

OXIDATIVE DEHYDROGENATION OF METHANOL ON CHROMIUM OXIDE/ MONTMORILLONITE K10 CATALYSTS

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ABSTRACT

Methanol conversion was carried out on one of mesoporous materials, Chromia / Montmorillonite K10 (MK10) in a pulse microcatalytic system. Methanol was converted to formaldehyde and ethylene by two different mechanisms. Methanol dehydrogenation increases by reaction temperature (300-400°C) and as chromia loading decrease. In contradiction, the dehydration of methanol takes place at higher temperature (400-500°C) and as chromia loading increase, 3-18%Cr. Redox and exposed non-redox Cr³⁺ are responsible for HCHO formation. There is relationship between increasing of C₂H₄ production and the increase of Cr⁶⁺ phase (from TPR & UV-Vis) according to the acidity of chromia catalysts 34 and 76 μL tert-Butylamine /gram catalyst for 3%Cr and 18%Cr, respectively. Formaldehyde formation is diffusionally controlled at high temperature (400-500°C) and kinetically controlled at lower reaction temperature (300-400°C) while methanol dehydration to ethylene is surface reaction controlled at 400-500°C.

INTRODUCTION

Montmorillonite K10, a commercial acid activated clay and a quasi-crystalline material has most of its pores falling in the mesoporous range 20-75 Å diameter ⁽¹⁾. Both Brönsted and Lewis acid sites have been identified on montmorillonite K10 ⁽²⁾.

Impregnated and ion exchanged montmorillonite K10 have proved to be good catalysts for a number of reactions ⁽³⁻⁶⁾. The strength and nature of interaction between the metal oxide (vanadia, zirconia and chromia) and the support may influence the acidity by affecting the valence state of the metal ⁽⁶⁾.

Methanol, one of the most important chemical intermediates used in industrial chemistry, is the starting materials for the synthesis of various products such as hydrocarbons and oxidation products ⁽⁷⁾. Among the oxidation processes, formaldehyde production is dominant ⁽⁸⁾. This reaction has been found to be structure sensitive and selectivity depends on the arrangement of the surface atoms ^(9, 10).

Chromia supported on various oxides such as γ -alumina, SiO₂, ZrO₂, MCM-41 ⁽¹¹⁻¹⁵⁾ and SBA-15 ⁽¹⁶⁾ are well known active catalysts for different catalytic conversion of hydrocarbons as oxidative dehydrogenation to olefins, cracking and partial oxidation to oxygenate and CO ⁽¹⁷⁻²⁰⁾.

In this work, we prepared different chromia / Montmorillonite K10 catalysts to study the effect of chromia loading on the methanol conversion to formaldehyde and ethylene. Also to describe the active sites which are responsible for these reaction.

EXPERIMENTAL

Catalysts preparation:

The chromium oxide catalysts were prepared from chromium nitrate precursor. A predetermined amount of the precursor solution was added gradually with stirring to a crystallizing dish containing a predetermined amount of the support to make the specified weight percent 3, 6, 9 & 18 of the chromium on the montmorillonite K10. The contents were continuously stirred while excess distilled water was evaporated. A thick paste was obtained that was dried in an oven at 110°C overnight. The catalyst powder was calcined at 250°C (temp.ramp 5°C/min.) in air for four hours after that heated at 450°C in hydrogen for 4 hr.

Catalytic activity

The catalytic activities of the investigated catalysts were tested through the oxidative dehydrogenation of methanol by using a micro catalytic pulse technique. Methanol was injected in micro quantities (2µL) by micro syringe in the form of pulses into a micro reactor containing 0.5 gm of the tested catalysts. The catalyst bed was supported on fine quartz wool and an inert glass placed at the top of this bed to ensure good mixing of the reactants. The reactor effluent was passed through a chromatographic column for separation and determination using flame ionization detector. Computerized data acquisition system was used for integration and recording the effluent yield. The column used, 200 cm length and 0.3 cm diameter, packed with acid washed chromosorb AW (80-100 mesh size) from Merck, loaded with 15% by weight squallane (Merck).

The reactions were carried out under atmospheric pressure and temperature range 300-500°C. The hydrogen flow rate was kept constant at 50 mL per minute. Prior to catalytic activity test, the catalyst samples were heated in flowing H₂ up to 450°C with a heating rate of 100°C/h and kept for 2h at 450°C for their activation. Few doses of methanol were injected first to reach steady state of the activity. The chromatographic column temperature was adjusted and controlled at 80°C.

Acidity test

Pulse technique method was used to determine the acidity of the investigated catalysts. The catalyst sample (0.5 g) was activated at 450°C for 2 hr in a stream of H₂ at flow rate of 50 ml/min. The reactor temperature was adjusted at 150°C. 2µL of tert-Butylamine (TBA) was injected continuously till appear a peak corresponding to the excess of unadsorbed amine. This process was repeated in the same manner until the stationary state was achieved. The total of TBA uptake (µL), number and density of acid sites were calculated.

- Elemental analyses for chromium metal were performed by inductively coupled plasma using

ICP-AES Shimadzu ICP-7500 (Japan).

Designed chromium wt.%	3	6	9	18
Detected chromium wt.%	2.8	5.78	8.87	17

- Elemental analyses for MK10 were examined by X- ray fluorescence using Shimadzu XRF-1700 sequential X-ray fluorescence spectrometer, 40 kV, 30mA and Rh target Oxide.

Oxide	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	LOI	Total
%	75.89	10.47	0.48	2.40	1.34	0.37	0.24	1.38	0.02	0.04	7.18	99.81

RESULTS AND DISCUSSION

Mesoporous montmorillonite K10 (BET s.a.= 345 m²/g, Pore diameter = 36.7 Å and total pore volume = 0.63 cm³/g) ⁽²¹⁾ is an inactive toward methanol conversion, but after modification with chromia, the catalytic activity was enhanced. The products detected were formaldehyde due to dehydrogenation of methanol and ethylene resulted from methanol dehydration for all catalysts sample under investigation.

Methanol dehydrogenation

Table 1 and Fig.1 showed the catalytic dehydrogenation of methanol to formaldehyde over chromia / MK10 catalysts with different chromia loading.

Formaldehyde production increase by reaction temperature to maximum value at 300-400°C then declines at higher temperature up to 500°C. Methanol dehydrogenation affected by chromia loading i.e. as chromia percent increase, HCHO yield decrease from 3-18 % Cr loading.

Table 1: Catalytic activity and selectivity of various chromia catalysts for methanol dehydrogenation to formaldehyde

Y: Formaldehyde mole% & S: % formaldehyde selectivity

	300		350		400		450		500	
	Y	S	Y	S	Y	S	Y	S	Y	S
Cr (3) / MK10	26.3	100	49.7	100	68.1	100	69.8	75	33	33
Cr (6) / Mk10	21.1	100	63.2	100	66.1	88	41.8	42	8.9	9
Cr (9) / MK10	20.3	100	53.9	100	48.8	81	33.7	34	3.7	4
Cr (18) /MK10	12.7	100	38.2	100	46.2	88	14.9	17	2	2

Up to 350°C, the selectivity of HCHO reaches 88-100% for all chromia catalysts. The selectivity decrease for lower percent chromia catalysts as reaction temperature increase. This behavior due to the formation of another product (ethylene).

Chromia / Montmorillonite K10 catalysts with lowest Cr content (3%Cr) gave highest activity toward dehydrogenation of methanol even at 400°C. This due to redox Cr^{3+} is abundant in chromia catalyst with low chromia loading⁽²²⁾.

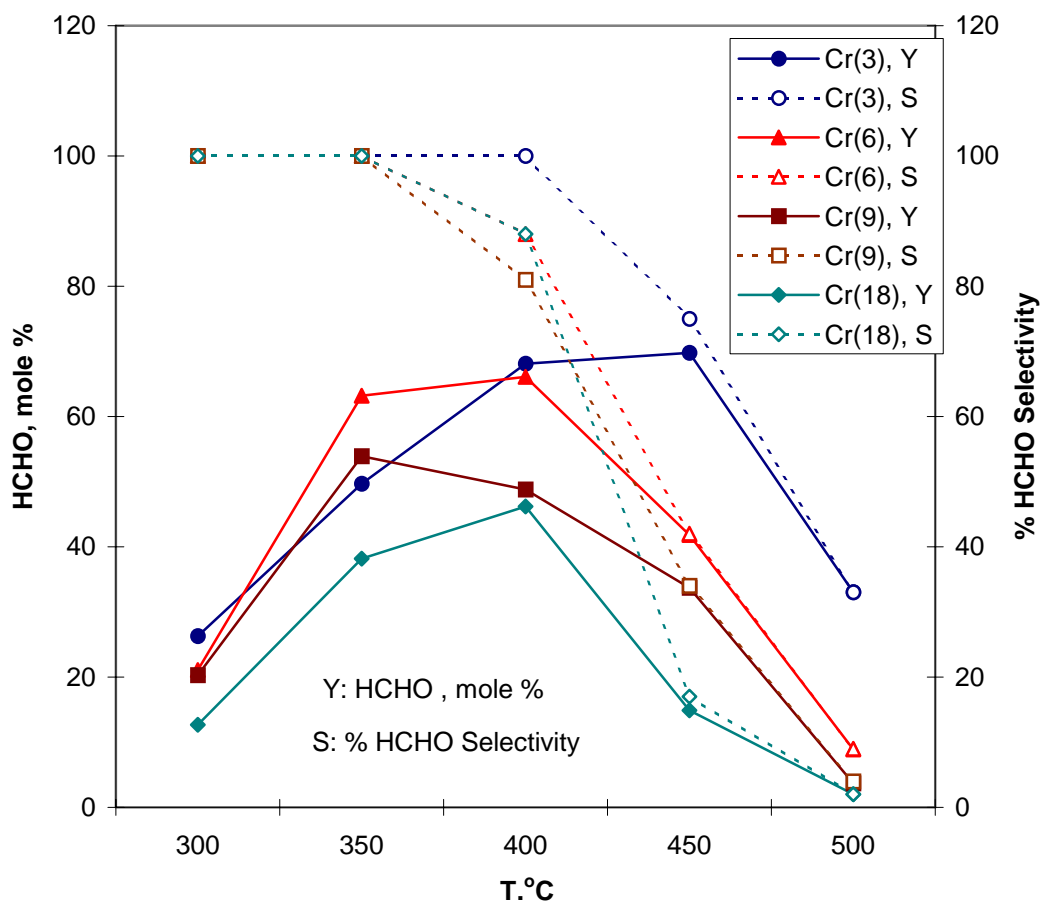


Fig.1: Catalytic activity and selectivity of chromia catalysts for methanol dehydrogenation to formaldehyde

Active site(s) responsible for methanol dehydrogenation:

Oxidized chromia catalysts contain chromium in oxidation state Cr^{6+} , Cr^{5+} and Cr^{3+} . Hydrogen, alkane and CO reduce Cr^{6+} and Cr^{5+} under typical dehydrogenation conditions (500-600°C) (22, 23, 24-28). The redox Cr^{3+} formed in the reduction of Cr^{6+} serve as active sites in the dehydrogenation (29).

Figure 2a shows the *different types of Cr^{3+} species* that are present in reduced chromia/alumina catalysts. Type 1 sites are surface Cr^{3+} sites, with subclasses type 1' and type 1'', which are presumably catalytically active. A type 1' site is an isolated (i.e., mononuclear) Cr^{3+} ion that does not interact with other chromium sites; it is sometimes referred to as

dispersed Cr^{3+} ⁽³⁰⁾. A type 1'' site is a Cr^{3+} ion that has one or more neighboring Cr^{3+} ions and thus is called multinuclear Cr^{3+} .

Type 1'' sites are also called “ Cr^{3+} clusters.” In addition there are type 2 and type 3 sites, where the Cr^{3+} is not a surface ion but is buried inside chromia crystallites (type 2) or the alumina support (type 3). Since types 2 and 3 are not surface species, they are not catalytically active. Chromia crystallites consist of type 1'' and type 2 sites together and may grow in size so that they become visible in X-ray diffraction (XRD).

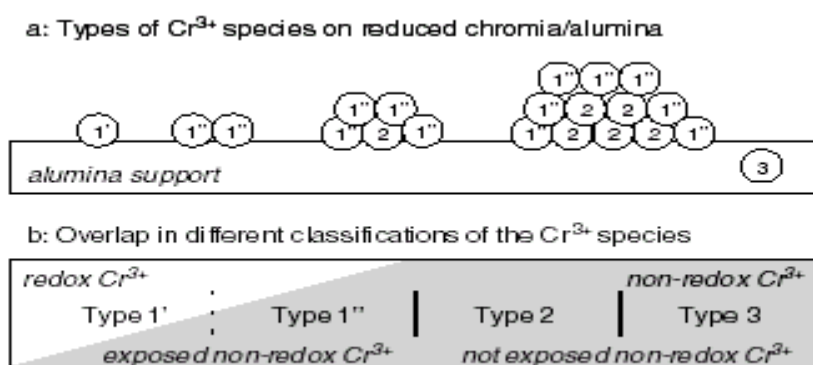


FIG. 2. (a) Schematic summary of the different Cr^{3+} species present on reduced chromia/alumina catalysts (oxygen ions between the Cr^{3+} ions are omitted for clarity), and (b) an illustration of the overlap in the different classifications of Cr^{3+} species.

The Cr^{3+} species have also been classified in terms of origin ^(22, 24,31). Those Cr^{3+} ions that have been formed through reduction of chromium in high oxidation states (Cr^{6+} and Cr^{5+}) in a reducing atmosphere are referred to as “redox Cr^{3+} ,” whereas those Cr^{3+} ions that have been stabilized as Cr^{3+} are referred to as “nonredox Cr^{3+} .” Redox Cr^{3+} is exposed on the surface and thus can be catalytically active. Nonredox Cr^{3+} may be exposed and catalytically active, but it may also be buried inside chromia crystallites or inside the alumina support and thus be catalytically inactive.

Redox Cr^{3+} is abundant in chromia/alumina catalysts with low chromium loading, whereas nonredox Cr^{3+} is mostly present in catalysts with higher loadings⁽²²⁾. Figure 2b shows how the classifications in terms of *type and origin overlap*. Thus redox Cr^{3+} probably falls in the category of type 1' sites. Exposed nonredox Cr^{3+} should be mostly classified as type 1'' with minor contributions from type 1' sites, and nonexposed nonredox Cr^{3+} should be classified as type 2 or type 3 sites.

However in our case the XRD, (UV-vis DRS), TPR and FT-IR spectroscopy⁽²¹⁾ have shown that Cr^{6+} ions present on oxidized chromia/MK01 catalysts may be present in highly dispersed state even at higher chromia loading (18%Cr). In conclusion, redox Cr^{3+} of type 1' site is responsible for methanol dehydrogenation especially for lower Cr content sample (namely, 6%Cr).

Methanol dehydration

Ethylene is formed by base reactions (dehydration) and is promoted by catalysts having acidic properties⁽³²⁾. In fact, the catalyst with lower chromia loading, the chromia species are perhaps present predominantly in higher oxidation state like Cr^{5+} and or Cr^{6+} , which are more acidic than the lower oxidation state like Cr^{3+} species⁽³³⁾.

Beside the formation of formaldehyde, ethylene was formed over chromia/MK10 catalysts. Montmorillonite K10 contains Lewis acid sites (Al^{3+}), which are involved in reactions of alcohol to ethers, which is the intermediate step to form ethylene. Montmorillonite K10 also contains Brønsted acid sites that promote dissociation of the alcohol hydroxyl group during olefin formation. So that the formation of ethylene and ether on MK10 can be explained by the presence of acid sites presented on the surface.

Moreover, the ethylene formation increases as chromia loading increase from 3 to 18 % Cr (table2 and fig.3). The activity and selectivity reach ~98% at higher reaction temperature (500°C)

Table 2: Catalytic activity and selectivity of various chromia catalysts for methanol dehydration to ethylene

	300		350		400		450		500	
	Y	S	Y	S	Y	S	Y	S	Y	S
Cr (3) / MK10	-	-	-	-	-	-	23.5	25	67	67
Cr (6) / Mk10	-	-	-	-	8.8	12	58.2	58	91.1	91
Cr (9) / MK10	-	-	-	-	11.3	19	65.3	66	96.3	96
Cr (18) / Mk10	-	-	-	-	6.5	12	73.2	83	98	98

Y: ethylene mole% & S: % ethylene selectivity

and for highest chromia loading sample (18%Cr). This behavior was due to increase of chromia loading and that the sample is rich with Cr⁶⁺ phase according to TPR analysis ⁽²¹⁾. This means that large fraction of Cr⁶⁺ is present even in the reduced atmosphere (H₂ gas). It is attributed also to that the sample containing 18%Cr is more acidic (table 3), active and selective toward ethylene formation.

Surface acidity of chromia/MK10 catalysts

As mentioned previously, pulses of tert-Butylamine (TBA) were injected over the catalyst. The TBA chemisorbed completely and occupied one acid site per molecule, assuming that TBA occupies preferentially the stronger sites before weaker ones.

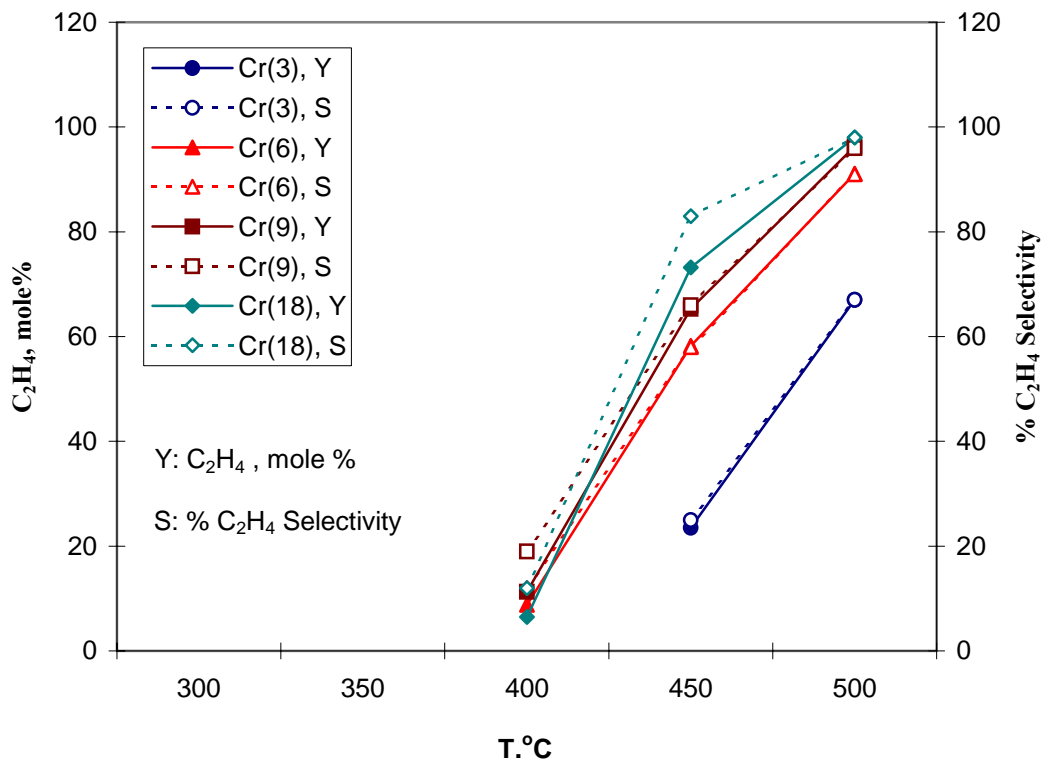


Fig.3:Catalytic activity and selectivity of chromia catalysts for methanol dehydration to ethylene

The results obtained for active sites of investigated catalysts are illustrated in table 3. The determined active acid sites on Cr (3)/MK10 catalyst is 34 μ L of TBA corresponding to 1.97×10^{24} molecules/g. whereas, in Cr (18)/MK10 catalyst is 76 μ L corresponding to 4.3×10^{24} molecules/g. This indicates more activity of the catalyst containing 18%Cr; rich with Cr⁶⁺

(21)

Table 3: Acidity function and surface areas of the investigated catalysts

<i>Sample</i>	<i>Wt. of TBA/g.</i> 1*	<i>N</i> ^{2*} (<i>acid site/g.</i>)	<i>BETs.a</i> ^{3*} (<i>m²/g.</i>)	<i>d</i> ^{4*} (<i>mole/m²</i>)
Cr (3)/MK10	(34μL) 24	1.97X10 ²⁴	242	0.82 X10 ²²
Cr (6)/MK10	(49μL) 34	2.8 X10 ²⁴	215	1.3 X10 ²²
Cr (9)/MK10	(59μL) 41	3.4 X10 ²⁴	136	2.5 X10 ²²
Cr (18)/MK10	(76μL) 52	4.3 X10 ²⁴	177	2.4X10 ²²

1*: corresponding to μL of tert-Butylamine adsorbed X density of TBA for one gram catalyst,

2*: *N* is the number of acid sites/g.,

3*: BET s.a. is the surface area of the catalyst sample, and

4*: *d* is the density of acid sites/m².

From these obtained data, it appeared, of great interest, to follow the density of active acid sites, (number of molecules of TBA adsorbed per unit surface area, molecules/m²). The expected data should reflect the type of distribution of the investigated active sites rather than their absolute number being related to absolute activity.

Inspections of these results reveals that the density of active sites, responsible for methanol dehydration in Cr (18)/MK10 catalyst is triple that of Cr (3)/MK10 catalyst. This is also in harmony with the catalytic activity. However, the density of active sites responsible for methanol dehydration in Cr (18)/MK10 catalyst is nearly close to that of Cr (9)/MK10 catalyst, which is revealed to the distribution of active site on larger surface area (177m²) comparing to the small area (136m²) of the later one.

These larger of number and density of active sites for Cr (18)/MK10 catalyst indicate that more Cr⁶⁺ species is present which it responsible for the higher yield of ethylene.

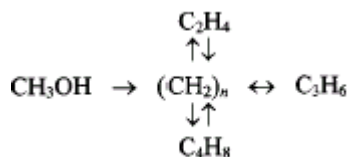
Formaldehyde and Ethylene formation mechanisms:

The rate determining step of formaldehyde formation has been found to be C-H bond breaking within an adsorbed methoxy group leading to the formation of an adsorbed form of formaldehyde⁽³⁴⁻³⁶⁾. The ability to break a C-H bond will depend on the basic or nucleophilic character of oxygen species close to the methoxy group^(37, 38). On the other hand, the desorption of the reaction products will be more favored by a weak than by a strong acid site⁽³⁹⁾. The selective formation of formaldehyde may require both weak acid and basic sites to limit the H abstraction and to prevent a too strong adsorption of formaldehyde, respectively.

If the acid sites are too strong, the residence time of formaldehyde species becomes long enough to form a dioxymethylene species^(40, 41). This reaction does not occur at high temperature, because the desorption rate of formaldehyde is enhanced more by a temperature increase than is the reaction rate to form dioxymethylene species⁽⁷⁾. The product distribution of methanol oxidation depends on the acidic and basic properties of catalysts. For example, the formation of dimethyl ether is produced on catalysts with high acidic character, carbon oxides on catalysts of high basic character and mild oxidation products such as formaldehyde, methyl formate and dioxymethylene on bi-functional catalyst with acid-base character.

Three reaction steps are distinguished for the conversion of methanol to olefins: (i) the dehydration of methanol to dimethyl ether, (ii) the conversion of a mixture of methanol and dimethyl ether to olefins and (iii) a bond chain

polymerization of olefins and isomerization⁽⁴²⁾. Most of the recently published theoretical works investigate the mechanisms for the first C–C bond formation. Dahl and Kolboe^(43, 44) explained the formation of olefins by a “hydrocarbon pool” mechanism, which represents adsorbates such as



According to this mechanism, “big” carbonaceous species exist inside the micro pores of zeolite and add and split off reactants and products, respectively^(43,44). The “hydrocarbon pool” represents adsorbates with many characteristics of ordinary coke and would perhaps be better represented by $(\text{CH}_x)_n$ with $0 < x < 2$ ⁽⁴⁵⁾.

Kinetic behavior of dehydrogenation and dehydration of methanol over chromia/MK10 catalysts.

The kinetic behavior of vapour-phase methanol dehydrogenation and dehydration Fig.4 was followed up through the Arrhenius plot of $\ln k$ against $1/T$, where the rate constant (k) was estimated in all cases from the relationship, $k = F \ln 1/1-x$, x being the degree of conversion, assuming the reaction is of first order.

The activation energies for both reactions proceeded over the surface of the examined catalysts were calculated and summarized in Table 4.

Table 4: Activation energies and pore radius of the investigated catalysts

Catalyst name	Pore radius (Å)	Formaldehyde formation (K.cal./mole)		Ethylene formation (K.cal./mole)
		300-400°C	400-500°C	400-500°C
<i>Cr (3)/MK10</i>	18.6	10.2	-24.4	31
<i>Cr (6)/MK10</i>	18.7	11.9	-39	33
<i>Cr (9)/MK10</i>	17.1	8.6	-53.3	33.4
<i>Cr (18)/MK10</i>	18.1	11.9	-46.6	41.1

Arrhenius plots for methanol dehydrogenation to HCHO over all the studied catalysts, exhibits two regions (Fig.4a), one in low temperature range and the other in the high temperature range. When the surface reaction is relatively slow as compared to the other rate processes (mass transfer adsorption of reactants-desorption of products), the reaction is kinetically controlled. The reaction is diffusionally controlled when it is limited by gas film reactants as well as by pore diffusion resistance.

The reaction is kinetically controlled in the lower temperature region 300-400°C (surface reaction controls), and diffusion controlled in the higher temperature region, viz., 400-500°C. All catalysts under study, at higher temperature region reveals that the gas film is predominantly with (-ve) activation energies. This behavior is due to formation of other product observed (namely, ethylene).

As regards to the ethylene formation on all catalysts, Fig.4 (b) shows only one region behavior, which reveals that the reaction is purely kinetically controlled (31-41 K.cal./mole).

The energy value assigned for Cr (18)/MK10 is considerably more than that for other catalysts (table 4) although this sample has higher degree of conversion which may be related to the higher chromia content. Also attributed to their higher acidity rather than the others.

In conclusion, the chromia content, the acidity of catalysts and the states of chromium species seems to be more contributing in the behavior of the methanol conversion to HCHO and C_2H_4 , rather than the other parameters as the textural characteristics.

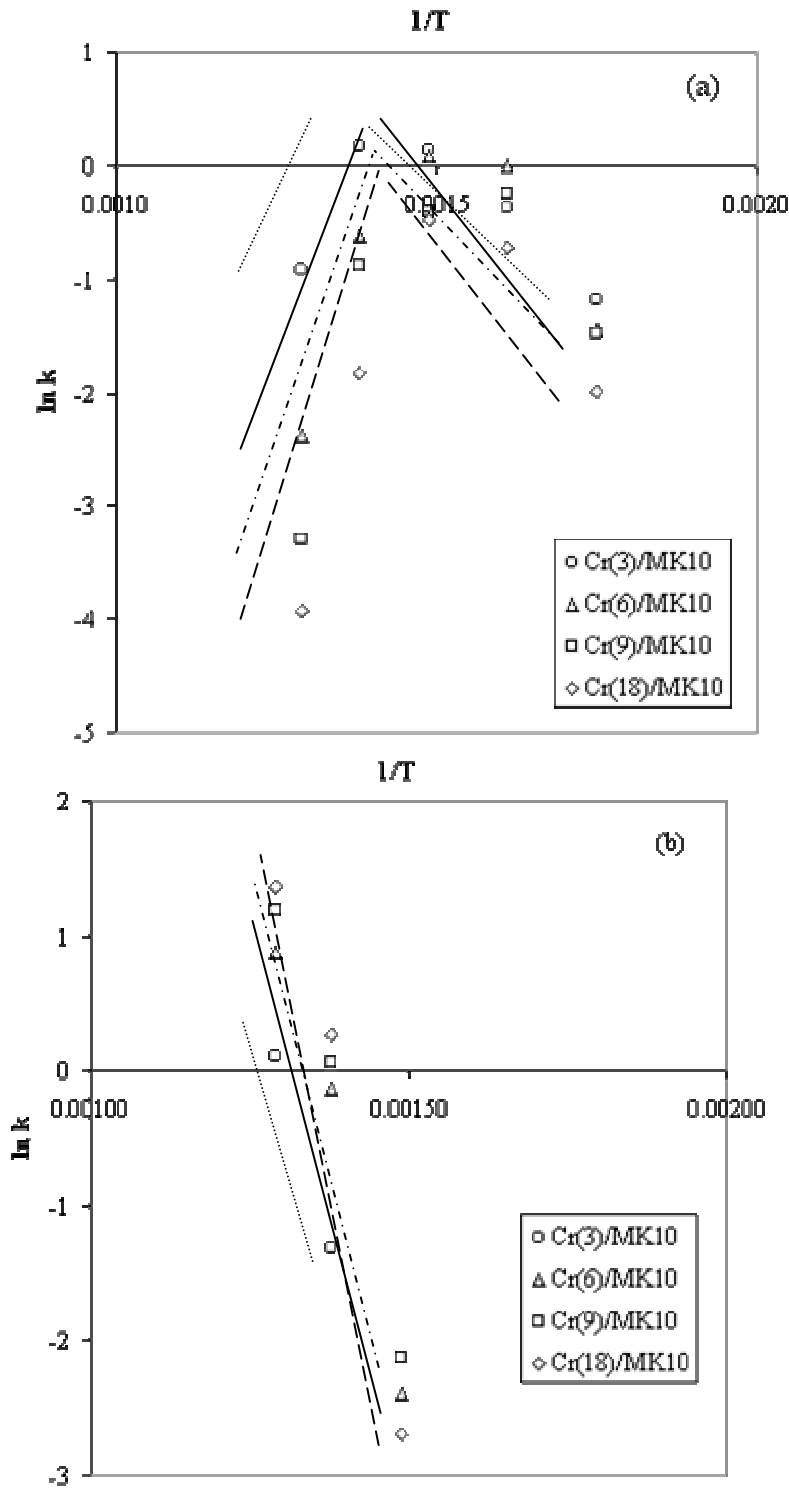


Fig.4: Kinetic behavior of (a) HCHO formation and (b) C_2H_4 formation

CONCLUSION

Chromia catalysts under investigation are suitable to apply in the natural gas liquefaction, since methane is the main constituent in the natural gas so that it is easily to use it in the formation of olefin which is the starting material for petrochemicals and liquid petroleum products as gasoline and so on. Also we can apply these catalysts in the production of hydrogen gas by complete oxidation of methane. Catalyst containing 18%Cr is more active and selective for methanol dehydration to ethylene especially at higher reaction temperature according to its higher acidity, rather than the sample containing 3%Cr. So that the catalyst containing 18%Cr is suitable to use in natural gas liquefaction to liquid hydrocarbons through the formation of olefins. According to the kinetic behavior and activation energies for the methanol conversion to HCHO and C₂H₄, the chromia content, the acidity of catalysts and the states of chromia species seems to be more contributing rather than the textural characteristics.

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