

Cu/W/HZSM-5 for METHANE CONVERSION TO LIQUID HYDROCARBONS

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Abstract

The direct conversion of natural gas, and in particular, the principal component, methane, to useful products has been intensely studied over the past decades. ZSM-5 zeolite has been known to be a suitable catalyst for olefin oligomerization, but it is not resistant to high temperatures. In this work, HZSM-5 was modified with copper and tungsten to develop a highly active and heat resistant bifunctional oxidative-acid catalyst. The performances of Cu modified W/HZSM-5 were compared with HZSM-5 for the oxidation of methane to liquid hydrocarbons. The characterization results revealed that the addition of tungsten to HZSM-5 zeolite improved its thermal stability. Response Surface Methodology (RSM) was employed to determine the optimum methane conversion and C₅⁺ selectivity. Numerical results indicated the optimum methane conversion of 29.4 % with the corresponding C₅⁺ selectivity of 57.2% were achieved at 12.3 vol.% of O₂, 203.9 ml/min of total feed flow rate, and % W doped of 3.2 wt.%. The optimum C₅⁺ selectivity of 70.2 % was attained at 7.6 vol.% of O₂, 208.9 ml/min of total feed flow rate, and 3.2 wt.% of W content with the corresponding methane conversion of 26.7%. By means of variance analysis and additional experiments, the adequacy of this model was confirmed.

Keywords

Methane conversion; Tungsten; Copper; HZSM-5; Liquid Hydrocarbons

Introduction

Crude oil is a non-renewable resource and cannot be solely relied as the feedstock or energy source in future. New natural gas deposits are being continuously discovered; hence, natural gas is a new potential resource. Methane, the largest component of natural gas, can be converted to valuable liquid fuels or other important chemical intermediates. In general, there are two routes for converting methane to gasoline: indirectly or/and directly. The indirect route is a two-step process whereby natural gas is first converted into synthesis gas (a mixture of hydrogen and carbon monoxide), and then into gasoline range. The direct route is the one step process in which the natural gas reacts

with oxygen (or another oxidizing species) to give the desired product directly.

Zeolites are unique materials. Unlike other catalysts, zeolites possess active sites on intracrystalline surface crystallographically. For each particular zeolite structure the acidity per active site reached a maximum value at a particular Si/Al ratio, which will determine the acidic strength of the zeolite. Ernst and Weitkamp [1] reported the presence of strong acid sites in the zeolite catalyst was detrimental for the selective oxidation of methane to higher hydrocarbons; otherwise oxidized products, CO_x (carbon monoxide and carbon dioxide) predominate. When the acidity is reduced by exchanging the zeolite with alkali metal cations, the selectivity to higher hydrocarbons is slightly enhanced. Han et al. [2] demonstrated the successful production of higher hydrocarbons from methane oxidation using ZSM-5 zeolite catalyst loaded with metal oxides. The metal oxides with sufficiently high dehydrogenation and low olefin oxidation activities reduce the acidity of ZSM-5 resulting in higher hydrocarbons production.

The incorporation of two different metals could create materials with well-defined or new catalytic and acidic properties. One recent study has revealed that acidic and catalytic properties of these materials depended on the location and surroundings of the metal ions [3]. De Lucas et al. [4-6] discovered that the introduction of Cu (II) ions by an ion-exchange method could remarkably increase the activity of Mo/HZSM-5 for methane aromatization and improved its stability to some extent. Mo species is the most active component for methane non-oxidative aromatization so far, but its activity and stability need to be improved.

Molybdenum supported on H-ZSM-5, is active and selective for benzene formation from methane [7-9]. It was clearly established that at high temperature molybdenum in Mo/HZSM-5 was reduced and formed Mo₂C species [10]. Further, during the activation process of Mo/HZSM-5, molybdenum species migrated towards exchangeable sites in the zeolite framework [10,11]. It is generally reported that the activation of methane occurred on molybdenum active species forming ethylene as the primary intermediate before being converted into benzene. By using pure methane feed, it was found that methane conversion and rates of benzene formation drastically decreased for a few hours owing to

significant coke formation. To reduce coke formation, some preliminary efforts have been made to add selected oxidative reagents such as oxygen and carbon dioxide (10% or higher) to the methane gas feed, but the aromatic product formation was completely inhibited on Mo/HZSM-5 catalyst as reported previously [12,13].

On the basis of the chemical similarities between MoO₃ and WO₃ it seems reasonable to expect a parallelism in their catalytic properties. Ding et al. [14] reported the non-oxidative methane reaction over W/HZSM-5 produced C₂-C₁₂ hydrocarbons. Under condition of 700°C, and a flow rate of methane + argon at 12.5 cm³/min, the C₂-C₁₂ hydrocarbons selectivity was 70-80%. However, methane conversion was small, between 2% and 3%.

Tungsten and Mo are under the same group in the periodic table of the elements (VI B), and hence the chemical properties of oxides or carbides of W and Mo are similar. Therefore, the structural and catalytic resemblance between W and Mo-HZSM-5 is expected. Xiong et al. [15,16] studied the incorporation of metals Zn, Mg, Mn, La, and Zr into the W/HZSM-5 catalyst. The W/HZSM-5 based catalyst was suitable for reaction temperatures as high as 800°C to obtain a much higher methane conversion and yields of aromatic hydrocarbon without loss of W component [15]. They confirmed that the intensity and concentration of Brønsted acid sites have affected the catalyst activity for ethylene selectivity and the rate of aromatization of ethylene [16]. The incorporation of Mg²⁺ and Zn²⁺ into the W/HZSM-5 resulted in the elimination of a large portion of strong Brønsted acid sites, but new medium strength Brønsted acid sites emerged. The medium strength Brønsted acid sites enhanced the benzene selectivity and suppressed coke formation, thus prolonging the lifetime of the catalyst.

Cu loaded ZSM-5 catalyst via acidic ion exchange method has been identified to be the potential catalyst for conversion of methane to liquid fuels [17,18]. However, the infrared study of metal loaded ZSM-5 catalyst indicated that the catalysts are not resistant to high temperatures. At 800°C one study has indicated that metal loaded ZSM-5 did not exhibit vibration bands at 3610 cm⁻¹ and 3660 cm⁻¹, but ZSM-5 showed a weak vibration band at 3666 cm⁻¹ (ascribed to OH groups on non-framework Al species) [18]. The result suggested that the framework and non-framework aluminum were either extracted to acidic solution or became silanol defect form when calcined at 800°C and made the catalysts inactive.

Response Surface Methodology (RSM) is a method to determine the optimum condition of a process. RSM has similarity with regression analysis. In regression analysis, empirical mathematical model are derived from the experimental data. RSM is a set of technique designed to

find the optimum value of the response and the influencing factors.

In this paper HZSM-5 was modified with tungsten and copper and the catalyst performance was tested for the oxidation of methane to liquid hydrocarbons (C₅⁺). The roles of W and Cu, the Brønsted acid sites, and catalytic activity will be studied by means of hydrogen-TPR, ammonia-TPD, FTIR, nitrogen adsorption (NA) and methane oxidation. The optimization of the direct conversion of methane using 3.0Cu loaded W/ZSM-5 catalyst was studied to obtain maximum methane conversion and C₅⁺ selectivity by utilizing experimental design and empirical modeling.

Experiment

Catalyst Preparation

ZSM-5 zeolite with a SiO₂/Al₂O₃ mole ratio of 30 was supplied from Zeolyst International Co. Ltd, Netherlands. The surface area of the zeolite was 400 m²/g. Cu (3% weight)-HZSM-5 catalyst was prepared by impregnating a certain amount of the HZSM-5 zeolite carrier with copper nitrate solution. The copper nitrate solution was prepared by dissolving copper nitrate hydrate (Cu(NO₃)₂·3H₂O) in deionized water and adding a small amount of H₂SO₄ to regulate the pH value of the solution to 2-3. The sample (10 ml of solution per gram zeolite) was dried in an oven at 120°C for two hours and then calcined at 500°C for four hours.

The 3.0 wt.% of Cu loaded W/HZSM-5 was prepared by first impregnating a certain amount of the HZSM-5 zeolite carrier with a calculated amount of tungsten hydrate in aqueous solutions. The tungsten hydrate solution was prepared by dissolving ammonium tungsten hydrate ((NH₄)₆W₁₂O₄₀·H₂O) in deionized water and adding a small amount of H₂SO₄ to regulate the pH value of the solution to 2-3, followed by drying at 120°C for two hours and calcining at 400°C for four hours, and subsequently impregnating with a calculated amount of H₂SO₄ acidified copper nitrate aqueous solution (pH= 2-3). Finally, the sample was dried at 120°C for two hours and calcined at 500°C in air for five hours.

Characterization and Catalyst Testing

The catalysts were characterized by XRD, hydrogen-TPR, ammonia-TPD, FTIR and nitrogen adsorption. The performance of the catalysts was tested for methane conversion to liquid hydrocarbons (LHC) via a single step reaction in a fixed-bed micro reactor-GC combination system under reaction condition at atmospheric pressure and 800°C. The feed gas was composed of methane (99.9% purity) and oxygen. An on-line Gas Chromatography equipped with TCD and Porapak-N column was utilized to analyze the gas. The liquid products were analyzed using GC FID and HP-1 capillary column.

Methane conversion and C₅⁺ hydrocarbons selectivity were calculated, based on equations (1) and (2), respectively.

$$CH_4 \text{ conv.} = \frac{\text{mole of } CH_4 \text{ (in)} - \text{mole of } CH_4 \text{ (out)}}{\text{mole of } CH_4 \text{ (in)}} \times 100\% \quad (1)$$

$$\text{Product(i)Select.} = \frac{\text{mole of Product (i)}}{\text{mole of } CH_4 \text{(in)} - \text{mole of } CH_4 \text{(out)}} \times 100\% \quad (2)$$

where i = CO, CO₂, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₅⁺, and H₂O.

Results and Discussions

Optimization of Methane Conversion by Regression Analysis

The application of response surface methodology produced the following regression equation, which is an empirical relationship between methane conversion and the test variable in coded unit given in Eq. (3).

$$Y = -28.54597 + 9.5251 x_1 + 4.4146 x_2 + 0.1549 x_3 - 0.0500 x_1 x_2 - 0.0042 x_1 x_3 - 0.0003 x_2 x_3 - 1.2751 x_1^2 - 0.1713 x_2^2 - 0.0003 x_3^2 \quad (3)$$

The goodness of the fitting of the model can be checked by several criteria. Table 1 shows the Analysis of Variance (ANOVA) for the model that corresponds to methane conversion. The value of coefficient R² = 0.940 indicates that only 6% of total variation is not explained by the model. The value of F is compared to the table value F_(p-1, N-p, α), which is the upper 100 α percent point of the F distribution, with p-1 and N-p degrees of freedom, respectively. The adequacy of the fitted model from Eq. (3) is tested using static F. Since F value at 10.4633 exceeded the table value F_(9,6,0.1) = 7.9761, the Fisher F test demonstrated a high significance for the fitted regressions model.

Table 1- ANOVA for the methane conversion

Source	Sum of squares	Degree of freedom	Mean Square	F Value	F 0.01	R ²
S.S. Regression	430.508	9	47.834	10.4632	7.9761	0.94
S.S. Error	27.430	6	4.572			
S.S. Total	457.938	15				

From Figure 1 (Pareto Chart), the most significant parameters are clearly the % vol of O₂ (X₂) and its quadratic effect (X₂X₂). The quadratic of total flow of feed gases (X₃) and quadratic of % wt of W (X₁) are significant but less important. The % wt of W and total flow of feed gases actually appear low, as well as the interactions % wt of W-total flow (X₁X₃) and % wt of W-% vol of O₂ (X₁X₂). The interaction of % vol of O₂ - total flow of feed (X₂X₃) was insignificant.

Optimisation of C₅⁺ Selectivity by Regression Analysis

The application of response surface methodology yielded the following regression equation, which is an empirical relationship between C₅⁺ selectivity and the test variable in coded unit given in Eq. (4).

$$Y = -67.0195 + 32.0514 x_1 + 8.1699 x_2 + 0.5304 x_3 - 0.0833 x_1 x_2 - 0.0008 x_1 x_3 - 0.0012 x_2 x_3 - 5.1206 x_1^2 - 0.5386 x_2^2 - 0.0012 x_3^2 \quad (4)$$

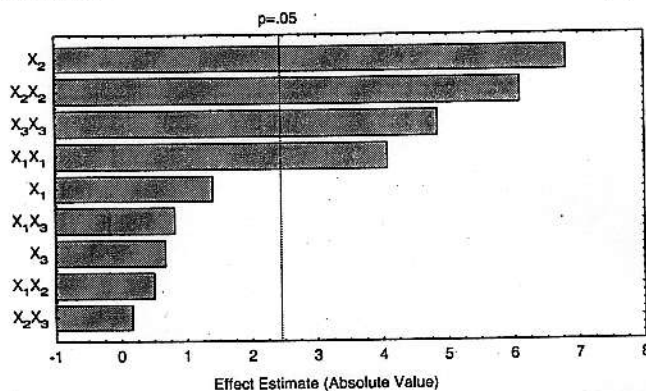


Figure 1 - Pareto chart of standardized effects of methane conversion

Table 2 shows the Analysis of Variance (ANOVA) for the model that explains the response of the C₅⁺ selectivity. The Analysis of Variance (ANOVA) for the model explains the response of the C₅⁺ selectivity. The coefficient R² = 0.95 indicates that only 5% of total variation is not explained by the model. The value of F is compared to the table value F_(p-1, N-p, α), which is the upper 100 α percent point of the F distribution, with p-1 and N-p degrees of freedom, respectively. Since the value F = 11.5647 exceeded the table value F_(9,6,0.1) = 7.9761, the Fisher F test also demonstrated its high significance for the fitted regressions model.

Table 2- ANOVA for the C₅⁺ selectivity

Source	Sum of square	Degree of freedom	Mean Square	F Value	F0.01	R ₂
S.S. Regression	4866.406	9	540.712	11.564 72	7.9761	0.95
S.S. Error	280.532	6	46.755			
S.S. Total	5146.938	15				

The results in Table 3 pertain to the catalytic reaction test at the optimized reaction condition when compared with the modeling result. The experimental values are 27% and 69% for CH₄ conversion and C₅⁺ selectivity, respectively. The results in Table 3 also indicated that to achieve a high C₅⁺ selectivity the percentage of O₂ in the feed gas is very critical; otherwise the oligomerization activity will be suppressed. Meanwhile the % error between the predicted and experimental results for CH₄ conversion and C₅⁺ selectivity are 8% and 2 %, respectively. The discrepancies between the predicted and experimental results are probably due to the characteristic of the catalysts which have not been taken into account by the statistical model. Nevertheless, the differences are within the acceptable limit. From these results, it is verified that the statistical model is useful for the accurate prediction of C₅⁺ selectivity and CH₄ conversion.

Table 3 - Comparison between predicted and observed optimized values

	W doped (%)	O ₂ (% vol)	Total flow of feed	Pred.	Obs.	% Error
CH ₄ conv.	3.2	12.3	203.9	29.4%	27.0%	8.0%
C ₅ ⁺ select.	3.2	7.6	208.9	70.2%	69.0%	2.0%

Note: Pred. = predicted; Obs. = observed

The composition of liquid fuels and RON over 3.0Cu/3.2W/ZSM-5 catalyst is shown in Table 4. The Research Octane Number (RON) was estimated [19] to be 86.1. The gasoline composition has a low n-paraffin and high aromatics content, at 9% and 17%, respectively while the majority is olefins at 52% as indicated in Table 4.

Table 4 - The RON and composition of liquid fuels over 3.0Cu loaded 3.2W/ZSM-5 catalyst

Composition of Liquid Fuels	%
Gasoline range (C ₅₋₁₀)	82.8
C ₁₁ ⁺ range	18.2
Composition of Gasoline range	
n-Paraffins	9.0
Iso-Paraffins	22.0
Olefins	52.0
Aromatics	17.0
RON	86.1

Characterization of 3.0Cu/3.2W/HZSM-5 Catalyst

The isotherm adsorption of 3.0Cu/3.2W/ZSM-5-Fresh and 3.0Cu/3.2W/ZSM-5-Used, as shown in Figure 2 as an example, is a combination of types I and IV. The presence of hysteresis loop was associated with capillary condensation, where in the case of zeolite, it indicated the formation of mesopores. The profile for 3.0Cu/3.2W/ZSM-5-Used indicated enlargement of some micropores resulting in more mesopores being formed.

The ammonia-TPD spectra of the catalyst provided useful information about the intensity and the concentration of the acid sites on the catalysts surface as tabulated in Table 5. The concentration of the surface acid sites (acidity) of the ZSM-5 and 3.0Cu/3.2W/HZSM-5-Fresh zeolite were the same. The acidity of 3.0Cu/3.2W/HZSM-5-Used was undetected (~ 0) because the aluminium in the framework was probably extracted. after reaction at 752°C for a period of five hours.

Table 5 - Total volume, pore distribution and acidity of the catalysts

Catalysts	Av. Pore Diam. (Å)	Acidity (mol/kg)
HZSM-5	24.3	0.87
3.0Cu/3.2W/HZSM-5 - Fresh	26.1	0.87
3.0Cu/3.2W/HZSM-5 - Used	45.2	0

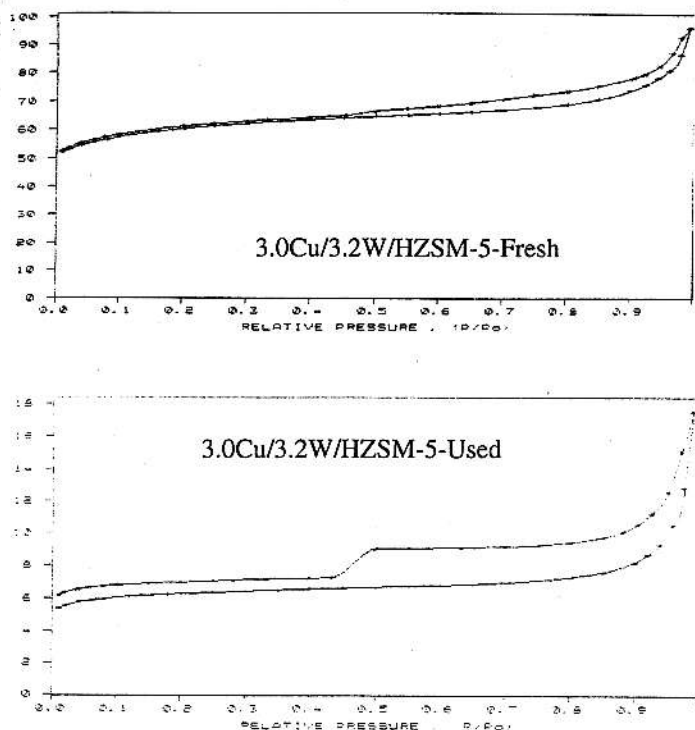


Figure 2 - The diagrams isotherm adsorption of catalysts

Figure 3 depicts the ammonia-TPD spectra of the HZSM-5 and modified HZSM-5 with loading of W and Cu. For the HZSM-5, the ammonia-TPD peaks appeared at $\sim 237^\circ\text{C}$ and $\sim 430^\circ\text{C}$, which may be ascribed to the desorption of two kinds of ammonia species adsorbed on weak acid (mostly Lewis acid) sites and strong acid (mostly Brönsted acid) sites, respectively [20].

The addition of 3.2% W and 3.0% Cu to HZSM-5 led to the reduced intensity of the high temperature ($\sim 430^\circ\text{C}$) peak and a small downshift of its position as revealed in Figure 3. This is similar to the results found by previous researchers [15,16], where the incorporation of Mg^{2+} and Zn^{2+} into the W/HZSM-5 host catalyst resulted in the elimination of strong surface Brönsted acid sites. For the 3.0%Cu/3.2W/HZSM-5-Used, the ammonia-TPD peaks disappeared at $\sim 237^\circ\text{C}$ and $\sim 430^\circ\text{C}$. This indicated that after reaction, the acid sites of the 3.0%Cu/3.2W/HZSM-5 had weakened.

Cu and W loaded HZSM-5 samples showed that in the OH stretching vibration three IR bands at $\approx 3610\text{ cm}^{-1}$, due to bridge Si-OH (Al) acidic groups, at $\approx 3660\text{ cm}^{-1}$ due to non-framework Al sites, or octahedral, and at $\approx 3740\text{ cm}^{-1}$, attributed to terminal Si-OH non-acidic groups [21].

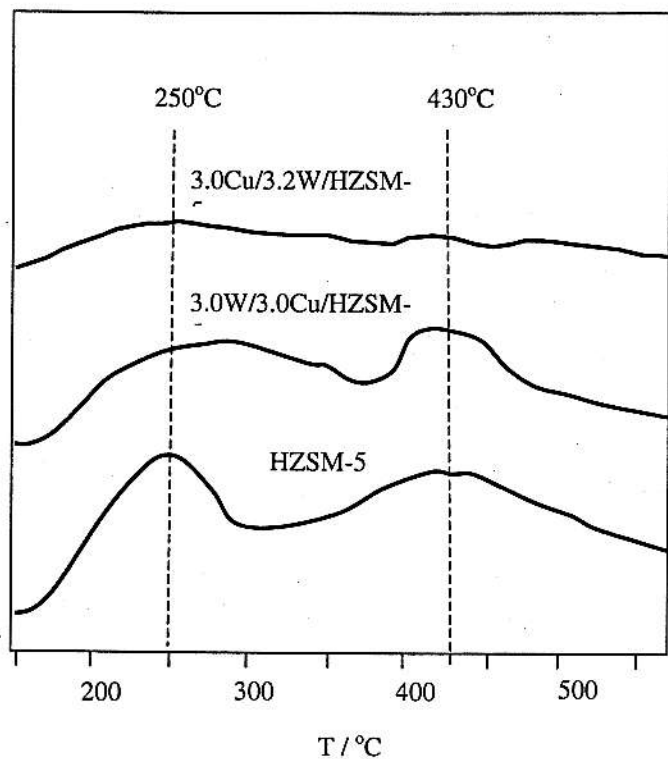


Figure 3 - Ammonia TPD spectra of samples

Further reaction with methane and oxygen at 753°C for five hours resulted in the disappearance of the band at $\approx 3,610\text{ cm}^{-1}$ for 3.0Cu/3.2W/HZSM-5-used sample. This is probably due to the extraction of aluminum in the zeolitic framework into the non-framework or due to the deposition of carbonaceous residues. The deposition of the coke led to catalyst deactivation after five hours of reaction.

The H_2 -TPR profiles of 3.0W/3.0Cu/HZSM-5, 3.0Cu/3.2W/HZSM-5 for fresh and used samples are depicted in Figure 4. As observed, all the curves contain several peaks in the temperature range of 200-900°C. The TPR patterns of both catalysts exhibited two peaks with the maximum at $\approx 800^\circ\text{C}$ which could be due to the reduction of W species. The reducibility of this type of catalyst decreased as the strength of the interaction between the metal oxide species and the surface of the support increased.

The observed hydrogen-TPR peak at $\approx 400^\circ\text{C}$ for 3.0Cu/3.2W/HZSM-5-fresh could be due to the reduction of Cu^{2+} species. The spectra demonstrated the existence of a single reduction peak of Cu^{1+} to Cu^0 at 420°C . However, after reaction at 800°C the peak disappeared. One interesting feature of Figure 4 is the H_2 -TPR spectra of 3.0Cu/3.2W/HZSM-5-used which indicated a peak at 340°C (Figure 4). This small peak may be attributed to the reduction of Cu^{2+} to Cu^{1+} . Nevertheless, the peak of W^{n+} did not change before and after the reaction. The TPR profile for tungsten revealed that the addition of tungsten had increased

the thermal stability of the catalyst, as the W component was not lost by sublimation after reaction at 753°C.

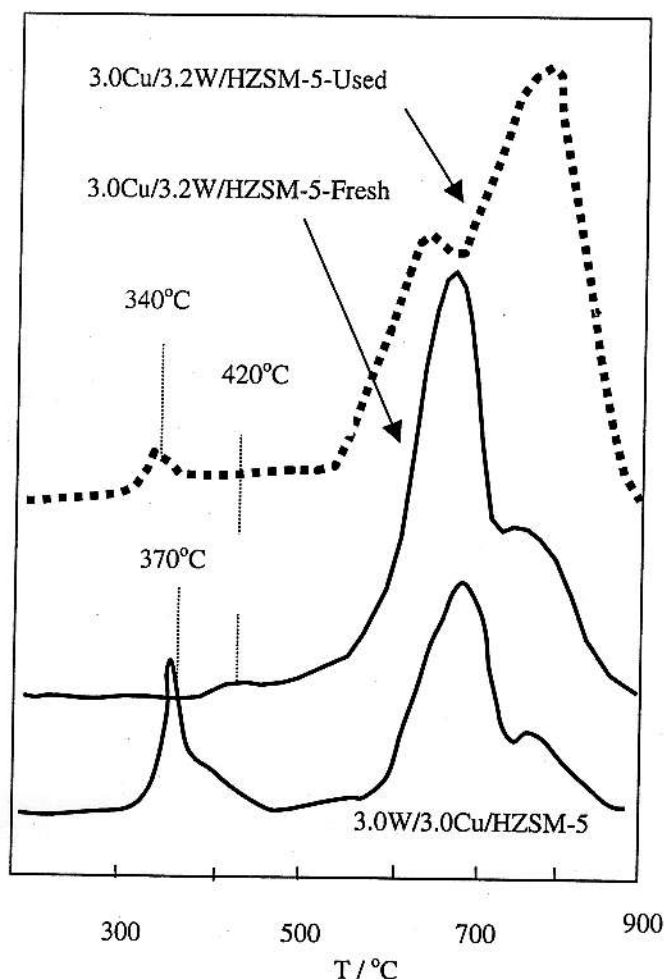


Figure 4 - Hydrogen-TPR spectra of samples

Conclusions

The direct conversion of methane was optimized over Cu-W/ZSM-5 catalyst using 'Statsoft Statistica' version 6.0 software. The three independent variables involved in the optimisation are %wt. of W-doped, %vol. of O₂, and total flow of feed gases. The Pareto chart indicated that the variable with the largest effect was % vol. of O₂ (X₂) and its quadratic effect (X₂X₂). This is followed by flow total of feed gases (X₃), % wt. of W doped (X₁) and its quadratic effects (X₃X₃ and X₁X₁). The interactions between any two of the independent variables can be neglected. From the RSM results the optimal methane conversion, C₅⁺ selectivity, and C₅⁺ yield of 29.4%, 70.2%, and 20.6%, respectively were obtained. The adequacy of this model was confirmed by means of variance analysis and additional experiment.

From the characterization studies, the 3.0Cu/3.2W/HZSM-5 had more potential to catalyze the methane oxidation

reaction to form liquid fuels. The advantages of 3.0Cu/3.2W/HZSM-5 included higher crystallinity, higher amount of Brönsted acid sites and medium strength of Brönsted acid sites. TPR analysis indicated that the resistance of HZSM-5 towards temperature was enhanced by loading W and the high reaction temperature (753°C) did not lead to the loss of W component by sublimation. 3.0Cu/3.2W/HZSM-5 catalyst is a potential catalyst, because under optimum conditions high methane conversion (27%) and C₅⁺ selectivity (69%) were obtained.

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