Synthesis of lower olefins from methanol and subsequent conversion of ethylene to higher olefins via oligomerisation

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Abstract

Catalytic conversion of methanol to hydrocarbons with the special emphasis on lower olefins (ethylene and propylene) was carried out using 12-heteropoly acids of W and Mo and P or Si and salts of 12-heteropoly acids. Amongst the metal salts of tungstophosphoric acid, cesium salt exhibited better activity and selectivity for the formation of ethylene and propylene. The maximum selectivity for C_2–C_4 olefins was 60.7%. Physico-chemical characterization of the catalysts has been made by FTIR spectroscopy, XRD, DTA, acidity by n-butyl amine titration and surface area. Acidity and surface area of the catalysts influence the activity and selectivity for the olefins.

Oligomerization of ethylene to higher olefins was carried out in liquid phase using $TiCl_4$–$Et_3Al_2Cl_3$, $TiCl_4$–Et_2AlCl, $TiCl_4$–Et_3Al and $Ti(OBu)_4$–$Et_3Al_2Cl_3$ catalyst systems. Among the catalysts tried, $TiCl_4$ and $Ti(OBu)_4$ based catalysts showed better activity and selectivity to alpha olefins in the range C_4–C_{14}. For vapour phase, HZSM-5, nickel salt supported on SAPO-5 molecular sieve, ZSM-5 and γ-alumina, heteropoly acid supported on ZSM-5 and potassium salt of tungstophosphoric acid were tested. The maximum selectivity of C_4–C_6 olefins was 10.0 wt.% with HZSM-5 catalyst with a Si/Al ratio of 100. The selectivity for higher olefins was less than that obtained by liquid phase oligomerization of ethylene.

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1. Introduction

A large part of raw materials of the chemical industries consists of lower olefins, which at present are produced from petroleum. Dependence of chemical industries on this feedstock has been a weak point in the past due to uncertainty of continued supply. Coal with extensive reserves distributed all over the world is potentially an important feedstock for the chemical and energy related industries. The conversion of coal into synthesis gas and subsequently into methanol is a well-known technology. The production of lower olefins from methanol could be an attractive proposition depending on the local, geographical, economic and political situation. Thus, it would reduce the dependence on petroleum naphtha.

The conversion of methanol to olefins over zeolites [1–3] has been intensively studied. It has been well established that Bronsted acid sites and adjacent basic sites are active in the olefin formation. Heteropoly compounds have received considerable attention in the last two decades for use as heterogeneous and homogeneous catalysts [4–10] particularly in the dehydration of alcohols [11–13] of low molecular weight. Ehwald et al. [14] also reported the synthesis of olefins from methanol on silica supported $Ag_4(SiW_{12}O_{40})$ and alumina-supported $H_4(SiW_{12}O_{40})$. They have indicated that the best results with respect to the production of olefins were obtained in medium range of surface concentration.

Natural gas available at remote places is currently not been utilized and in some cases being flared. This can be utilized by

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conversion to syngas and subsequent down stream processing by known technologies. Furthermore, coal bed methane (CBM) is also available in some countries, which can be augmented in the same way.

With lower olefins as feedstock, practically the entire spectrum of organic chemicals can be conveniently built up as the technology is well established. The manufacture of higher olefins in the C_5–C_{11} range for processing to plasticizer alcohols as well as to C_9–C_{18} hydrocarbons for the production of detergent raw materials is possible through further processing of the lower olefins produced from syngas by oligomerization to higher olefins. The implications of these developments are, that with coal/natural gas/CBM as raw material, it is possible, at least in principle, to produce higher olefins, which are normally produced from petroleum naphtha.

The work has been divided into development of catalysts and optimization of reaction parameters for (a) conversion of methanol to lower olefins and (b) oligomerization of lower olefins to higher olefins in liquid phase and vapour phase.

2. Experimental

Pure heteropoly acids (LR, Loba) as such were pelletised and sized to −6 +14 BSS and used as catalysts. Heteropoly acid salts were prepared by neutralization of pure acids by the corresponding alkali carbonates. Supported heteropoly acid catalysts were prepared by wet impregnation method.

Catalytic conversion of methanol to lower olefins was carried out in a continuous fixed bed glass reactor of 20 mm i.d. and 30 cm length, packed in three sections with bottom 10 cm with unglazed porcelain insulating beads, middle 7 cm catalyst mass (−6 +14 BSS) and top 5 cm layer with insulating beads. Reactor temperature was controlled by regulating the heat input through electrical heating. The reaction products mostly consist of hydrocarbons in C_1–C_4 range, both saturated and unsaturated. The identification and estimation of the gaseous products was done by gas chromatography using alumina column at ambient temperature.

Liquid phase oligomerization reaction of ethylene to higher olefins was carried out with organometallic catalysts, prepared in a glove box under inert atmosphere at different mole ratios of Al:Ti (7.67–7.68) in toluene medium. Toluene was freshly distilled and dried. This was transferred to a 300 ml autoclave (PAAR) under inert atmosphere. Ethylene was charged into the autoclave at 200 psig pressure and the temperature was maintained at 80 ± 5 °C. The reaction mixture was constantly stirred under controlled temperature. The reaction was completed within 30 min when the ethylene pressure dropped to 1 atm. The autoclave was then externally cooled with water at room temperature and opened after taking two gas samples for analysis. Secondary butanol (7–8 ml) was added to the product mixture to deactivate the catalyst in the medium. The autoclave was then washed with few ml of methanol and the liquid product was transferred to a stoppered conical flask. The gaseous and liquid prod-

ucts were analyzed by gas chromatograph (Shimadzu) using OV-17 packed column (PONA).

Vapour phase oligomerization of ethylene to higher olefins was carried out in a glass reactor (32 cm length and 20 mm i.d.) at atmospheric pressure. The reactor was electrically heated to the desired temperature. A requisite amount of catalyst (2.0 g) was charged into the reactor and a mixture of nitrogen and ethylene (each 10 ml/min flow rate) passed from the top of the reactor. The product was collected at the bottom of the reactor and the gaseous samples were collected at different time intervals and passed through gas meter. The reaction products have been analyzed by VARIAN Gas chromatograph using capillary column PLOT Al_2O_3/KCl. The individual product against a particular retention time (RT) was identified by GC-MS and computer library search.
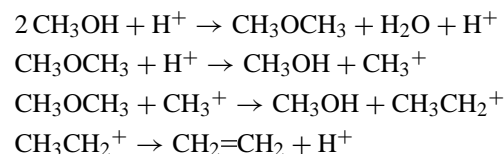
Catalysts were characterized by DTA, IR spectroscopy, XRD and acidity by *n*-butyl amine titration method. The surface area was measured by Quantasorb (Quantachrome Corporation, USA) using nitrogen as the adsorbate.

3. Results and discussion

3.1. Methanol to lower olefins

It is known that heteropoly acids are active for the dehydration of alcohols through Bronsted acid sites. In the present work, the effect of impregnating the heteropoly acid on a support towards the conversion of methanol to hydrocarbons has been studied. Emphasis has been placed on the elemental composition of heteropoly anion with Keggin structure on the product pattern and yield of hydrocarbons specially lower olefins.

The carbonium ion mechanism for the formation of olefins from methanol may be postulated as follows [12].

$$2\,CH_3OH + H^+ \rightarrow CH_3OCH_3 + H_2O + H^+$$
$$CH_3OCH_3 + H^+ \rightarrow CH_3OH + CH_3^+$$
$$CH_3OCH_3 + CH_3^+ \rightarrow CH_3OH + CH_3CH_2^+$$
$$CH_3CH_2^+ \rightarrow CH_2{=}CH_2 + H^+$$

According to this mechanism a carbonium ion is formed from dimethyl ether as a first step on the acidic sites of the catalyst. The carbonium ion thus induces a series of reactions, leading to lower olefins as primary reaction product. It is likely that catalysts having the Bronsted acidity should catalyse the above reaction, since Bronsted acidity favours the formation of carbonium ion.

From the results listed (Table 1) it can be seen that molybdophosphoric acid is selective to methane at both the temperatures studied with negligible amount of ethylene. For tungstophosphoric acid, the selectivity for olefins at 250 °C is 31.8% and on increasing the reaction temperature to 300 °C, the selectivity decreased to 20.0%. In case of tungstosilicic acid (300 °C), the selectivity is 16.0%. The trend observed for the heteropolyacid towards the formation of olefins is of the

Table 1
Conversion of methanol to hydrocarbons

S.No	Catalyst	Temperature (°C)	Distribution of hydrocarbons (wt.%)					
			CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}
1	HPMo	300	96.8	0.6	2.6	–	–	–
2	HPMo	350	97.5	0.7	1.6	–	–	–
3	HSiW	300	72.0	2.0	11.0	7.0	4.0	4.0
4	HPW	250	26.5	2.2	23.8	26.1	8.0	12.5
5	HPW	300	54.0	1.6	16.0	13.0	4.0	11.4
6	HPW/SiO_2	300	33.9	–	44.1	–	22.0	–
7	HPWV/SiO_2	300	84.9	–	15.1	–	–	–
6	HPWV$_2$/SiO_2	300	95.3	0.2	3.6	–	–	–
9	KPW	300	69.3	0.2	16.3	–	6.4	–
10	RbPW	300	80.4	0.2	16.3	–	2.6	–
11	CsPW	300	52.2	1.6	26.2	–	20.0	–
12	CsPW	330	28.9	0.9	34.1	2.1	26.6	7.4

HPMo: molybdophosphoric acid; HSiW: tungstosilicic acid; HPW: tungstophosphoric acid; HPWV: 11-tungsto-1-vanadophosphoric acid; HPWV$_2$: 10-tungsto-2-vanado phosphoric acid; KPW: potassium salt of tungstophosphoric acid; RbPW: rubidium salt of tungstophosphoric acid; CsPW: cesium salt of tungstophosphoric acid.

order HPW > HSiW > HPMo. Thus tungstophosphoric acid (HPW) is the preferred catalyst in this series of heteropoly acids because of higher acidity, hydrolytic and thermal stability compared to tungstosilicic acid (HSiW) and molybdophosphoric acid (HPMo). Although the surface area for HPW is low (Table 2), the acidity is higher than that observed for the corresponding salts. When HPW is supported on SiO_2, it has increased the surface area as well as the acidity. This preparation has shown the maximum selectivity for the olefins (66.1%). The acidity of heteropolyacids arises from protons, partial hydrolysis, acidic dissociation of water coordinated to metal ion and Lewis acidity of metal. In case of HPW/SiO_2 the maximum selectivity can be due to the increased surface area, which has provided a high dispersion of the heteropolyacid, thereby providing more acid sites for the reaction. When the corresponding salt of heteroployacid having different cations were tested, the results show a maximum of 46.2% for CsPW at 300 °C which has further increased to 60.7% when the reaction temperature was increased to 330 °C.

The IR spectra of the K and Cs salts are shown in Fig. 1. The adsorption band around 1600–1700 cm^{-1} indicate protonated water and the band about 3200–3300 cm^{-1} molecular water. The Cs salt reveals two small humps between 2500 and 3000 cm^{-1}, characteristic of free heteropoly acid. It appears that Cs could not fully replace the H^+ of the tungstophosphoric acid. The XRD for the three salts (Fig. 2) show similar

Table 2
Surface area and acidity of catalysts

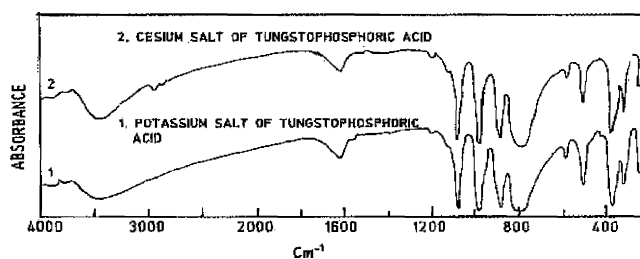| S.No	Catalysts	Surface area (m^2/g)	Total acidity (mmol *n*-butyl amine/g cat.)
1	HPW	3.0	0.83
2	KPW	184.7	0.62
3	RbPW	126.6	–
4	CsPW	68.6	0.40
5	HPW/SiO_2	246.8	1.18

Fig. 1. IR spectra of heteropoly compounds.

pattern except that there is a shift in the 2θ for Rb and Cs. All the salts are in crystalline form. The *n*-butyl amine titre values are shown in Table 2. Between potassium salt of tungstophosphoric acid (KPW) and cesium salt of tungstophosphoric acid (CsPW), the titre value for CsPW is lower and its surface area is also lower, thereby creating an optimum acid site density and acid site dilution which seems to be responsible for higher olefins selectivity. The decomposition of the K-salt begins
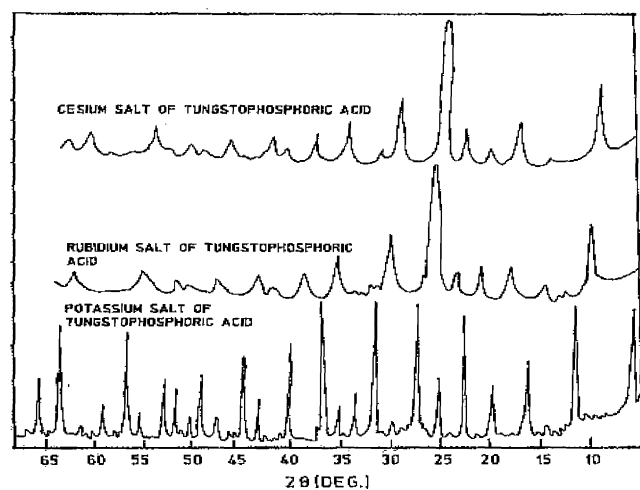

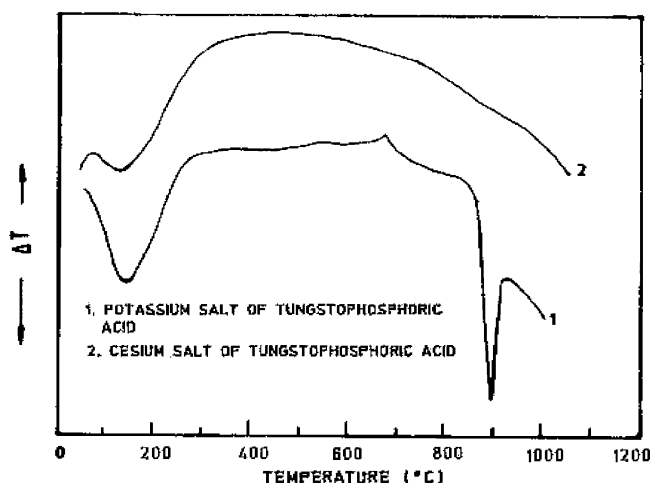Fig. 2. XRD patterns of heteropoly compounds.

Fig. 3. DTA of heteropoly compounds.

beyond 500 °C (Fig. 3). The free acids are characterized by multiple dehydration peaks (endotherm) around 150 °C. The dehydration endotherm is larger for the K-salt compared with Cs-salt and consequently, the retention power together with the presence of some free heteropolyacids as was observed by IR, may be responsible for higher activity of the Cs salt. When W in tungstophosphoric acid is substituted with one or two atoms of V in PW_{12}, olefin yield is found to be decreasing from 15.1% for single atom substitution to 3.6% for two atoms substitution.

Thus, from the study, it appears that HPW/SiO_2 has promise for olefin synthesis followed by CsPW. The results show that carbonium ion mechanism seem to be responsible for the olefin formation.

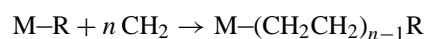### 3.2. Oligomerization of ethylene to higher olefins

This reaction was studied both by employing Ziegler–Natta catalysts in liquid phase as well as by solid acid catalysts in vapour phase. Liquid phase oligomerization of ethylene to higher olefins:

$TiCl_4–Et_3Al_2Cl_3$, $TiCl_4–Et_2AlCl$, $TiCl_4–Et_3Al$, and $Ti(OBu)_4–Et_3Al_2Cl_3$ catalyst systems were employed for the oligomerization of ethylene (Table 3) at 190 psig ethylene and 80 °C in toluene solvent. In all the catalyst systems ethylene conversion is > 96.5%. All the systems generated linear alpha olefins as the major products and polyethylene as by-product. The selectivity to olefins follows the order: $TiCl_4–Et_3Al_2Cl_3$ > $TiCl_4–Et_3Al$ > $Ti(OBu)_4–Et_3Al_3Cl_3$ > $TiCl_4–Et_3AlCl$.
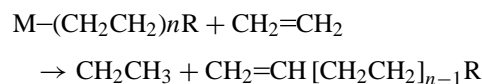
All the systems produce predominantly $C_4–C_{14}$ olefins. It is observed that the maximum selectivity to 1-butene is obtained using $Ti(OBu)_4–Et_3Al_2Cl_3$ system. Better selectivity to $C_6–C_{12}$ alpha olefins is obtained using the catalysts $TiCl_4–Et_3Al$ and $TiCl_4–Et_2AlCl$.

Polyethylene selectivity follows the order: $TiCl_4–Et_2AlCl$ > $Ti(OBu)_4–Et_3Al_2Cl_3$ > $TiCl_4–Et_3Al$ > $TiCl_4–Et_3Al_2Cl_3$. This is in the reverse order of olefin formation with the above catalyst systems. Both the catalytic oligomerization and polymerization can be represented as a combination of chain growth and displacement reactions that take place at an organometallic site (M–R). When the chain transfer takes place at a sufficient rate low molecular olefins [15,16] are produced. If chain growth takes place at a rate faster than the displacement reaction then polyethylene is produced. Conventional chain growth and displacement reactions are represented by the following reactions [17,18].

Chain growth

$$M–R + n\,CH_2 \rightarrow M–(CH_2CH_2)_{n-1}R$$

Displacement

$$M–(CH_2CH_2)nR + CH_2=CH_2$$
$$\rightarrow CH_2CH_3 + CH_2=CH\,[CH_2CH_2]_{n-1}R$$

This study clearly indicates that the catalyst systems studied produce active sites facilitating both the oligomerization and polymerization of ethylene. This is significantly influenced by the ligands of the titanium metal as well as the co-catalysts employed.

3.3. Vapour phase oligomerization

Oligomerization of propylene [19] and higher olefins [20] is reported on zeolites and supported clays. Ethylene was best oligomerized over phosphoric acid. Because of corrosion problem solid acid catalysts have been studied to replace H_3PO_4 containing catalysts [19].

H-ZSM-5 (Si/Al = 100), Ni-SAPO-5, 12-tungstophosphoric acid supported on H-ZSM-5 (Si/Al = 100), $NiSO_4$, $NiSO_4$ /ZSM-5 (Si/Al = 40), $NiSO_4/\gamma$-alumina and potassium salt of tungstophosphoric acid were prepared and tested for the oligomerization of ethylene. The results are shown in Table 4.

Using $NiSO_4$/ZSM-5 catalyst the selectivity to C_4-olefins and C_5-olefins reached a maximum during the time period 90–120 min (at reaction temperature of 300 °C and GHSV =

Table 3
Liquid phase oligomerization of ethylene to higher olefins

S.No	Catalyst (Mol. ratio)	1-$C_4^=$	1-$C_6^=$	1-$C_8^=$	1-$C_{10}^=$	1-$C_{12}^=$	1-$C_{14}^=$	1-$C_{16}^=$	1-$C_{18}^=$	1-$C_{20plus}^=$	Polymer	Sel. (%)	Conv. (%)
1	$TiCl_4/Et_3Al_2Cl_3$ = 7.67	29.2	24.3	12.6	3.0	8.5	7.3	–	–	–	15.1	84.9	96.6
2	$TiCl_4/Et_2AlCl$ = 7.67	20.3	12.2	4.5	1.6	3.8	4.7	4.7	–	–	48.2	51.8	98.2
3	$TiCl_4/Et_3Al$ = 7.67	6.2	3.7	52.2	–	–	–	–	–	–	37.9	62.1	97.8
4	$Ti(OBu)_4/Et_3Al_2Cl_3$ = 7.67	37.8	9.0	2.2	0.6	1.6	1.2	0.7	0.6	1.1	45.2	54.8	97.2

Feed: Ethylene: 190 psig, reaction temperature: 80 °C; solvent: toluene; Sel.: selectivity; Conv.: conversion.

Table 4
Vapour phase oligomerization of ethylene

S. No	Catalyst	GHSV	Composition of the products (wt.%)										
			Ethane	Ethene	C_3	$C_3^=$	C_4	$C_4^=$	C_5	$C_5^=$	C_6	$C_6^=$	*
1	HZSM-5(Si/Al = 100)	882	0.14	85.74	0.92	0.79	1.89	8.92	0.87	0.36	0.19	0.10	0.08
2	Ni-SAPO-5	1710	16.01	82.94	0.35	0.32	0.11	0.20	0.01	0.02	–	–	–
3	HPW/HZSM-5(Si/Al = 100)	819	–	82.24	–	0.91	11.52	0.48	4.13	0.72	–	–	–
4	NiSO$_4$/ZSM-5(Si/Al = 40)	849	96.54	–	0.72	0.45	0.72	0.47	1.10	-	–	–	–
5	NiSO$_4$/γ-Al$_2$O$_3$	1042	–	95.94	–	–	–	1.36	1.24	1.32	–	0.14	–
6	KPW	424	–	77.67	–	2.54	16.0	0.04	0.50	3.75	–	–	–

Ethylene: 10 ml/min; nitrogen: 10 ml/min; temperature: 300 °C; pressure = 1 atm.; catalyst weight: 2.0 g.

* Dienes.

849). Using NiSO$_4$/γ-alumina as catalyst the selectivity to C$_5$ and C$_6$ olefins were maximum at 120–150 min duration (at 300 °C and GHSV = 1042). When 12-tungstophosphoric acid supported on H-ZSM-5 is employed as catalyst the selectivity to C$_4$-olefins and C$_5$-olefins reached a maximum at 0–30 min duration at a reaction temperature of 300 °C and GHSV = 819. Using H-ZSM-5 (Si/Al = 100) as catalyst the selectivities to C$_4$-and C$_5$–C$_6$-olefins is maximum at 30–60 min and 0–30 min duration, respectively. Selectivity to iso-butane and iso-pentane is also found to very high at reaction temperature of 300 °C and GHSV = 882.

The maximum selectivity of C$_4$–C$_6$ olefins achieved is 10.0 wt.% with HZSM-5 catalyst (Si/Al = 100). The selectivity to higher olefins was less in comparison with that obtained by liquid phase oligomerization of ethylene. Further the olefins obtained in vapour phase oligomerization is a mixture of linear, internal and branched olefins. This indicates cracking, isomerization and oligomerization reactions are taking place on the acidic sites of the solid acid catalysts.

4. Conclusion

In the conversion of methanol to C$_2$–C$_3$ olefins the maximum activity and selectivity of the catalysts depends on an optimum acidity and specific surface area.

In the liquid phase oligomerization of ethylene, among the catalysts tried TiCl$_4$ and Ti(OBu)$_4$-based catalysts showed better activity and selectivity to α-olefins in the range C$_4$–C$_{14}$. Polyethylenes are obtained as by-products.

In vapour phase oligomerization of ethylene C$_3$–C$_6$ olefins are achieved besides the corresponding saturates with the solid acid catalysts studied. The selectivity to higher olefins was less in comparison with that obtained by liquid phase oligomerization reaction. Further the olefins are a mixture of terminal, internal and branched compounds.

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