



Effect of Alkali and Transition Metal Cations-Modified-ZSM-5 Catalysts in Oxidative Dehydrogenation of Propane to Propylene

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In this work, ZSM-5 modified with lithium, potassium, caesium, chromium and molybdenum were produced by solid state reaction and their respective catalytic properties were investigated using a laboratory fixed bed reactor in oxidative dehydrogenation of propane to propylene. The results showed that the incorporation of the metals influenced the conversion of propane and the selectivity to propylene due to their adjustments of the catalyst's acidity and led to a reduction in average pore diameter and pore volume. However, the crystalline structure of the original parent zeolite was not strongly affected by the presence of the metals as observed from the XRD and FTIR analyses. Li-ZSM-5 showed the highest selectivity to propylene and low conversion of propane. Mo-ZSM-5 showed good activity and reasonable selectivity at both low and high temperatures of the reaction (70 % selectivity and 43 % conversion). All the catalysts tested showed good activity and reasonable selectivity at the highest temperature of the reaction.

Keywords: Oxidative Dehydrogenation, Propane, Propylene, Selectivity.

INTRODUCTION

Catalytic oxidative dehydrogenation (OXD) of propane to propylene has attracted considerable attention, because propylene constitutes an important and versatile intermediate in the petrochemical industry. It is the raw material for the production of polypropylene, polyacrylonitrile, acrolein, acrylic acid, propylene oxide and so on. Currently the majority of propylene is obtained as a by-product of ethylene production by the steam cracking and fluid catalytic cracking of naphtha and gas oils. Steam cracking and fluid catalytic cracking will not be able to cover the expected demand of propylene in the coming decades¹⁻³. Dehydrogenation of propane is an endothermic reaction; therefore, relatively high reaction temperatures are needed to obtain high propane yields. The high reaction temperatures favour thermal cracking reactions to form light alkanes and alkenes leading to decreased product yield and increased catalyst deactivation¹. Catalytic oxidative dehydrogenation of propane by oxygen is an attractive alternative because it is an exothermic and non-thermodynamic limited reaction¹⁻². However, the low propylene selectivity of the process caused by propane over-oxidation, remains an unsolved problem. Consequently, this prompted extensive research to get an effective and efficient catalyst with high selectivity. The main reason for the low selectivity of propylene is the relatively higher reactivity of the desired product molecule;

propylene, that can undergo rapid consecutive over-oxidation in the presence of catalyst able to activate the much less reactive alkane molecule⁴. In order to address this problem, a large variety of different catalysts were investigated by many researchers. The mixed oxides and modified heteropoly compounds (HPC) containing molybdenum or tungsten as terminal atoms have been considered for the propane oxidation⁵. Corberan⁶ developed novel approaches to address the problem with oxide hydrogenation along three complimentary directions: (1) Oxide nanocatalysts preparation by non-conventional routes, to tune the nature of the active center; (2) Oxidant selection, to avoid over oxidation; (3) Catalyst arrangement, to take advantage of the reaction mechanistic features.

Among all the studied catalysts, zeolite supported metal-oxide-based catalysts have been proved as the most promising ones due to their high catalytic activity^{2,5,7}. Zeolites are class of microporous crystalline materials that find wide spread use in the petrochemical industry. ZSM-5, a typical MFI-type zeolite is considered to be a good catalyst or catalyst support^{1,8-11} because of its unique properties, including tridimensional micropore structure, high surface area, high thermal and hydrothermal stability, special molecular sieving and shape selectivity. Transition metals, alkali, alkaline earth and rare earth metals modified ZSM-5 catalysts have been investigated and proven to be good and promising catalysts for propane conversion to propylene. Recently, Sazama *et al.*¹² studied the

structure and function of Fe and acid sites in propane oxidative dehydrogenation over Fe-ZSM-5 catalyst using N_2O as mild oxidant. Also in a recent research work on the use of zeolites as support in propane dehydrogenation, mononuclear pseudo-tetrahedral vanadium species of VSiBEA zeolite catalysts was discovered as the active sites for the reaction¹³. The influence of various promoters and the performance of the resulting catalyst in enhancing the selectivity to light olefins have also been studied^{1,2,7,11,14}.

Cations can be introduced into ZSM-5 through different ways such as aqueous and solid-state ion exchange, chemical vapor deposition, mechanical mixing and synthesis¹⁵. Among the various processes used to introduce metal ions into ZSM-5 solid-state ion-exchange avoids handling of large volume of solution and their waste¹⁶. Solid-state ion-exchange results in the formation of extraframework species which have different reactivity from that of the exchanged ions conducted in liquid phase¹⁷.

Numerous publications are available on the extra framework species supported catalyst. Chromium species on various supports such as Al_2O_3 , TiO_2 , SiO_2 , MgO , ZSM-5 have been reported¹⁸⁻²⁰. The stabilities of these species were related to the strength of their interactions with the supports. In case of propane oxidative dehydrogenation on chromium-based catalysts, the active centers are identified to be Cr^{3+} clusters generally resulting from the reduction of higher oxidation states²⁰. Wu *et al.*²¹ reported that Cr^{6+} as the key factor in achieving high activity in oxidative dehydrogenation of propane over Cr_2O_3 - ZrO_3 catalysts using CO_2 as mild oxidant. Potassium on ZSM-5 on the other hand has been reported to show high catalytic activity for oxidation of hydrocarbon²². There have been several explanations on the role of potassium in the catalytic reaction. Its affinity to adsorb oxygen and intermediate formation of its eutectic compounds with other components to form further active phase are among the factors that are considered to be important²³. Molybdenum oxide precursors on ZSM-5 are suggested to be initially located on the external surface and subsequently transformed to molybdenum oxo species which are redistributed at the external and the internal structure²⁴. Burns *et al.*²⁵ demonstrated that the resultant molybdenum oxo species leads to the distortion of ZSM-5 framework and the reduction of the bronsted acid site strength.

In this work, HZSM-5 was ion-exchanged with some metal precursors using solid-state procedure. This work involves the preparation of lithium, caesium, potassium, chromium and molybdenum supported by HZSM-5. The influence of the extra framework species on the ZSM-5 properties and the catalytic performances were studied.

EXPERIMENTAL

Catalyst preparation: Na-ZSM-5 ($SiO_2/Al_2O_3 = 40$) zeolite was transformed to H-ZSM-5 by ion-exchange with ammonium chloride (1M, Sigma-Aldrich, 99.8 %) at room temperature. NH_4^+ exchange was repeated three times using fresh NH_4Cl and subsequently washed to remove the chloride. NH_4ZSM-5 sample was calcined at 600 °C for 3 h to obtain H-ZSM-5. The 10 wt % metals from their respective precursor; anhydrous lithium chloride (BDH, 99 %), potassium chloride (BDH, 99 %), caesium nitrate (BDH, 99 %), chromium (III)

nitrate monohydrate (Sigma-Aldrich, 99 %) and ammonium molybdate were incorporated on the H-ZSM-5 by solid-state reaction. The H-ZSM-5 and the precursor salt were grounded and then calcined under air in a furnace at 600 °C for 3 h.

Catalyst characterization: The samples obtained were characterized using adsorption-desorption of N_2 at 77.4 K, on a Quantachrome Autosorb 1C analyzer. The samples were outgassed at 300 °C for 3 h, under flow of helium prior to analysis. The properties obtained are: BET surface area (m^2/g) and pore volumes from nitrogen held at $P/P_0 = 0.00965$ (VP, cm^3/g). The B.J.H method was employed to determine the average pore radius. Philips analytical X-ray diffractometer (PW1710) was used for the structural characterization scanning at 2θ angle range of 3 to 70° at a step size of 0.020° using Cu radiation. The FTIR spectra were collected on Perkin Elmer 2000 using KBr as the diluent and binder.

Catalyst performance test: Propane reaction was carried out in fixed bed stainless tubular microactivity-reference reactor (PID Eng and Tech, Spain). The microactivity reference unit is an automated and computer-controlled laboratory reactor for catalytic microactivity tests. It consists of stainless steel tubular reactor of 305 mm length and 9 mm internal diameter heated by a tube furnace whose temperature is monitored by an axially located thermocouple in contact with the catalyst bed. The reactor furnace and flow lines are enclosed in a hot box system heated by an electric forced convection heater that allows the process route to be kept at temperature of 170 °C to avoid possible condensation in the system. The feed was introduced into the hot box under the following conditions: feed flow rate of 20, 5 and 50 mL/min for propane, oxygen and argon, respectively, at reaction temperatures of 350, 400, 450, 500 and 550 °C. The reactor bed comprised of 0.5 g of lithium, potassium, caesium, chromium or molybdenum on HZSM-5 and 1 g glass bead diluent. Conversion and selectivity data were obtained using gas chromatography (Perkin Elmer, Clarus 500) attached to the reactor outlet. The GC was equipped with 50 m long alumina PLOT capillary and 13X molecular sieved packed columns.

The oven temperature was specified to achieve fast separation of light hydrocarbons and permanent gases. Oven temperature program: 60 °C hold for 1 min, increase to 80 °C at a rate of 20 °C/min, then increase to 200 °C at a rate of 30 °C/min. The packed column temperature: 150 °C. The detectors-thermal conductivity and flame ionization were operated at 200 °C. It was calibrated to identify low molecular weights of alkanes, alkenes, hydrogen, oxygen, CO and CO_2 .

RESULTS AND DISCUSSION

Catalyst characterization: The surface area, pore volume and average pore diameter of the catalytic samples are given in Table-1. Reductions in the above quantities were observed in the initial parent HZSM-5 when the metals were incorporated into the zeolite matrix. The reduction in average pore diameter and pore volume when compared with parent HZSM-5, lead to decrease in surface area noticed in all the catalyst samples. The decrease in the average pore diameter suggests disposition of metals in the wider pore, thereby increasing the proportion of the narrower pores. This decreases

the average diameter. In addition, the reduction of the surface area of the modified catalysts compared to the HZSM-5 support may be due to the pore filling of the supports by the respective metal species since they occupied both internal and external surfaces. The metals may also block part of the narrow pores. This leads to overall decrease in the surface area. In addition, the changes in the surface areas and porosity may suggest structural changes in the catalyst.

TABLE-1
PHYSICOCHEMICAL PROPERTIES OF CATALYSTS SAMPLES

Catalyst sample	S_{BET} (m^2/g)	Pore volume (m^3/g)	Pore diameter (nm)
Li/HZSM-5	62.22	0.005045	0.9835
K/HZSM-5	351.00	0.03468	1.198
Cs/HZSM-5	242.10	0.02571	0.9626
Cr/HZSM-5	383.70	0.03420	1.264
Mo/HZSM-5	200.60	0.01418	1.265
HZSM-5	424.80	0.05349	1.69

The diffraction peaks from the XRD analysis as shown in Fig. 1 indicated that all catalyst samples have good crystallinity and exhibited the typical characteristic XRD profile² of ZSM-5. However, the intensity of the diffraction peaks of the mother zeolite (HZSM-5) is a bit higher than that of the other samples which indicates it has a higher crystallinity. The XRD patterns showed different degrees of surface structural modifications of the catalysts due to the introduction of different alkali and transition metals. Addition of Cs (perhaps on account of its bigger size) led to substantial decrease in characteristic peaks at $2\theta = 24$ associated with ZSM-5. Other metals exhibited less effect on the structure. This indicates extra-framework addition of the metals. Cr-HZSM-5 catalyst clearly reveals additional XRD lines at $2\theta = 34, 38, 42, 51$ and 56° attributable to $\alpha\text{-Cr}_2\text{O}_3$ which can be formed and aggregated during the thermal decomposition of nitrate ions²⁶. Also, K-HZSM-5 displays additional peaks attributed to potassium silicate ($\text{K}_x\text{Si}_y\text{O}_z$) and K_2O which might have originated from the reaction between potassium atoms and extra framework silicate phases of the zeolites²².

The IR spectra of the catalyst samples in the region of $1600\text{-}400\text{ cm}^{-1}$ are shown in Fig. 2. The metal modified zeolites spectra did not show alteration from the mother sample (HZSM-5) indicating that the metals are not in framework positions. An exception to that is K-HZSM-5 which shows the disappearance of the spectra bands at 450 and 500 cm^{-1} . The 450 cm^{-1} band is related to the bending modes of Si-O bonds in the SiO_4 tetrahedra²⁷ while the band at 500 cm^{-1} is due to double ring vibration peculiar to pentasil structure²⁸. The formation of potassium silicate phase ($\text{K}_x\text{Si}_y\text{O}_z$) from the reaction of potassium atoms and the extra framework silicate phases of the zeolite as confirmed by XRD is responsible for this alteration. An intense IR skeleton vibration bands at 550 cm^{-1} which is attributed to the vibration of larger parts of the structure (external) indicates that the silica tetrahedra are locally organized according to a zeolitic structure^{26,29}. The absorption bands related to the internal vibration of TiO_4 tetrahedra which is a characteristic peaks of ZSM-5 ($1080, 800$ and 450 cm^{-1}) in the zeolitic matrix were found^{4,30}.

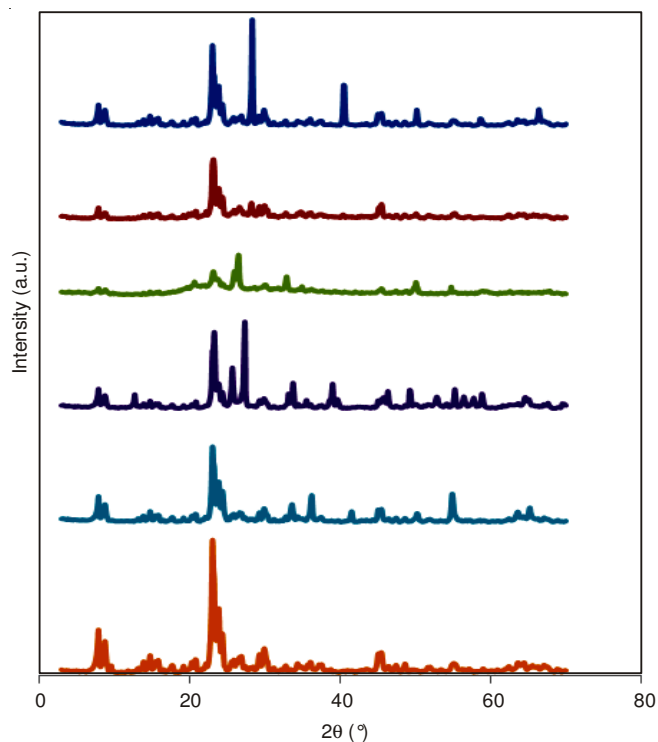


Fig. 1. XRD patterns of the catalytic samples

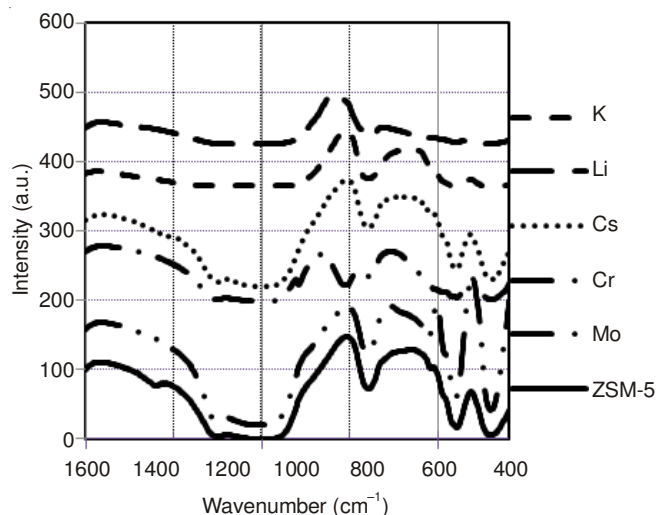


Fig. 2. IR spectra of the catalyst samples from FTIR analysis

Performance of catalyst: Exchanging zeolites with a less electronegative charge balancing cations of alkali metals such as Li, K, Cs and/or occlusion of alkali metal oxide clusters in zeolite cage makes the zeolite basic. Lithium modified ZSM-5 catalyst showed little activity in propane oxide hydrogenation at both low and high temperatures of the reaction and had the lowest conversion of propane compared to other modified catalysts tested. Because of the presence of structural microporosity in the parent zeolite which allows diffusion of guest ions, Li^+ blocks some micropores in the structure as evident from the sharp reduction in surface area from the parent zeolite and this leads to low activity. In contrast to the conversion, Li-HZSM-5 demonstrated high selectivity to propylene at all reaction temperatures tested. This may not be unconnected with the ability of Li^+ to selectively eliminate strong acid sites (NH_3 desorption temperatures above 400°C)³¹

and decrease weak and moderate acid sites (desorption temperatures of < 350 and 350-400 °C, respectively). Strong acid sites have been associated with the formation of cracking products (Fig. 3).

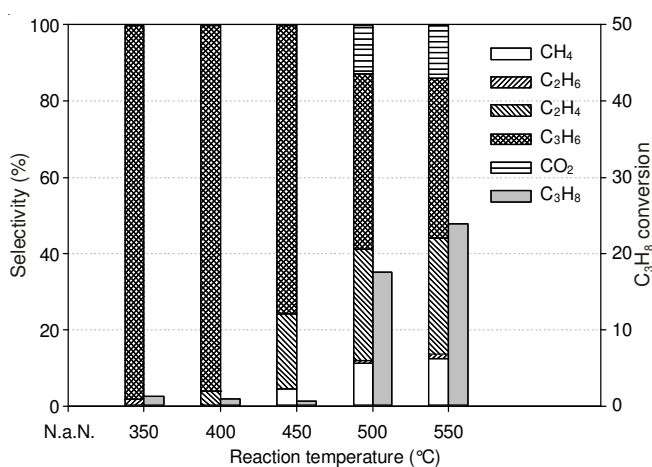


Fig. 3. Selectivity and conversion as a function of temperature for Li-ZSM-5 catalyst

Potassium and caesium modified ZSM-5 showed good activity in oxidative dehydrogenation of propane to propylene. The conversion increased with increasing temperature from 350 to 550 °C as shown in Figs. 4 and 5. The highest conversions achieved were 42.94 and 38.45 % at 550 °C for K-ZSM-5 and Cs-ZSM-5, respectively. K⁺ and Cs⁺ influenced the activity of the catalyst by eliminating all kind of acid sites (strong, moderate and weak) at the 10 wt % catalyst loading used. In addition, potassium reaction with the extra framework silicon to produce a new phase within the framework of the zeolite may have led to generation of strong bronsted acid sites like Si(OH)K responsible for high activity observed.

The cracking ability of zeolites depends on acidity. The global acidity of a given zeolite is the result of two parameters of bronsted sites (active sites), *i.e.*, their density (or their concentration) and their strength¹¹. The density of bronsted acid sites decreases when the Si/Al ratio of the zeolitic framework increases, since the ion exchange capacity corresponds to the Al³⁺ content of the zeolite. The strength of the bronsted acid sites depends on the interaction between the proton and the

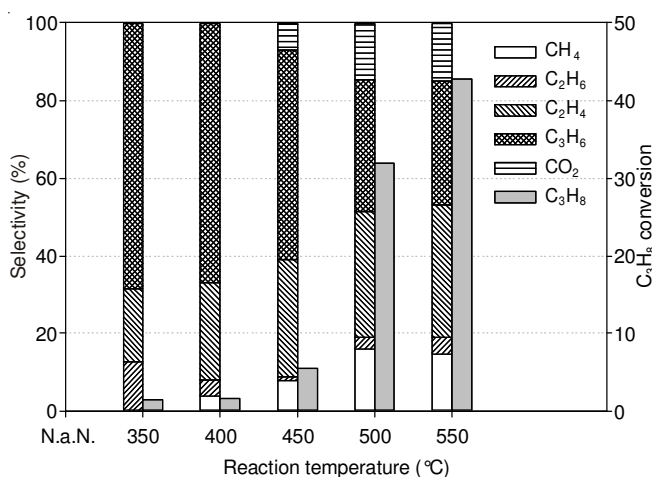


Fig. 4. Selectivity and conversion as a function of temperature for K-HZSM-5

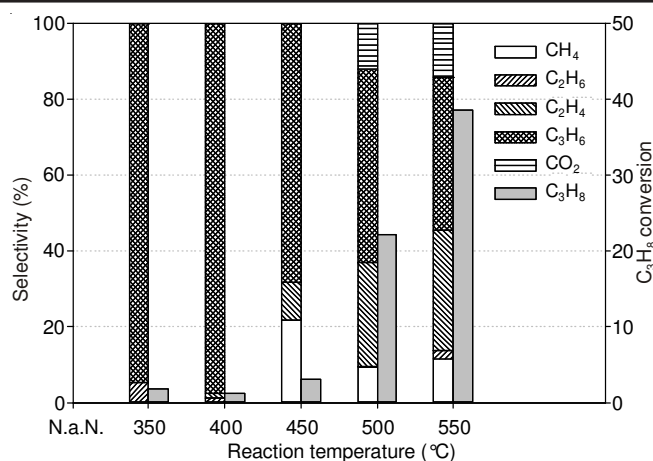


Fig. 5. Selectivity and conversion as a function of temperature for Cs-HZSM-5

zeolitic framework or the environment of the framework Al. Also, the strength of the Brønsted acid sites is affected by isomeric substitution and on the type of hetero atom.

One of the major roles of the alkali metals is the modification of the acid character by weakening acid strength or reducing acid sites. In summary, the modification of HZSM-5 with Li, K and Cs influences differently on the zeolitic acidity, which is directly related to the alkalinity. With the increase of alkalinity of alkali metal ion from Li⁺, K⁺ to Cs⁺, the ability to reduce the zeolitic acidity is increased but the selectivity to eliminate the strong acid sites on zeolite is decreased accordingly. This is the reason why Li-HZSM-5 showed high selectivity to propylene but low propane conversion.

Transition metals modified zeolites behave as bifunctional catalysts where active sites on the metal are used for hydrogenation or dehydrogenation and the acidic sites on the zeolite for cracking, isomerization and so on. In addition to bifunctional mechanism, modification of ZSM-5 with transition metals adjusts the catalytic acidity¹¹. Transition metals have partially occupied *d*-orbitals the symmetry of which is suitable for formation of chemical bonds with neutral molecules. These metals also have several stable oxidation states and different coordination numbers as a result of the changes in number of *d*-electrons. The catalysis by transition metals (organometallic compounds) is based on activation of the substrate by coordinating it to the metal, which lowers the activation energy of the reaction between the substrate¹⁰.

The dehydrogenation of propane to propylene in the presence of oxygen over ZSM-5 supported chromia and molybdena catalyst were investigated at temperatures from 350 to 550 °C. The results are shown in Figs. 5 and 6. Propylene is the major product formed, other by-products produced are methane, ethane, ethylene and carbon dioxide. Oxygenates and aromatics were not detected. As can be seen from the results, at low reaction temperature (350-450 °C) conversion of propane was low while high selectivity to propylene was observed for both Cr-HZSM-5 and Mo-HZSM-5.

Cr-HZSM-5 shows high conversions at low reaction temperatures compare to other catalysts but low selectivity to propylene. Transition metals, such as Cr, introduced into Pentasil type zeolites are generally used as active components for hydrogenation, dehydrogenation or aromatization reactions.

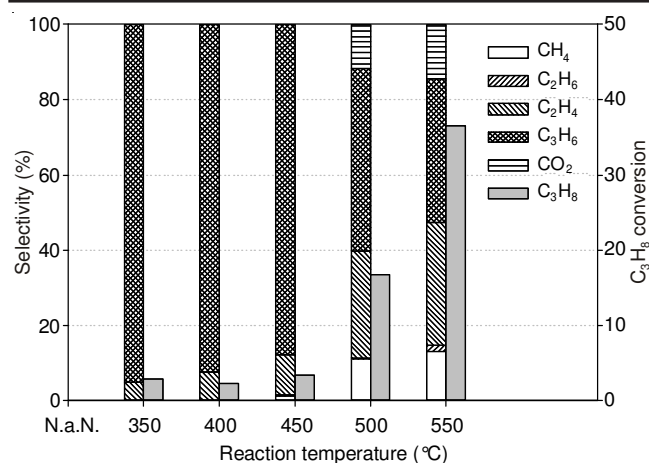


Fig. 6. Selectivity and conversion as a function of temperature for Cr-HZSM-5

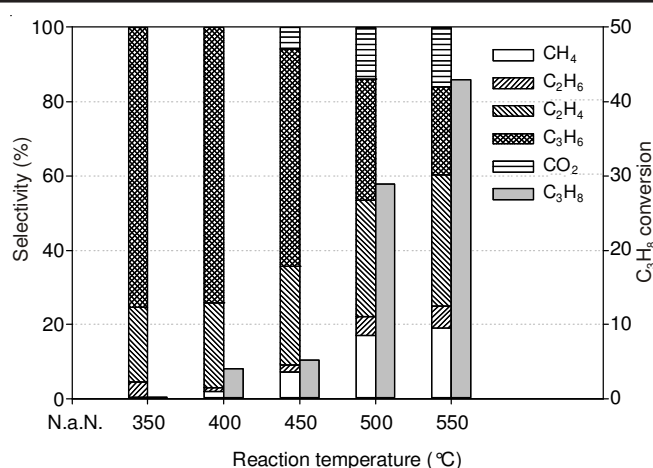


Fig. 7. Selectivity and conversion as a function of temperature for Mo-HZSM-5

Lewis acid sites play a role in the initial stages of cracking as reported by many researchers¹¹. It results in the olefin formation that can, initiate, or at least enhance the cracking reaction. Zhang *et al.*² proposed that Cr(III) species are responsible for high catalytic activity of supported chromia catalysts in light alkane dehydrogenation whereas Wu *et al.*²¹ found out that the presence of Cr⁶⁺ enhances the activity of the same type of catalysts using CO₂ as mild oxidant. When Mo-HZSM-5 was used for the dehydrogenation of propane in the presence of oxygen, high conversion and selectivity to propylene were observed at both low and high temperatures of the reaction. Molybdena is reported by many researchers as a good catalyst for selective oxidation of light hydrocarbons³². Mo-HZSM-5 proved to be a promising catalyst for the production of light olefinic hydrocarbons from propane as over 70 % selectivity to propylene and ethylene at 43 % conversion was recorded. Fu *et al.*³³ reported that coordinated Mo(V) that poison the stronger acid sites needed for cracking, leads to low selectivity to cracking products and high activity in propane dehydrogenation as shown by its high conversion. In the presence of strong acid sites, dehydrogenation and cracking occur simultaneously whereas over medium/weak sites, the process was found to occur *via* consecutive reactions³⁴. C-H bonds activation on weak and medium acid sites are known to lead to olefins as the products of the reaction, while C-C bonds that lead to cracking products are primarily activated on strong acid sites (Fig. 7).

In all the catalysts tested in this work the selectivity of propylene decreased with temperature and conversion (Figs. 8 and 9) as a result of increase in the amount of by-products methane, ethylene and carbon dioxide. The amount of carbon dioxide formed increased with temperature but was not detected at low temperatures of the reaction for the alkali metals modified ZSM-5. The carbon dioxide is formed due to the presence of total oxidation sites on the catalysts.

High conversion and low selectivity was noticed at the highest temperature of the reaction (550 °C) for all the catalyst systems as shown in Fig. 9. The reasons are: formation of cracking products and CO₂ and gas phase reactions typical of most hydrocarbons at high reaction temperature.

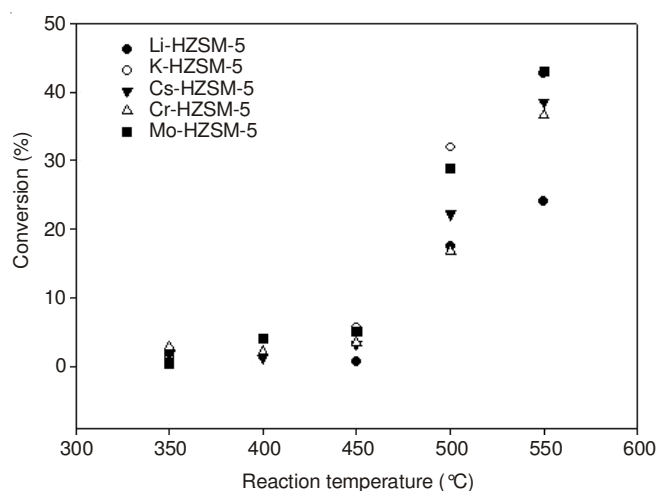


Fig. 8. Variation of Temperature with conversion for all the catalyst samples

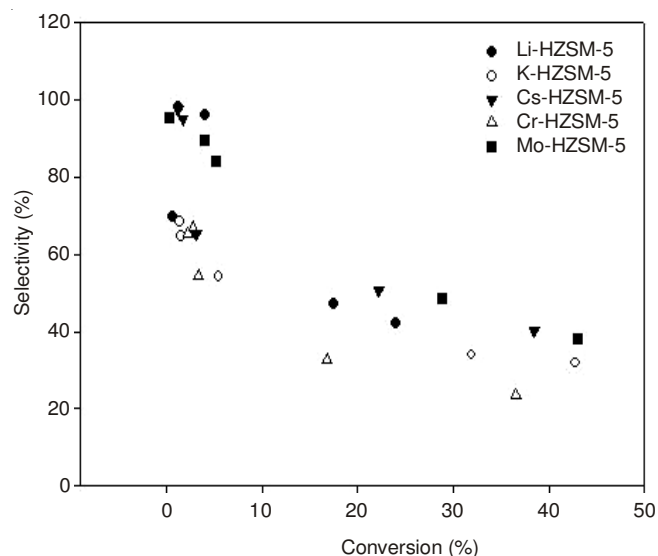


Fig. 9. Variation of conversion with selectivity at 550 °C for all the catalyst samples

Thus, on ZSM-5 modified lithium, caesium and potassium catalysts, it was shown that incorporating alkali metals decreased conversion but increased the selectivity of propylene at the expense of other by-products. The reason should be the basic surfaces facilitate the desorption of alkenes, more basic

compounds than the corresponding alkanes, thus preventing them from further reaction/oxidation³² to products/CO₂.

However, the effect of the acid base properties on selective oxidation of hydrocarbons is more complex since it should depend on the nature of the catalyst and hydrocarbon molecule. In the case of propane molecule, selective oxidation to propylene also needs Brønsted acid sites. The different routes to propylene and CO_x, respectively, are probably differently sensitive to the acid-base nature and strength of the used catalyst.

Conclusion

ZSM-5 modified with lithium, potassium, caesium, chromium and molybdenum were prepared by solid state reaction and their respective catalytic properties were investigated in oxidative dehydrogenation of propane to propylene. The catalytic analyses showed that incorporation of metals influenced the conversion of propane and selectivity to propylene, this may be due to the adjustments of the catalyst's acidity. Although most of the metals did not strongly affect the crystalline structure of the original parent zeolites (HZSM-5) based on the XRD and FTIR analyses, Cr-HZSM-5 and K-HZSM-5 revealed additional peaks. These peaks were attributed to α -Cr₂O₃ and K₂Si₂O₇, respectively. The former was formed and aggregated due to thermal decomposition of nitrate ions from the catalyst precursor [chromium(III) nitrate] while potassium silicate as a result of interaction of potassium atoms with extra framework species. Li-HZSM-5 showed high selectivity to propylene and low conversion of propane probably, this is due to its ability to eliminate strong acid sites which are responsible for the formation of other cracking products. Mo-HZSM-5 showed good activity and selectivity to propylene at both low and high temperatures of the reaction which can be attributed to the presence of molybdena and/or molybdenum oxo species after calcination of the catalyst at 600 °C. All the catalysts investigated in this work showed good activity and reasonable selectivity at high reaction temperatures (500-550 °C) which implies, they are all promising catalysts for the dehydrogenation of propane to propylene in the presence of oxygen.

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