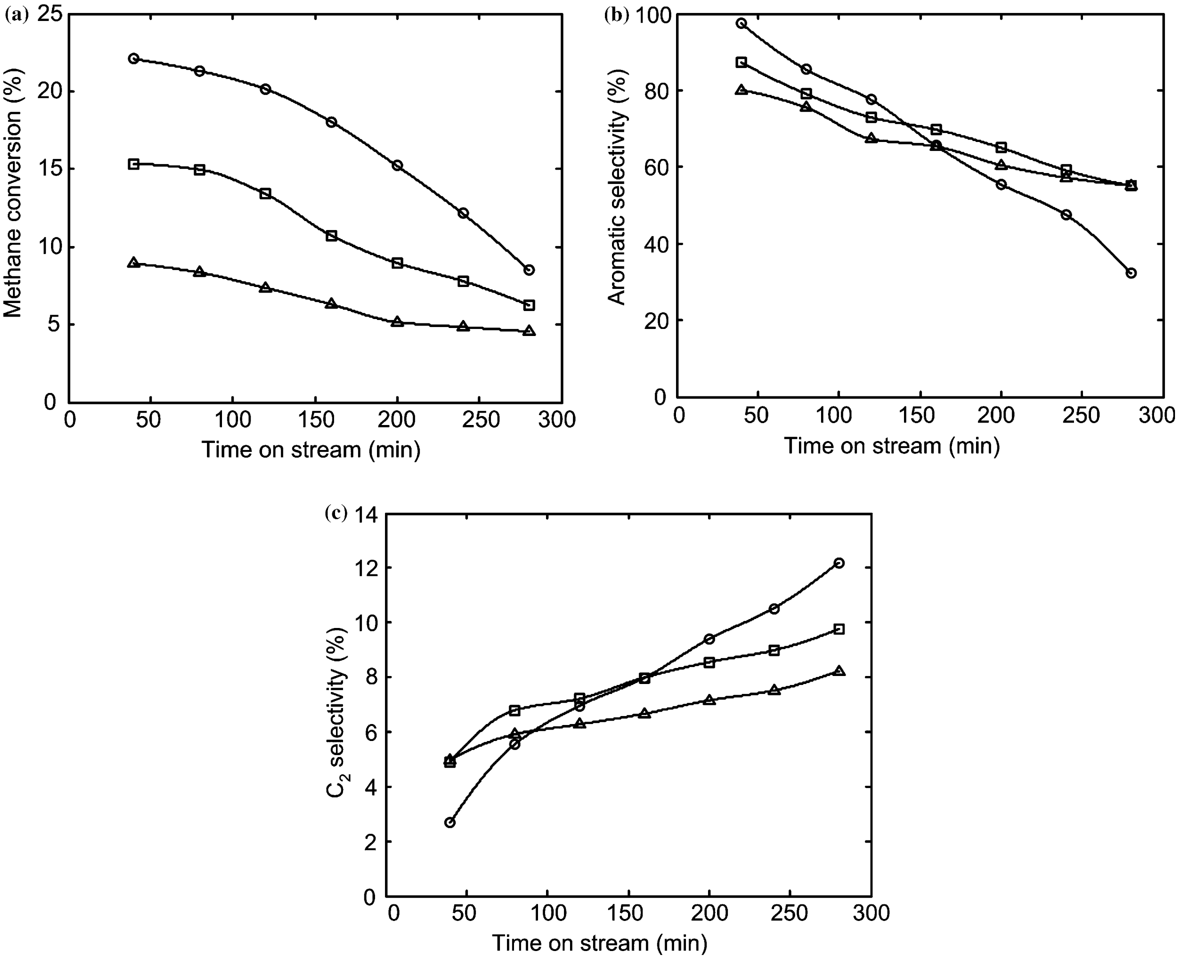

Figure 2. Effect of Si/Al ratio of HZSM-5 on the methane conversion and product selectivities over 3 wt.% W-H_2SO_4/HZSM-5 catalysts for dehydroaromatization of methane at 1073 K, GHSV = 1800 ml/(g.h). Feed Gas = CH_4 + 10% N_2, 1 atm. Catalysts: (○) W-H_2SO_4/HZSM-5 (Si/Al = 30); (□) W-H_2SO_4/HZSM-5 (Si/Al = 50); (△) W-H_2SO_4/HZSM-5 (Si/Al = 80).

C_2-hydrocarbons were detected with negligible amount of COx. From the results of the activity testing, in the presence of O_2 in methane feed, methane conversion decreases by 40.1% of its initial value (17.59%) and the corresponding selectivity to aromatics decrease slightly from 85.29% to 63.25% within 360-min time on stream. In the non-oxidative condition, the reduction of methane conversion is 81.75% of its initial value (15.46%) accompanied by a rapid decline of aromatic selectivity from 75.94% to 16.27% after 360 min of reaction. On the contrary, the C_2-hydrocarbons increase with increasing time on stream from 3.67 to 11.74% for the oxidative condition. In the absence of oxygen, C_2-hydrocarbons, initially increase, then decrease with increasing time which is probably due to the deposition of coke leading to diminishing C_2 hydrocarbons selectivity.

3.2. *Correlation between activity and characterization of supported W catalysts*

The different activities and stabilities exhibited by a series of the 3% W-based catalysts with different supports in the DHAM suggest that the physico-chemical properties of the catalyst support affect the performance of the catalysts. HZSM-5 possesses two-dimensional pore structure with a 10-membered ring. Its pore system consists of a straight channel with pore diameter of 5.3 × 5.6 Å. Hβ has a two-dimensional pore structure which consists of 12-membered rings with diameter of 7.6 × 6.4 whilst USY is a large-pore zeolite, with a three-dimensional straight channel with supercage pore system [15].

The BET surface area and micropore volume of supported W-based catalysts are given in table 1. It can be seen that the BET surface area decrease in the following order W/USY > W/Hβ > W/HZSM-5 > WAl_2O_3 while the micropore volume of the catalysts decrease in the sequence of W/USY > W/Hβ > WAl_2O_3 > W/HZSM-5. The BET surface area and micropore volume of the 3% W/HZSM-5 catalyst is slightly larger than the 3% W-H_2SO_4/HZSM-5 catalyst. The results may be attributed to the difference in the nature of W species present over the catalysts as a consequence of the acidic treatment used for the impregnation method.

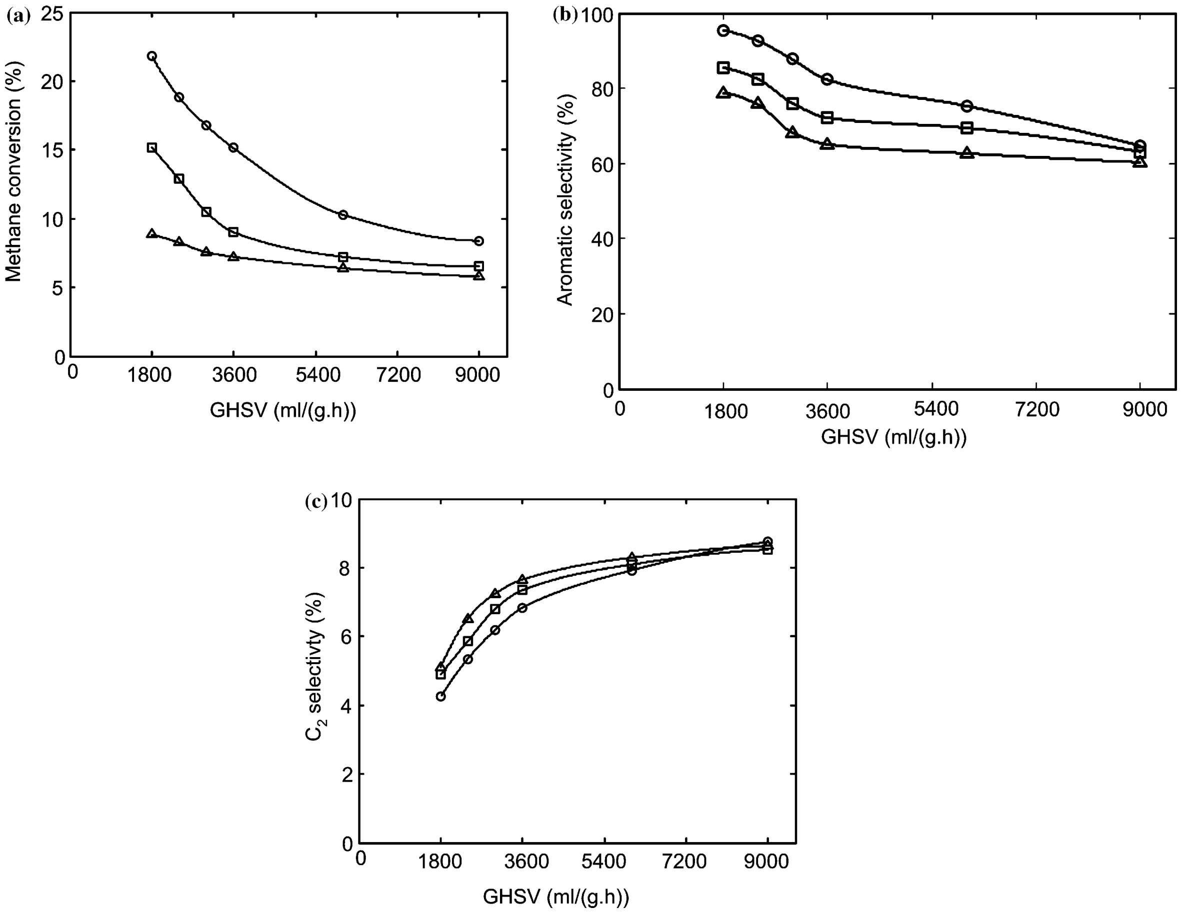

Figure 3. Effect of GHSV on : (A) methane conversion (B) aromatics selectivity and (C) C_2 hydroacrbons. Catalysts: (○) W-H_2SO_4/HZSM-5 (Si/Al = 30); (□) W-H_2SO_4/HZSM-5 (Si/Al = 50); (△) W-H_2SO_4/HZSM-5 (Si/Al = 80). Reaction conditions: 1073 K, feed gas: CH_4 + N_2, 1 atm, The data taken at 1 h after the reaction start.

Meanwhile, the BET surface area and micropore volume do not change significantly with increasing Si/Al ratio.

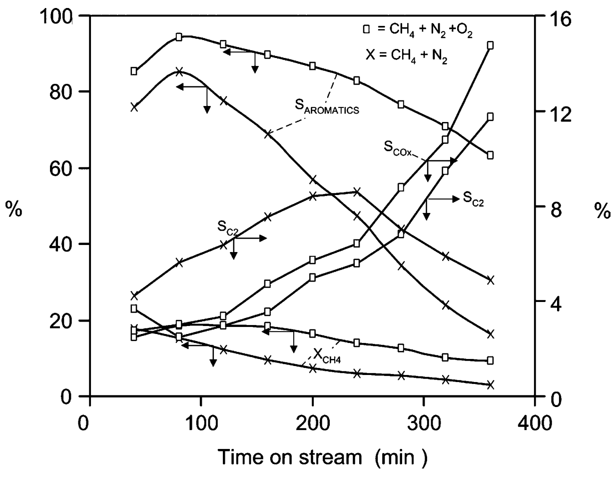

Figure 4. Comparison between oxidative and non-oxidative of DHAM reaction over 3% W-H_2SO_4/HZSM-5. (Si/Al = 30) at 1073 K, GHSV = 3000 ml/(g.h), 1 atm.

The performances of the W/USY, W/HZSM-5, and W/Hβ catalysts all prepared with neutral impregnation solution are slightly different at the initial stage of the reaction. Among them, the activities of the W/HZSM-5 and W/Hβ are relatively more stable with time on stream than W/USY. Moreover, HZSM-5 was found to be the best support as evident from the highest activity displayed while USY relatively had the lowest stability. The high activity of a catalyst may be related to its pore diameter which is shape selective to the diameter of a

Table 1

BET surface areas and micropore volumes of W supported catalysts

Catalyst	BET surface area (m^2/g)	Micropore volume (cm^3/g)
W/Hβ	484	0.319
W/USY	611	0.596
W/Al_2O_3	124	0.283
W/HZSM-5	363	0.232
W-H_2SO_4/HZSM-5 (Si/Al = 30)	321	0.195
W-H_2SO_4/HZSM-5 (Si/Al = 50)	356	0.201
W-H_2SO_4/HZSM-5 (Si/Al = 80)	358	0.186

benzene molecule. In contrast, a catalyst exhibiting relatively low performance is associated to aromatics-type carbon condensed ring deposited on the catalyst surface. The carbon is easily formed over the large pore zeolite which has three-dimensional structure and cages such as USY. Therefore, the channel is blocked rapidly leading to low aromatics selectivity [15]. This is evident from the aromatics selectivity results over the W/USY catalyst which is shown to decrease significantly whereas the C_2-hydrocarbons selectivity increased rapidly with time on stream. The lowest aromatics selectivity is displayed over the W/Al_2O_3 catalyst. If the acidified effect of W/HZSM-5 is not considered, the highest C_2 hydrocarbons selectivity is exhibited over the W/Al_2O_3 catalyst indicating that Al_2O_3 is less selective toward aromatics molecule.

The relationship between the acidity of the supports and the activity of the catalysts for DHAM is investigated further. The amount and the strength of the catalysts acidity were determined by means of TPD-ammonia. The number of acid sites of the supports and W supported on HZSM-5 catalysts are given in table 2, while the NH_3-TPD curves of the catalysts supports, i.e. USY, Hβ, HZSM-5 (Si/Al = 30), and Al_2O_3 are shown in figure 5. The amount of desorbed ammonia and desorption temperature are directly associated to the amount and strength of catalyst acidity, respectively. The NH_3-TPD curve of HZSM-5, exhibits two separate peaks at 523 K and 743 K which are attributed to weak and strong acid sites. The existence of the peaks has been reported for the acid characterization of HZSM-5 by the NH_3-TPD method [16,17]. Unlike HZSM-5, the

Table 2

The amount of NH_3 desorption and total number of acid sites of the various catalysts supports and W-supported HZSM-5 catalysts. Peak L (weak acidity) at T ~ 523 K; Peak H (strong acidity) at T ~ 743 K

Catalyst	Amount of NH_3-desorbed (mmol/g cat)		Total number of acid sites (mmol/g cat)
	Peak L	Peak H	
Hβ	1.311 *(L + M)	–	1.311
USY	2.329** (L + M)	–	2.329
Al_2O_3	0.348	–	0.348
HZSM-5	0.844	0.407	1.251
W/HZSM-5 (Si/Al = 30)	0.698	0.363	1.062
$W-H_2SO_4$/HZSM-5 (Si/Al = 30)	0.614	0.240	0.854
$W-H_2SO_4$/HZSM-5 (Si/Al = 50)	0.561	0.127	0.687
$W-H_2SO_4$/HZSM-5 (Si/Al = 80)	0.356	0.111	0.467

*(L + M) = Peak L (weak acidity) at T ~523 K and peak M (medium acidity) at T ~ 623 K.
**(L + M) = Peak L (weak acidity) at T ~523 K and peak M (medium acidity) at T ~653 K.

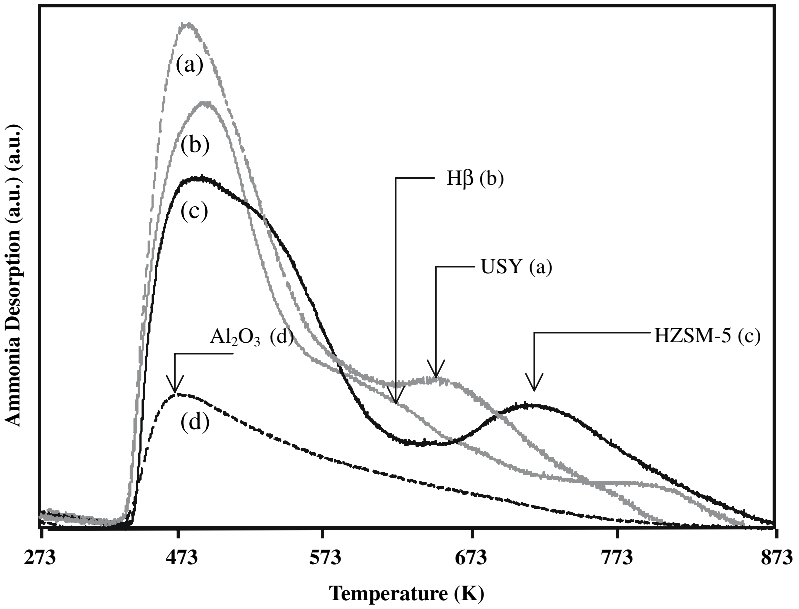

Figure 5. Ammonia-TPD profile of catalyst supports used in the present study: (a) USY (b) Hβ (c) HZSM-5 (Si/Al = 30) (d) Al_2O_3.

TPD curves of Hβ and USY show a major peak at temperature 523 K and a shoulder peak at temperature around 623 K and 653 K for Hβ and USY, respectively. The major peak at lower temperature can be assigned to weak acidity, while a shoulder peak can be attributed to medium acidity. Both Hβ and USY possess relatively high amount of total acid sites, as presented in table 2. The highest amount of ammonia-desorbed shown on USY zeolite is probably due to its high specific surface area. Meanwhile, the TPD-peak of Al_2O_3 mainly shows at low temperature indicating the absence of medium and strong acid sites and in addition, the results in table 2 confirms the low total number of acid sites. As can be seen that the amount of acid sites on W-H_2SO_4/HZSM-5 catalysts prepared with the addition of H_2SO_4 in the impregnation solution is reduced compared with the W/HZSM-5 catalyst prepared with neutral solution in the impregnation method. The results in table 2 shows that the amount of acid sites on W-H_2SO_4/HZSM-5 decreases with increased in Si/Al ratio.

Based on the activity results, it is found that 3% W-H_2SO_4/HZSM-5 (Si/Al = 30) exhibits a maximum aromatics selectivity which decrease significantly with time on stream as presented in figure 2(B). Moreover, the effect of GHSV ranging from 1800–9000 ml/(g.h) on the activity of 3% W-H_2SO_4/HZSM-5 catalysts with different Si/Al ratios indicates that the maximum activity appears on the catalyst with Si/Al = 30 as shown in figure 3(a), (B) for methane conversion and aromatics selectivity, respectively. It seems that in addition to the pore structures being shape-selective, the strength of the acid sites in the HZSM-5 catalyst also contribute to achieving optimum catalyst activity in DHAM reaction as has been reported by several authors [1–12, 16]. The decrease in aromatic selectivity after reaching a maximum value suggested the event of coke deposition in the catalyst. This fact might be due to the presence of extensive amount of strong Brönsted acid sites in the 3% W-H_2SO_4/HZSM-5 (Si/Al = 30) catalyst. The amount of acid sites on the W-H_2SO_4/HZSM-5 catalysts with different Si/Al ratios are presented in table 2. The data demonstrated that the amount of strong acid sites are dependent substantially on Si/Al ratios of HZSM-5 used. The highest amount of strong acidity is presented over the 3% W-H_2SO_4/HZSM-5 (Si/Al = 30) catalyst. It has been reported that the strong Brönsted acid sites on the catalyst were responsible for the formation of aromatics, however, an excess of the Brönsted acid sites led to severe coke formation [2]. The deactivation of the catalyst yielded the decrease in the selectivity for aromatics, whereas the C_2 selectivity increased markedly as evident from the results illustrated in figure 2B, C, respectively. This result suggests that the coke formation in the catalyst could reduce the amount of Brönsted acid sites and the catalyst pore size which may lead to the suppression of C_2-hydrocarbons oligomerization to form benzene. Meanwhile, a low amount of acid sites and the absence of strong acid sites on W/Al_2O_3 lead to a low DHAM activity. Likewise, figure 3C displays the increase in the C_2 hydrocarbons selectivity with increase in GHSV. Similar result has been reported [6], indicating C_2-species as the primary intermediates which are oligomerized subsequently to aromatics. In order to improve the activity and stability of 3% W/HZSM-5 (Si/Al = 30) catalyst, 2% O_2 was added into the methane feed, in this case GHSV of 3000 ml/(g.h) was applied. The activity of the catalysts enhance significantly with the presence of oxygen in methane feed as can be seen figure 4. The same effects are observed over the Mo/HZSM-5, Re/MCM-22, and W/HZSM-5 catalysts as has been reported by previous authors for DHAM reaction with co-feed such as CO, CO_2, and O_2 in the methane feed [1, 5, 7, 8, 17– 19]. The enhancement of the catalyst activity in the presence of oxidant is due to the partial removal of coke in the catalyst.

The UV-DRS method was performed to investigate the nature of tungsten species in different supports and the results are shown in figure 6. The wavelengths for the supported W species are reported to be at 220 nm, between 250–325 nm, and between 375–400 nm which could be assigned to tetrahedral monomeric tungstate species, octahedral polymeric tungstate species and WO_3 crystallites, respectively [20–22]. As portrayed in figure 6(A), the UV-DRS spectra of W loaded on different supports show a major band at 220 nm and a shoulder at 275 nm for zeolites as supports. In contrast, the W/Al_2O_3catalyst shows a band at 220 nm only and the results are consistent with the work reported for Al_2O_3 supported catalyst [20].

The different behavior exhibited by the W/HZSM-5 and W-H_2SO_4/HZSM-5 (Si/Al = 30) catalyst was probably due to the change in the nature of W species caused by the different preparation conditions employed in the impregnation of W on the HZSM-5. The UV-DRS characterization was carried out to provide the evidence for the existence of different kinds of tungsten species and the result is shown in figure 6(B). The UV-DRS spectrum of W-H_2SO_4/HZSM-5 consists of two major bands at around 220 nm and 310 nm which correspond to the presence of tetrahedral monomeric and octahedral polymeric tungstate species, respectively. Meanwhile, a major band at 220 nm and a shoulder at 275 nm appear on W/HZSM-5 indicating that tetrahedral monomeric tungstate species are predominant while octahedral polymeric tungstate species exist in a minor extent. The addition of H_2SO_4 in the impregnation solution can enhance the formation of polytungstate in the precursor which is in accordance with the work reported by several authors [15, 20–22]. As reported in the literatures, the structure of aqueous tungstate anions exist in two forms: a tetrahedrally coordinated WO_4^{2-} anion and an octahedrally coordinated $W_{12}O_{42}^{12-}$. The equilibrium between these two species is described by :

$$12WO_4^{2-} + 12H^+ \Leftrightarrow W_{12}O_{42}^{12-} + 6H_2O$$

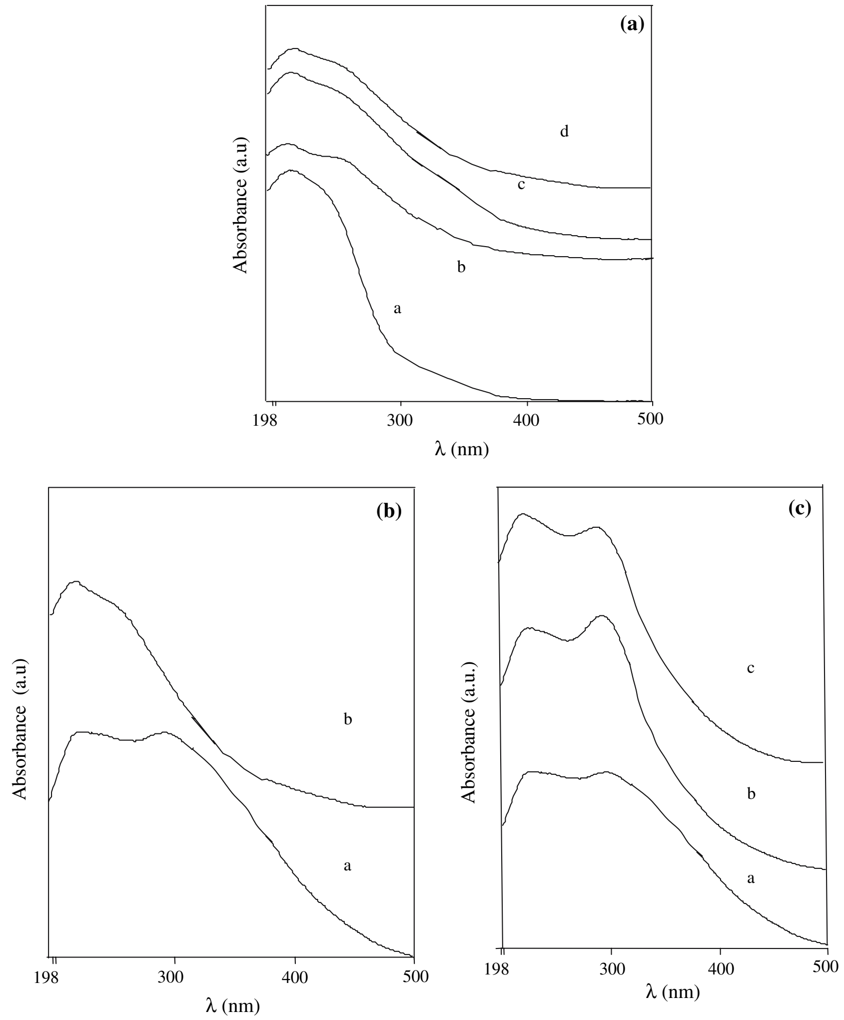

Figure 6. (A) UV-DRS of 3% W-based catalyst on different supports: (a) Al_2O_3; (b) USY; (c) Hβ; (d) HZSM-5 (Si/Al = 30). (B) UV- DRS of (a) 3% W-H_2SO_4/HZSM-5 (Si/Al = 30) and (b) 3% W/HZSM-5 (Si/Al = 30). (C) UV-DRS of 3% W-H_2SO_4/HZSM-5 with different Si/Al ratios: (a) 30; (b) 50; (c) 80.

Based on the reaction above, the polymeric tungstate species is the predominant species in acidic pH due to the shift of equilibrium to the right. In contrast, the tungstate monomer is predominant in the neutral or alkali solution. Thus, the catalyst prepared with the addition of H_2SO_4 in the impregnation solution exhibited considerable amount of polymeric tungstate present in the W-supported catalyst whereas the catalyst prepared in neutral solution had polymeric tungstate in minor amount. The higher activity obtained over the W-H_2SO_4/HZSM-5 catalyst than the W/HZSM-5 catalyst can be attributed to the existence of a considerable amount of octahedral polymeric tungstate species which promote the activity of the W-H_2SO_4/HZSM-5 catalyst. This result seems to be in good agreement with the results reported by Zeng *et al.* [4] who observed that octahedral polymeric tungstate species promoted the reducibility of W-H_2SO_4/HZSM-5 and as a consequence led to a high DHAM activity.

However, the rapid decrease in the methane conversion and aromatic selectivity over W-H_2SO_4/HZSM-5 (Si/Al of HZSM-5 = 30) as appeared in figures 1 and 2 may be attributed to the heavily deposited carbon that covered the acidic and metal active sites which led to the deactivation of the catalyst. Coke deposition also caused a severe drop in the selectivity to aromatics and at the same time the selectivity of C_2 increased substantially. Moreover as shown in figure 1, it was demonstrated that methane conversion and aromatic selectivity over the W-H_2SO_4/HZSM-5 catalyst were higher than that over W/HZSM-5 at the initial reaction stage. However, the activity of the W-H_2SO_4/HZSM-5 catalyst decreased quickly with time on stream.

The effect of Si/Al ratio on the W-H_2SO_4/HZSM-5 catalysts is to elucidate the correlation between the acidity of HZSM-5 and the nature of W species on the catalytic performance of the catalysts. The

NH_3-TPD results reveal that as the Si/Al ratio increases, the amount and the strength of the acid sites on the catalysts decrease which can be seen in table 2. Meanwhile, the UV-DRS spectra demonstrated that all the samples show two kinds of bands at 220 nm and 310 nm associated to tetrahedral monomeric and octahedral polymeric W species respectively as shown in figure 6(c). The increase in Si/Al ratio for HZSM-5 has not affected the monomeric and polymeric concentration ratio of W species as indicated by the A_{220}/A_{310} ratio in figure 7 implying that a considerable amount of active polymeric W species existed over the three catalysts. However, the results of the activity testing shown in figures 2 and 3 indicate that as the Si/Al ratio increases, the acidic strength weakens and the activity of the catalyst decreases. The same observation was confirmed in a previous study that correlated the activity of benzene formation in methane aromatization with the Brönsted acid sites for the Mo/HZSM-5 catalyst [10]. It was found that benzene formation on the Mo/HZSM-5 is substantially dependent on the SiO_2/Al_2O_3 ratios of the HZSM-5 used. Among the Mo/HZSM-5 catalysts series, the one having SiO_2/Al_2O_3 ratio between 30–45 contains maximum Brönsted acid sites and corresponds to maximum benzene formation.

This results of the activity testing for the catalysts with different Si/Al ratios indicate that the activity of W-H_2SO_4/HZSM-5 catalysts is not only affected by the existence of octahedral polymeric W species, but also by the catalyst acidity. Moreover, the result concludes that the optimum activity of W-based catalysts for DHAM are dependent on the balanced amount between the two active sites in the catalyst, i.e. acidity and existence of octahedral polymeric and tetrahedral monomeric tungstate species.

4. Conclusions

Dehydroaromatiztion of methane (DHAM) was studied over a series of 3 wt% W-based catalysts prepared with different supports (HZSM-5, USY, Hβ, and Al_2O_3), under different preparation conditions and a variety of Si/Al ratios. HZSM-5 catalyst was found to be the best catalyst support. The W-H_2SO_4/HZSM-5 catalyst prepared by acid treatment emerged as the most promising catalyst. The catalyst exhibited the maximum catalytic activity which is higher than that over W/HZSM-5 prepared by impregnating the HZSM-5 precursor with a neutral solution of ammonium tungstate. Further investigation on the activity of W-H_2SO_4/HZSM-5 with different Si/Al ratios revealed that W-H_2SO_4/HZSM 5 catalyst with Si/Al = 30 showed an optimum methane conversion and aromatic s electivity. However, a significant decrease in the activity of the 3%W-H_2SO_4/HZSM-5 (Si/Al = 30) catalyst was observed with increasing time on stream and GHSV suggesting the deposition of coke in the catalyst. The activity and stability of 3 % W-H_2SO_4/HZSM-5 (Si/Al = 30) catalyst improved after introducing 2% O_2 into the methane feed. The relationship between the activity and the characteristics of the catalyst indicated that suitable content of octahedral polymeric and tetrahedral monomeric tungstate species accompanied by proper amount and strength of acid sites in the catalyst contributed to the highest catalytic performance for DHAM.

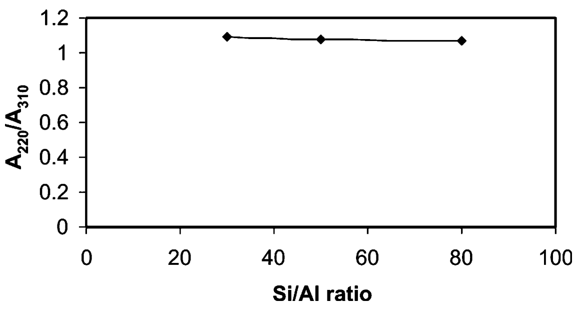

Figure 7. Effect of Si/Al ratio of HZSM-5 on A_{220} and A_{310} ratio attributed to monomeric and polymeric concentration of tungsten species.

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