

**Catalytic Conversion of Methanol on Metal Supported FSM-16
(Fe, Cu, Ag/FSM-16)**

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ABSTRACT

Pure SiO₂ having a FSM-16 structure was modified by the introduction of iron, copper and silver with 3, 6 and 9 wt% metal for each. The performances on methanol conversion for the prepared catalysts (Fe, Cu, and Ag/FSM-16) were different according to the properties of metals. The formation of formaldehyde is more pronounced than ethylene. Catalyst sample containing 3%Ag is more active with 100% selectivity toward methanol dehydrogenation. Methanol dehydrogenation to formaldehyde is an endothermic reaction and thermodynamically feasible. The obtained regression equations are adequate to the catalytic activity of the catalysts under investigation. The kinetic behavior for the methanol conversion was studied.

Keywords: Methanol conversion; Thermodynamic feasibility; Fe, Cu, Ag/FSM-16 catalysts; kinetic behavior.

INTRODUCTION

Mesoporous molecular sieves with a hexagonal array FSM-16 and tubular MCM-41 structures are of interest as silica based supports because of their larger surface area and pore diameter than conventional high-silica zeolites [1–8]. FSM-16 material has high thermal and hydrothermal stability than MCM-41 [9].

Methanol has been considered as a building block in the synthesis of various chemicals. Recently, the importance of methanol is stressed as one candidate for storage and transportation of hydrogen [10]. Formaldehyde [11] and methyl format [12] can be prepared by methanol dehydrogenation with production of hydrogen.

On the other hand, various mechanisms for the conversion of methanol to gasoline (dehydration of methanol to light olefins as ethylene and bond chain polymerization of olefins and isomerization) have been reported and established [13–15].

Cobalt oxide supported on FSM-16 catalysts [16] and chromium oxide loaded over montmorillonite K10 catalysts [17] are active for methanol dehydrogenation to formaldehyde for the catalysts containing low percent of cobalt and chromium (3 wt%) and efficient for methanol dehydration to ethylene for samples containing high metal percent (9wt % Co and 18 wt %Cr). The selectivity of ethylene formation is greatly affected by the acid-base properties of the support [18, 19], the density of the active sites and the metal oxidation state [17].

T. Tsoncheva et al. [20] suggested that MCM-41 silica modified with copper and iron oxide is useful as a catalyst for methanol decomposition to obtain alternative effective and ecological fuels for vehicles, fuel cells and gas turbines.

The activity of the partially oxidized silver surface was enhanced by the interaction of hydroxyl end of methanol molecules with the adsorbed surface oxygen atoms to form adsorbed CH_3O (methoxide). The methoxy surface species then decompose to form formaldehyde and hydrogen, or recombined with surface hydrogen to form methanol or interacted with surface formaldehyde to yield methyl format. CO_2 could be formed through further oxidation of formaldehyde through a format intermediate. The overall process is regarded as a combination of partial oxidation and dehydrogenation of methanol [21, 22]. The total reaction is highly exothermic and fast, requiring very short contact time (0.01 s or less) [23].

Full characterization of the catalysts under investigation was studied briefly in other work [24].

The aim of the present work is to study the catalytic activity of these catalysts toward methanol conversion. The thermodynamic feasibility, kinetics and mathematical modeling of methanol conversion were investigated.

EXPERIMENTAL

Catalyst Preparation

The parent mesoporous silica of the FSM-16 type with BET surface area of $931 \text{ m}^2\text{g}^{-1}$ and total pore volume of 1.098 mLg^{-1} was synthesized by standard procedure [12].

Iron, copper and silver impregnated FSM-16 (Fe/FSM-16, Cu/FSM-16 and Ag/FSM-16) were prepared by impregnating the synthesized FSM-16 with an aqueous solution of a prescribed concentration (3, 6, 9 wt % metal) of the metal nitrate from Aldrich, the slurry was stirred vigorously for 15 min. followed by the evaporation of excess water at 77°C . The samples were dried at 110°C overnight, and calcined at 250°C for 4 h in dried air stream. The resultant samples were heated at 450°C for 4 h in H_2 atmosphere.

Catalytic activity

Catalytic conversion of methanol on investigated catalysts was carried out under atmospheric pressure in the temperature range of $250 - 450^\circ\text{C}$. In a microcatalytic reactor, 0.25 g of the dried catalyst placed between two thin quartz layers. The catalyst was activated at 450°C for 2 h in a stream of H_2 gas. $2\mu\text{L}$ of the reactant was injected over the catalyst at a flow rate of $50 \text{ mL of H}_2 \text{ min}^{-1}$. The reactants and products were analyzed with an online gas chromatograph. Computerized data acquisition system, model 201 24-Bit (Italy) was used for integrating and recording the effluent yield. The column used was 200-cm length and 0.3-cm diameter, packed with chromosorb AW (80 – 100 mesh size) from Merck, loaded with 15 wt % squallane (Merck). The chromatographic column temperature was adjusted and controlled at 70°C . Doses of methanol were injected first to reach steady state of the activity.

RESULTS AND DISCUSSION

Catalytic conversion

Parent FSM-16 is catalytically dead but after metals loading it becomes active. This may be due to metals induced unbalance in the distribution of charge around OH group of FSM-16 silica framework.

The catalytic conversion of methanol over Fe, Cu, Ag supported on FSM-16 with different metal content (3, 6, 9 wt % metals) are shown in Fig.1. Dehydrogenation of methanol to formaldehyde is the most predominant reaction than the dehydration to ethylene which is in line with thermodynamics.

It is obvious that the dehydrogenation of methanol increases by increasing reaction temperature (250 – 450°C) for all the prepared catalyst samples due to increase of the activity of the catalyst at higher temperature (microkinetic factor). At higher reaction temperature (400 – 450°C), a little yield of ethylene was observed.

As metal percent increases 3 – 9 wt % metal; for catalysts containing silver, copper and iron; the selectivity of CH₂O decreases as reaction temperature increase (400 – 450°C) due to formation of ethylene.

For catalyst sample containing 3 wt % Ag, methanol is completely converted with 100 % selectivity to CH₂O and by increasing the silver content to 6 and 9 % Ag; ethylene was observed and the selectivity of CH₂O decreased a little bit at higher reaction temperature (400 – 450°C).

It is clearly shown that silver catalyst is more active and selective toward CH₂O formation than copper and iron supported on FSM-16 catalysts. This may be due to: (a) Silver active sites were almost present on the surface of the FSM-16 support due to its larger ionic radius (1.08 Å) rather than that of copper (0.71 Å) and iron (0.63 Å) which are present with higher quantity inside the pore system of FSM-16 [24]. This means that a large number of silver active sites are exposed to the methanol molecules. (b) Silver oxide is easily reduced to silver metal at lower reduction temperature (~143 – 177°C) than copper oxide at (~ 229 – 320°C) and iron oxide (~ 323 – 410°C) as clarified by Temperature Programmed Reduction (TPR) data [24].

Thermodynamic feasibility of methanol dehydrogenation.

Thermodynamic feasibility was theoretically calculated from known thermodynamic data of reactant and products [25-27]. Providing the suitable macrokinetic conditions (e.g. temperature, pressure, volume, contact time) and microkinetic conditions (e.g. surface area, pore size, metal particle size and number of active sites), the maximum thermodynamic feasible conversion can be attained.

The catalytic activity of the investigated catalysts (Fe/FSM-16, Cu/FSM-16 and Ag/FSM-16) was tested through methanol conversion. According to the high mole percent formaldehyde obtains. The thermodynamic feasibility for it was studied.



The reaction type is (A = B + C), therefore the feasible thermodynamic conversion (x) was calculated from the derived equilibrium conversion equation $K_p = [X^2 / (1 - X^2)] P$. This equation

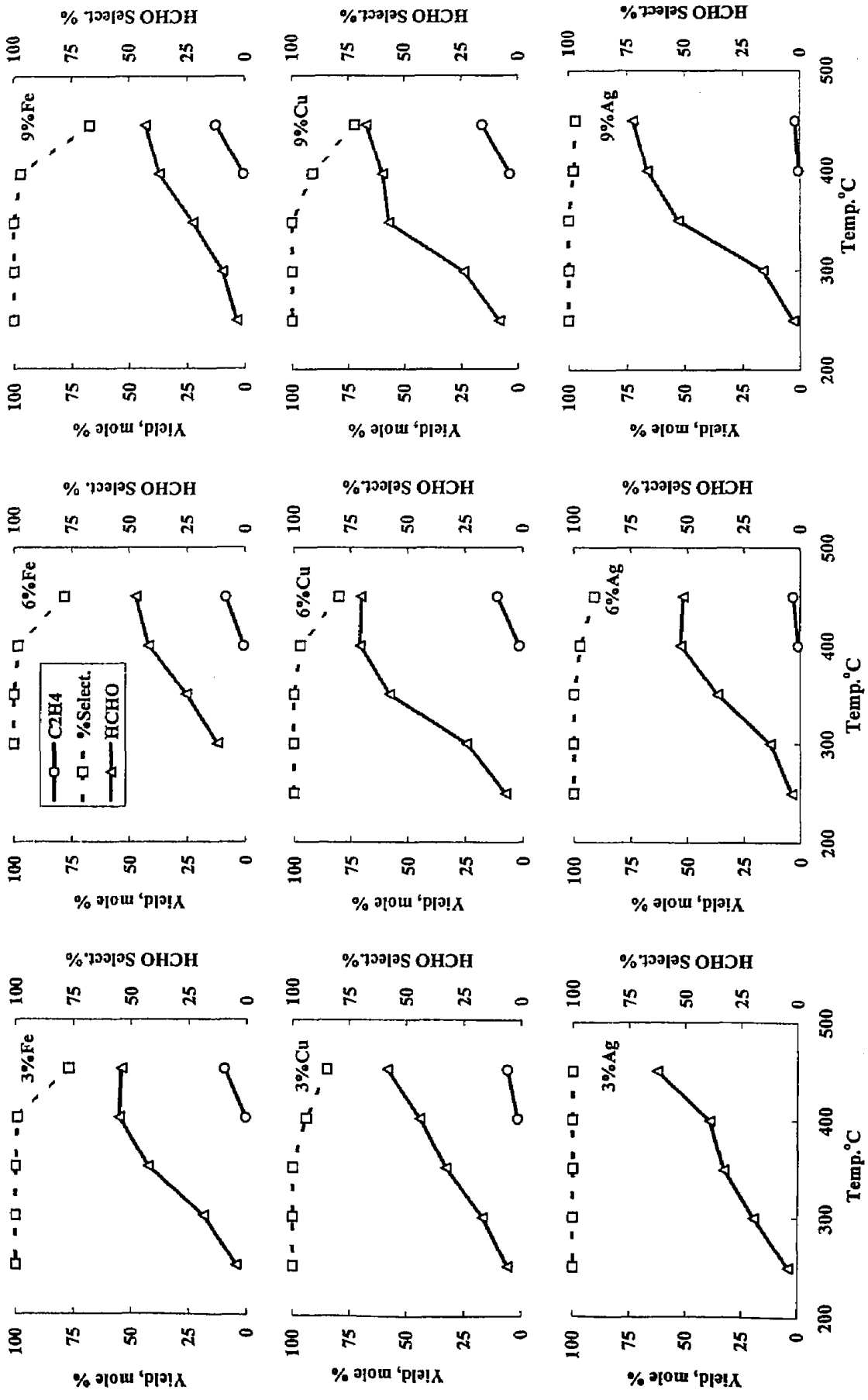


Fig.1. Catalytic conversion of methanol on iron, copper and silver supported on FSM-16 catalysts

shows also that the reaction is affected by pressure which leads to their decrease which is in line with Le-Chatelieu rule.

The reaction equilibrium constants K_p were calculated by Gibbs isothermic chemical reaction equation:

$$\Delta G_{\text{reaction}} = -RT \ln K_p$$

$$\text{Log } K_p = -\Delta G_{\text{reaction}} / 4.575 T$$

$$\text{where } \Delta G = \Delta H - T\Delta S$$

Where: T is the reaction temperature (K), ΔG is the isobaric potential of the reaction (kJ/mol), ΔH is the enthalpy (kJ/mol) and ΔS is the entropy (kJ/mol.K).

Therefore, the calculated free energy (ΔG) for methanol dehydrogenation is expressed in Table 1.

Table 1. Thermodynamic functions of methanol dehydrogenation ($\text{CH}_3\text{OH} \leftrightarrow \text{CH}_2\text{O} + \text{H}_2$)^{*}

t.°c	CH ₃ OH			CH ₂ O			reaction	
	ΔH°	ΔS°	ΔG	ΔH°	ΔS°	ΔG	ΔH	ΔG
27	-201.25	0.24	-273.25	-115.94	0.22	-181.64	85.31	91.6
227	-207.94	0.27	-340.94	-119.24	0.24	-238.74	88.70	102.2
427	-212.88	0.29	-414.48	-122.05	0.26	-300.55	90.83	113.9
727	-217.28	0.32	-534.28	-124.93	0.28	-399.93	92.35	134.4

* Both ΔH and ΔG for $\text{H}_2 = 0.0$ & $^{\circ}$: [27].

From Table 1, it is shown that methanol dehydrogenation to formaldehyde is an endothermic reaction.

Based on the equilibrium conversion equation, nomograms was constructed viz., $\log K_p$ vs. X (0.01– 0.9) [25]. From the obtained nomograms, the thermodynamics conversion (x) at different temperature was expressed in yield (y), mole %.

The estimated (y) values were plotted against the temperature. From the plot characteristic for the reaction, the thermodynamic feasibility was assessed.

According to the details of assessment, it is clear that, methanol dehydrogenation to formaldehyde, Table 2 and Figure 2, is feasible and its yield decreases with temperature.

Table 2. $\Delta \log K_p$ (reaction) = $\log K_p$ (CH₂O) - $\log K_p$ (CH₃OH)

t.°c	$\log K_p$ (CH ₃ OH)	$\log K_p$ (CH ₂ O)	$\Delta \log K_p$ (reaction)	Yield (mole %)
27	28.252	19.133	9.119	100
227	14.032	10.961	3.341	100
427	7.756	7.363	0.393	84
727	2.941	4.599	-1.658	16

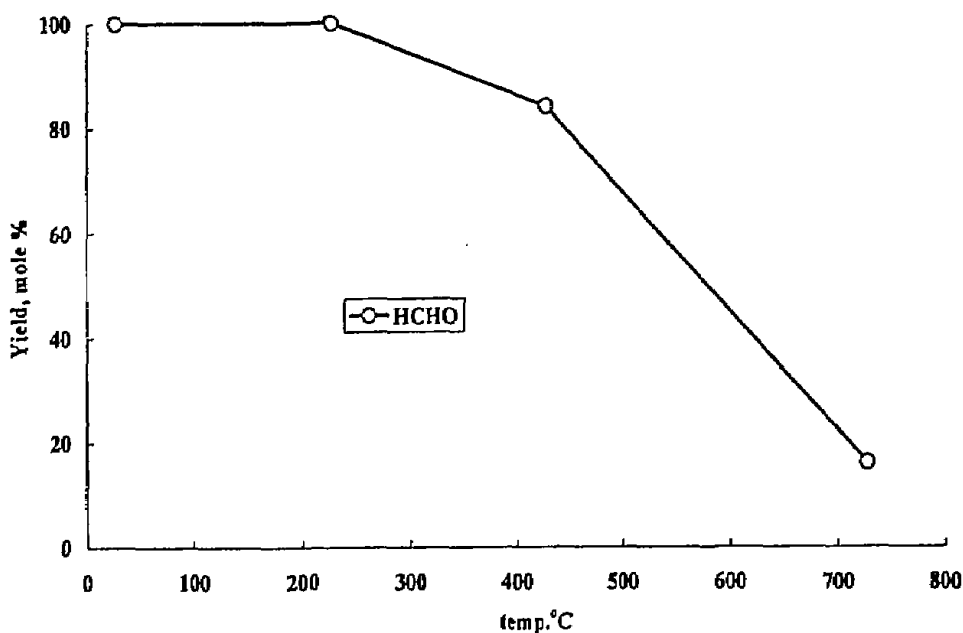


Fig.2. Thermodynamic feasibility of methanol dehydrogenation

Mathematical modeling of methanol conversion

Mathematical modeling in the last years is a good quantitative tool to evaluate the different factors on the reactions since it considers the reaction as black box, not depending on the mechanisms of reaction, which is an advantage compared with kinetic modeling that depends on the knowledge of mechanisms and consequently the order of reaction which in many cases is difficult.

In our case there are two factors (independent variables), metal percent (X_1) and reaction temperature (X_2). X_1 is expressed by 3, 6 and 9 wt % and X_2 as 300, 350 and 400°C. The upper levels or maximum values are 9 wt % metal and 400 °C; and the lower levels are 3 wt % metal and 300 °C. The central point is 6 wt % metal and 350 °C with $\Delta X_1=3$ wt % and $\Delta X_2 = 50$ °C.

Consequently the mathematical equation is in the following form: $Y = \beta_0 + \beta_1 Z_1 + \beta_2 Z_2$. Z_1 and Z_2 are a two variables and expressed as $[(X_1 - 6) / 3]$ and $[(X_2 - 350) / 50]$, respectively. β_0 , β_1 and β_2 are constants calculated from some arithmetic operation [28].

The resulted regression equations which evaluate the influence of both metal loading and temperature on the activity of the investigated catalysts toward methanol dehydrogenation to formaldehyde are expressed as follows:

$$\text{Fe / FSM-16} \quad Y = - 68.3 (-) 2.24 X_1 + 0.32 X_2 \quad \{1\}$$

$$\text{Cu / FSM-16} \quad Y = - 84.9 (+) 1.89 X_1 + 0.33 X_2 \quad \{2\}$$

$$\text{Ag / FSM-16} \quad Y = - 97.7 (+) 1.99 X_1 + 0.34 X_2 \quad \{3\}$$

Parentheses indicate stronger influence and sign indicate the direction of influence.

From the obtained regression equations {1, 2 and 3}, one can suggest that the formation of formaldehyde is greatly affected by the decrease of iron content {eq.1}. This is clearly observed from the negative sign between parentheses. However in case of copper and silver {eq. 2 and 3}, the formaldehyde formation is enhanced by increasing the metal content, viz. the positive sign between parentheses. The three mathematical models show that the yield increases with the temperature in all cases, and the effect of metal percent is stronger than temperature. This behavior is adequate and in harmony with the catalytic activity of the prepared catalysts, viz. Fig.1.

Both Student *t*-test and Fisher's test are used to ensure the adequacy of the regression equations and the significance of the regression coefficients. By running arithmetic operations [28], the Student *t*-test and Fisher's test can be calculated for the formaldehyde formation in the presence of the investigated catalysts shown in the following table:

Table 3. Statistical test for fitting accuracy

	F	t_1	t_2
Fe / FSM-16	9.555	8.943	21.243
Cu / FSM-16	10.645	8.923	24.646
Ag / FSM-16	116.534	8.53	24.661

For a significance level of $\alpha = 0.05$ and $V = 2$ of freedom, the tabulated Student *t*-distribution is $t_{\alpha}(V) = 4.3$. From Table 3, all regression coefficient are higher than 4.3 and become significant for both t_1 and t_2 (metal content and reaction temperature, respectively).

Another parameter (Fisher's test) is used to see the fitness of regression equation with the experimental observations. The tabulated value of Fisher's test for $\alpha = 0.05$ and $V_1 = 1$ and $V_2 = 2$ is $F_{1-\alpha}(V_1, V_2) = 18.5$. Accordingly, the F values for both catalysts iron and copper modified FSM-16 is less than the tabulated value, hence the obtained experimental data was adequately fit the mathematical models derived. But for Ag/FSM-16, the F value is much greater than tabulated one. Accordingly the regression equation is not identical for the obtained data because of all methanol are converted to formaldehyde at all reaction temperature in presence of catalyst contain 3 wt % Ag. (viz. Fig. 1).

Kinetics of methanol conversion

Kinetics of methanol conversion was studied for all the catalyst samples prepared in this work.

Results showed that all the reactions are first order since they obeyed Habgood first order equation for pulse system [29]. Values of the activation energies, calculated by Arrhenius equation are given in Table 4 together with the characteristics of each catalyst.

Results in this table show that activation energies for formation of formaldehyde is always lower than that for the formation of ethylene (for any catalytic system; feed-catalyst-products) which indicates the easier formation of formaldehyde than ethylene over our catalysts. It can be observed

Table 4. Activation energies of HCHO and C₂H₄ formation on iron, copper and silver supported on FSM-16

Catalyst name	Physical properties	T, °C	HCHO	T, °C	C ₂ H ₄
3 % Fe	s.a. = 702 m ² g ⁻¹ , P.D. = 22.8 Å, P.V. = 0.707 cm ³ g ⁻¹ , α ₀ = 30 Å	400 – 450	- 0.4	400 – 450	63.5
		300 – 400	10.6		
		250 – 300	17.9		
3 % Cu	s.a. = 748 m ² g ⁻¹ , P.D. = 23.4 Å, P.V. = 0.779 cm ³ g ⁻¹ , α ₀ = 38.1 Å	350 – 450	7.1	400 – 450	27
		250 – 350	12.2		
3 % Ag	s.a. = 802 m ² g ⁻¹ , P.D. = 23.2 Å, P.V. = 0.831 cm ³ g ⁻¹ , α ₀ = 41.6 Å	350 – 450	8.2	400 – 450	-
		250 – 350	14.5		
6 % Fe	s.a. = 703 m ² g ⁻¹ , P.D. = 24 Å, P.V. = 0.688 cm ³ g ⁻¹ , α ₀ = 30 Å	400 – 450	3.4	400 – 450	52.3
		300 – 400	10		
		250 – 300	11.9		
6 % Cu	s.a. = 684 m ² g ⁻¹ , P.D. = 23.4 Å, P.V. = 0.723 cm ³ g ⁻¹ , α ₀ = 30 Å	350 – 450	8.9	400 – 450	41.4
		250 – 350	15.7		
6 % Ag	s.a. = 702 m ² g ⁻¹ , P.D. = 23.2 Å, P.V. = 0.712 cm ³ g ⁻¹ , α ₀ = 41.6 Å	350 – 450	4.4	400 – 450	25.1
		250 – 350	16.1		
9 % Fe	s.a. = 652 m ² g ⁻¹ , P.D. = 24.2 Å, P.V. = 0.639 cm ³ g ⁻¹ , α ₀ = 34.6 Å	400 – 450	3.7	400 – 450	57.9
		300 – 400	11.7		
		250 – 300	12.6		
9 % Cu	s.a. = 625 m ² g ⁻¹ , P.D. = 22.8 Å, P.V. = 0.653 cm ³ g ⁻¹ , α ₀ = 38.1 Å	350 – 450	2.4	400 – 450	30
		250 – 350	14.9		
9 % Ag	s.a. = 680 m ² g ⁻¹ , P.D. = 23.2 Å, P.V. = 0.788 cm ³ g ⁻¹ , α ₀ = 41.6 Å	350 – 450	4.9	400 – 450	12.2
		250 – 350	20.9		

also that increase of temperature leads to lower activation energy of formaldehyde formation which indicates its more easier formation due to increase of the activity of the catalysts at higher temperature. The high activation energy of formaldehyde formation at lower temperature may also indicate that its diffusional hindered beside the lower activity of the catalyst at lower temperature.

Chaotic decrease and increase of the activation energy with metal loading percent is observed. This may be due to the chaotic dispersion of metal particles in each case and accordingly the properties of catalysts, i.e. there are no definite parameters for this behavior.

CONCLUSION

Silver/FSM-16 catalysts have good activity and selectivity toward methanol dehydrogenation to formaldehyde especially the sample containing the lower silver percent (3 wt % Ag), rather than copper and iron supported on FSM-16 catalysts. This behavior is related to the ionic radii of the different metal cations of silver > copper > iron. Therefore more silver active sites are present on the support surface and exposed to methanol molecules rather than iron active sites which may be present in large quantity inside the pore system of FSM-16. Methanol dehydration to ethylene was observed at higher reaction temperatures (400 – 450 °C). Thermodynamic feasibility of methanol dehydrogenation is possible and it is endothermic reaction. The obtained regression equation showed that the metal loading is more effective factor than reaction temperature for formaldehyde formation. Both calculated Student t-test and Fisher's test show that the regression equation and the experimental data are adequate to the mathematical models. Kinetic study shows that formation of formaldehyde is a first order and the activation energy decrease with increase of temperature due to increase of catalyst activity. Chaotic decrease and increase of the activation energy with metal loading in the kinetic behavior is related to the chaotic dispersion of metal in each case.

ACKNOWLEDGMENT

The author wishes particularly to convey his great thanks to Dr. Fikry Hinry Khalil professor of catalysis in Egyptian Petroleum Research Institute for his financial support, most helpful advice, for the discussions, and valuable revision.

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