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Ethanol Conversion to Ethylene Using Metal-Mordenite Catalysts

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Abstract: The aqueous ethanol conversion was investigated on dealuminated mordenite (DM) and a series of DM/metal catalysts prepared by impregnation (IMP) and solid-state ion exchange (SSIE). The catalysts were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), nitrogen adsorption method (BET). The conversion of aqueous ethanol (10.0%) on mordenite/metal catalysts was compared at temperature of 350°C. reaction time of 1 h, WHSV (weight hourly space velocity) of 1 h^{-1} and catalyst weight of 1 g. The product is mainly ethylene with small quantity of other light olefins. At higher temperature (550°C) methane was formed as a result of decomposition reaction. Among several metals (Zn, Mn, Co, Rh, Ni, Fe and Ag) which were incorporated onto the mordenite to prepare DM/single and mixed metal catalysts tested in this work, it was found that DM/Zn and DM/Zn-Ag catalysts prepared by impregnation method gave the highest selectivity to ethylene. For DM/Ni catalyst, it showed high selectivity to ethane due to its hydrogenation ability.

Keywords: ethanol conversion; metal-supported mordenite; catalyst; ethylene

1. Introduction

Conversion of methanol and ethanol to gasoline and other hydrocarbons has received wide attention due to the global energy crisis and the heavy demand for hydrocarbons. The ethanol obtained by fermentation of vegetable biomass and agricultural residues (a renewable and relatively abundant raw material) is an interesting alternative in developing countries wishing to reduce their dependency on petroleum as well as revitalize both agricultural activity and the local fermentation industry [1]. Fermentation of biomass to ethanol results in mixtures containing about 95% water and 5% ethanol. Methods for separating water including distillation or extraction with liquid solvents or with CO_2, azeotropic distillation to obtain absolute ethanol are energy-consuming and expensive. Catalytic transformation of alcohol into hydrocarbons is useful for petrochemical raw materials or as a motor fuel. The process is called BTG (bio-ethanol-to-gasoline), one major product is ethylene [2, 3]. Several catalysts were developed inclding zeolites [4, 5]. Zeolites have been widely studied because of their particular structure. The concentration and strength of acid sites is an important factor in both the activity and the selectivity of the zeolite cata-

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lyst. Ways of modifying the acidity of zeolites are dealumination [6] and cation exchange [7]. The presence of metal on these catalysts may modify the Bronsted centers of the zeolite and the metal state may be modified by the influence of the support [8]. Various techniques are available to introduce metals into zeolites, for example, impregnation and solution ion exchange [9, 10]. Solid state ion exchange (SSIE), is a highly efficient procedure, which has attracted increasing attention in recent years. [11] Light alkenes are produced from methanol with a modified ZSM-5 zeolite [12, 13], or dealuminated mordenite [14]. Mordenite is naturally-occurring silica-rich aluminosilicate. It has a one-dimensional, 12-ring channel system with side pockets involving 8-ring channel [15].

The aim of this work is centered on upgrading aqueous ethanol, transforming it to light olefins, which are themselves the starting materials for industrial products. Using aqueous ethanol is a benefit that the operation involving ethanol concentration can be avoided. The results of ethanol conversion over dealuminated mordenite as well as the effect of modification of mordenite with various metal promoters on activity and selectivity to ethylene are presented.

2. Experimental

2.1. Preparation of H-mordenite and dealuminated mordenite (DM)

The Na-form mordenite ($SiO_2/Al_2O_3 = 5.66$) was converted into the ammonium form by an ion-exchange method with an ammonium chloride solution. The H-form was obtained by calcining in air at 500°C for 6 h. Dealuminated mordenite (DM) was prepared by leaching H-mordenite in 8 M hydrochloric acid at 80°C for 5 h, dried at 100°C and calcined at 550°C.

2.2. Preparation of DM/metal

Metal incorporation (Zn, Mn, Co, Rh, Ni, Fe and Ag) was carried out using two different methods. In solid state ion exchange (SSIE) method, the dealuminated mordenite was mixed with metal salt (1% by wt of mordenite) and ground, dried at 120°C and then air-calcined at 550°C for 5 h. For mixed metals catalyst, after the incorporation of the first metal, the second metal (1% by wt) was then mixed into the DM/first metal and air-calcined at 550°C for 5 h. In impregnation (IMP) method, 5 mL aqueous chloride solution of selected metal **(**1% by wt of mordenite) was slowly dropped onto the dealuminated mordenite and mixed thoroughly, then the calcination was performed as above. For mixed metals catalyst, the solution of the second metal **(**1% by weight of mordenite) was then added and mixed with the DM/first metal.

In the catalytic reaction, each catalyst was packed in the reactor and activated under flowing N_2 at 500°C for 1 h and then reduced with flowing H_2 at 500°C for 1 h.

2.3. Catalyst characterization

The structures of the mordenite and DM/metal catalysts were recorded using Powder X-ray diffractograms by Rigaku, DMAX 2002/ Ultima Plus diffractometer equipped with a rotating anode using Ni filtered Cu-Kα radiation between 2 and 30^o (2θ) with a scanning rate of 2^o/min. Silicon (Si), aluminum (Al) in the catalysts were determined by XRF using a SISONS instrument ARL 8410 X-ray fluorescence spectrometer. The surface area was measured by nitrogen adsorption method (BET). Fourier transform infrared spectra were measured on Nicolet FT-IR Impact 410 spectrometer (resolution 4 cm^{-1}). The solid samples were prepared by pressing the sample with KBr. Temperature programmed desorption of ammonia (NH_3-TPD) was used to identify the acid site of the catalyst.

The amount of coke deposited during reaction was measured by thermogravimetry (TG) on a TA instrument thermogravimetric analyzer (SDT 2960) at the heating rate of 10°C/min under nitrogen atmosphere. The %coke on the catalyst was also confirmed by the difference in mass before and after calcinations at 550°C for 2 h.

2.4. Catalytic activity measurements

The experimental set-up is shown in Fig. 1. Catalytic test reactions were carried out in a fixed bed downstream quartz tubular reactor of 10 mm inner diameter. One gram of catalyst sample (crushed into 2 x 2 x 0.7 mm^3) was loaded into a middle part of a reactor and held in place using quartz wool support. The catalyst portion was covered with small amount of quartz wool. The height of the catalyst portion was 25 mm. The aqueous ethanol was fed using a Milton Roy syringe pump into nitrogen stream, passed from the top through the catalyst at a WHSV (weight hourly space velocity) of 1.00 h^{-1}, time on stream = 1 h. The temperature of the catalyst bed was monitored using a thermocouple located at the center of the reactor. Desired temperature was set using temperature controller to the range of 350-550°C. The reaction products were passed through a cooling system to separate condensable components from light gaseous products. The gaseous products were collected into a Tedlar bag and were analyzed by gas chromatography (Hewlett Packard-6890) by means of detectors based on thermal conductivity (TCD) and flame ionization (FID). The separation of products was carried out by means of a system made up of following columns: Carbowax Porasite column, Chromosorb column, Carbowax column, Carbopak B column, Hayesep Q, Hanesep T column, Molecular Sieve 5A column, Hanesep Q column and Molecular Sieve 13X column. The liquid products were analyzed by using a PONA capillary column.

Sets of experiments were carried out at atmospheric pressure, by feeding 10.0% ethanol (aqueous). For each sample, at least two runs were performed with the same feed. The activity data are reported in terms of ethanol conversion and product distribution, which is defined as mol% of each product/ mol % of hydrocarbons.

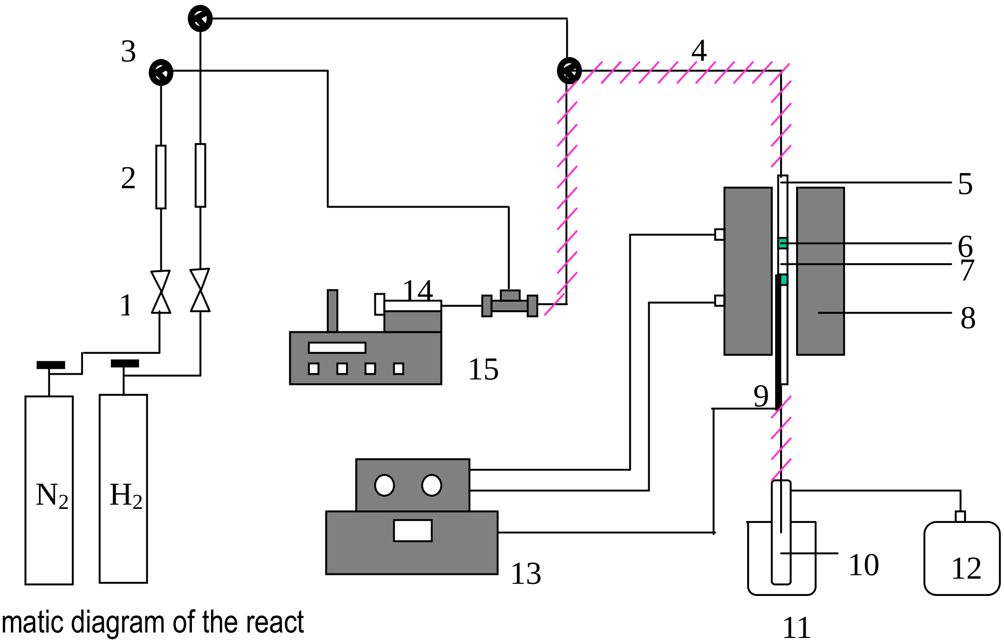

Figure 1. Schematic diagram of the react

1 = needle valve, 2 = flow controller, 3 = three-way valve, 4 = heater cable, 5 = tubular reactor, 6 = quartz wool, 7 = catalyst, 8 = electric furnace, 9 = thermocouple, 10 = cold trap,11 = dry ice-acetone bath, 12 = Tedlar bag, 13 = temperature programmed controller, 14 = syringe, 15 = syringe pump.

Table 1. Si/Al ratio (XRF) and surface area (BET).

Catalysts	Si/Al (% mol)	BET surface area (m^2/g)
Na-MOR	5.66	79
DM	26.90	244
DM/Zn	25.24	189
DM/Zn-Mn	24.91	165

Na-MOR = sodium mordenite, DM = dealuminated mordenite.

2.5. Catalyst regeneration

Catalyst regeneration consisted in oxidizing the coke deposited onto the catalyst in air flow for 2 h at 550°C. The regenerated catalyst was reused in the reaction.

3. Results and discussion

3.1. Catalyst characterization

Sodium mordenite (Na-MOR) with Si/Al = 5.66 was used as starting material, it was dealuminated with 8 M hydrochloric acid to increase its acidity (Si/Al to 26.90). Table 1 shows Si/Al ratios (determined by XRF) of mordenites before and after loading metal and also surface area (determined by BET).

It can be seen that after dealumination, the Si/Al mole ratio of DM was increased. This was due to the leaching of aluminium from the framework of mordenite when refluxed with hydrochloric acid. The DM has a higher surface area than the original sodium mordenite as the dealumination removes the extra-framework alumina, leading to an enlargement of the effective pore size and to the uncovering of the Bronsted acid sites located in the ring channels. The dealuminated mordenite was reported to show improved catalytic activity [16].

Temperature programmed desorption of ammonia (NH_3-TPD) was used to measure the acid amount and strength of catalysts. All NH_3-TPD profiles exhibit two types of acid sites. They are generally assigned to weaker acid sites (the desorbed ammonia peak at lower temperature with a maximum at 180°C) belonged to Bronsted acidity and a stronger acid sites (the desorbed ammonia peak at higher temperature with a maximum at 430°C) due to Lewis acidity. This result corresponds with the result reported [17]. After loading metal, the surface areas of the representative mordenite containing metal catalyst; DM/Zn and DM/Zn-Mn were decreased due to metal oxide deposition into the mordenite pores.

The XRD patterns of the dealuminated mordenite (DM), all of the DM/metal catalysts (M = Zn, Mn, Co, Rh, Ni, Fe and Ag), which were prepared by impregnation and solid-state ion exchange methods, revealed diffraction lines characteristic of mordenite with no significant change in diffraction angle and intensity [18]. No extra peaks due to metal incorporation were observed. Since metal concentration in the catalysts is very low, the XRD measurements are not able to show the presence of metals in these catalysts.

The IR spectrum of dealuminated mordenite showed characteristic bands: O-H stretching at 3642 cm^{-1}, O-H bending at 1640 cm^{-1} and Si-O stretching at 1073 cm^{-1} [19]. The spectra of all DM/metal catalysts are found very similar and showed no observable effect of the metal incorporation, this might be due to the very small amount of metal loaded. These data were consistent with those reported [20].

3.2. Catalytic results

The gaseous products detected are light hydrocarbons, i.e. methane (C_1), ethane (C_2), ethylene (C_2=), propane (C_3), propene (C_3=), butene (C_4=) and paraffins (C_4 –C_5). For product which has quantity less than 0.05 mol%, it is reported as trace.

Metal loading method

In Table 2, the data of ethanol conversion on DM/metal catalysts (metal = Zn, Co and Mn) prepared by SSIE and IMP were compared. Activity of some other metals (M = Rh, Cu, Fe, Ag and Ni) prepared by IMP was shown in Table 3. All the experiments were carried out using 10.0% ethanol as feed with the same condition, at 350°C, WHSV of 1.00 h^{-1}, time on stream = 1 h.

In Table 2, all DM/metal catalysts show high selectivity to ethylene and higher than dealuminated mordenite (DM). Higher yields of ethylene are registered in the catalysts prepared by impregnation method than that from solid state ion exchange method. This might result from the more homogeneous distribution of metal active species on the support [8]. The highest selectivity to ethylene was found in the DM/Zn catalyst. The order in selectivity to ethylene was DM/Zn > DM/Co ~ DM/Mn. For DM, the selectivity to ethane is higher than that of DM/metal. This can be explained by the acid strength of D-MOR, which is higher than DM/metal catalysts. It should be noted that no ether was produced.

Table 2. Ethanol conversion on DM/metal catalysts prepared by SSIE and IMP.

Product distribution (mol %)	DM	DM/Zn		DM/Co		DM/Mn	
		SSIE	IMP	SSIE	IMP	SSIE	IMP
C_1	45.1	0.2	0.1	0.2	0.1	0.1	0.1
C_2	7.5	trace	0.8	1.9	1.6	2.3	1.4
C_2=	46.2	96.0	96.6	89.7	94.7	86.3	94.3
C_3	0.1	0.2	0.2	2.2	0.6	3.7	0.9
C_3=	0.4	2.0	1.8	3.8	2.2	4.8	2.4
C_4=	0.3	1.5	0.3	0.9	1.4	1.1	0.5
C_4-C_5	0.2	trace	0.1	1.0	0.2	1.3	0.2
% Conversion	100	100	100	100	100	100	100
% Coke	1.0	2.4	1.8	2.7	1.5	2.1	1.9

DM = dealuminated mordenite, SSIE = solid state ion exchange, IMP = impregnation.

It is noticed that amount of coke that determined using TGA and also by the difference in the loss in weight for the samples before and after the calcinations is small.

In Table 3, the incorporation of metals (Rh, Cu, Fe and Ag) into the DM by impregnation method produced catalysts which yielded high amount of ethylene in the ethanol conversion. In the case of DM/Ag catalyst, %ethylene was moderate whereas DM/Ni catalyst gave very low %ethylene. The results from this work are better than previous report that 1% Rh/Al_2O_3 catalyst produced 60% ethylene at 400°C [21]. For the DM/Fe catalyst, the result obtained in this work is in contrast to the result reported on mordenite/Fe catalyst (100% Fe content) prepared by solid-state ion exchange which gave 75.9% ethane and 24.1% methane at 400°C with 96.4% conversion [22].

On the contrary, predominantly ethane and smaller amount of ethylene were observed on the DM/Ni catalyst. Metallic Ni is formed on the mordenite upon reduction with hydrogen gas and it is effective catalyst for hydrogenation of ethylene. It has been reported that NiSAPO-34 exhibits the activities for methanol decomposition to hydrogen and carbon monoxide and consequently methanation resulting in the decrease in ethylene selectivity [23].

Mixed metals

To investigate effect of mixed metals, the DM/Zn catalyst was chosen for the incorporation of the second metal as it yielded the highest %ethylene. The impregnation method was used for the preparation of DM/mixed metal catalysts. The reaction condition was same as used in the DM/single metal catalysts using 10.0% ethanol as feed. The results of the catalytic performance are given in Table 4**.**

Table 3. Ethanol conversion on DM/metal catalysts prepared by IMP.

Product distribution (mol %)	DM/Rh	DM/Cu	DM/Fe	DM/Ag	DM/Ni
C_1	2.4	trace	0.1	trace	0.6
C_2	0.0	1.5	1.2	2.1	62.5
C_2=	96.5	92.4	91.5	85.6	35.4
C_3	trace	1.4	1.8	4.1	0.1
C_3=	0.4	3.1	3.8	5.0	0.1
C_4=	0.8	0.8	0.9	2.0	1.2
C_4-C_5	trace	0.7	0.5	1.5	trace
% Conversion	100	100	100	100	100
% Coke	1.2	1.2	1.2	0.7	0.6

IMP = impregnation.

Table 4. Ethanol conversion on DM/mixed metal catalysts prepared by IMP.

Product distribution (mol %)	DM/Zn-Ag	DM/Zn-Mn	DM/Zn-Co	DM/Zn-Fe
C_1	0.1	0.5	0.1	0.2
C_2	0.3	0.8	0.5	0.3
C_2=	98.0	97.3	96.9	96.9
C_3	0.1	0.1	0.1	0.1
C_3=	1.3	1.1	1.9	2.1
C_4=	0.2	0.1	0.3	0.3
C_4-C_5	trace	trace	trace	trace
% Conversion	100	100	100	100
% Coke	2.0	1.8	2.9	1.8

IMP = impregnation.

It can be seen that incorporation of the second metal onto the DM/Zn catalyst led to an additional increase in ethylene. These data are consistent with results reported for ZSM-5/Zn-Mn catalyst [24].

Temperature

To investigate the effect of temperature, experiments were carried out at 350, 450 and 550°C using the DM/Zn-Mn catalyst prepared by solid state ion exchange method and used 99.9% ethanol as feed. The results are shown in Table 5. At high temperature, the concentration of both primary and secondary products on the surface decreased, and so the probability of formation of higher molecules also decreased [25]. It was found that there was a change in product distribution, and the highest selectivity to ethylene was obtained at 350°C. The selectivity to ethylene was decreased when temperature was increased. These data are consistent with the results obtained in the conversion of ethanol over H-ZSM-5 [26]. The highest selectivity to methane at 550°C was due to the cracking of hydrocarbon. A similar result was reported on methanol conversion [16].

Comparison of the concentration of ethanol between 99.9% and 10.0% at the same temperature, it can be seen that dilute ethanol gave higher yield of ethylene. It has been reported that water in aqueous ethanol and water from the product of the dehydration of the ethanol caused reduction in the acid strength of the active sites (poisoning of Bronsted sites) [27]. When water was adsorbed, it yielded a hydroxonium ion. Thus, the Bronsted acid sites are not available for interaction with alkene molecules to form higher alkenes and alkanes. In addition, water can also transform Lewis into Bronsted acid centers. The reduction of the concentration of Lewis acid centers leads to lower deactivation by coke, since coke formation seems to be faster on this type of sites [28]. The result from this work demonstrated that lower coke was formed for the aqueous ethanol. This agrees well with the result reported [29].

Table 5. Ethanol conversion on DM/Zn-Mn prepared by SSIE on various reaction temperatures.

Product distribution (mol %)	10.0 % ethanol	99.9 % ethanol		
	Temperature (°C)			
	350	350	450	550
C_1	0.6	2.3	13.1	77.9
C_2	1.6	1.0	2.3	6.9
C_2=	96.4	94.9	81.0	14.6
C_3	0.1	0.3	0.2	0.1
C_3=	1.1	1.0	2.9	0.4
C_4=	0.1	0.3	0.3	0.3
C_4-C_5	trace	trace	trace	trace
% Conversion	100	100	100	100
% Coke	1.5	4.3	2.5	2.1

SSIE = solid state ion exchange.

Alumina addition

In order to reduce amount of catalyst used in the reaction, alumina was added on the top of the catalyst (catalyst:alumina = 0.5g:0.5g). The result obtained using the representative mixed metal catalyst; DM/Zn-Ag is shown in Table 6. Alumina itself results in low amount of ethylene. The olefins were adsorbed and dehydration proceeded involving the action of an acid and a basic center of alumina [30]. Comparing between the catalyst with alumina and without alumina, the result showed that selectivity to ethylene was still present even though the former yielded a little lower %ethylene. This means that lower amount of catalyst can be used by diluting it with alumina.

Amount of metal

From the previous experiments, the catalysts loaded with 1%metal were used. In order to see effect of metal amount on product distribution, 5% metal catalysts were prepared by IMP method and tested activity using 10.0% ethanol as feed. The results are shown in Table 7.

From the above results, % selectivity to ethylene was decreased when the amount of metal loading of catalyst was increased from 1% to 5%. This result could be explained by the agglomerization of metal. In the case of the DM/Ni, increasing amount of Ni to 5% resulted in high selectivity to methane. This was in good agreement with the previous report of 5%Ni on Al_2O_3 [27]. In the case of coke formation, higher amount of metal gave higher %coke.

Catalyst regeneration

After the reaction, the catalyst was calcined to remove coke. It was reused at the same condition as for fresh catalyst. The result was shown in Table 8. It was seen that after many regeneration and use cycles (up to 7 times), the catalyst still showed activity with decreasing in ethylene selectivity and increasing in methane and ethane selectivity. This might be due to the agglomeration of metal, which caused the deactivation of the catalyst in long term operation.

Table 6. Ethanol conversion on DM/Zn-Ag catalyst prepared by IMP diluted with alumina.

Product distribution (mol %)	1.0 g Al_2O_3	g DM/Zn-Ag	0.5 g DM/Zn-Ag + 0.5 g Al_2O_3
C_1	12.6	0.1	8.1
C_2	12.8	0.3	0.3
C_2=	73.4	98.0	90.8
C_3	trace	0.1	trace
C_3=	0.2	1.3	0.6
C_4=	0.2	0.2	0.2
C_4-C_5	0.1	trace	trace
% Conversion	100	100	100
% Coke	3.0	2.0	3.9

IMP = impregnation.

Table 7. Ethanol conversion on DM/5% metal catalysts prepared by IMP.

Product distribution (mol %)	DM/1%Zn	DM/5%Zn	DM/1%Ni	DM/5%Ni
C_1	0.1	13.3	0.6	97.4
C_2	0.8	trace	62.5	trace
C_2=	96.6	84.7	35.4	trace
C_3	0.2	0.1	0.1	0.1
C_3=	1.8	1.8	0.1	trace
C_4=	0.3	trace	1.2	2.4
C_4-C_5	0.1	trace	trace	trace
% Conversion	100	100	100	100
% Coke	0.1	4.5	0.6	3.8

IMP = impregnation.

Table 8. Ethanol conversion on fresh and reused DM/Zn catalyst prepared by IMP.

Product distribution (mol %)	Fresh	Reused 2 times	Reused 7 times
C_1	0.1	2.8	6.7
C_2	0.8	1.2	13.2
C_2=	96.6	95.7	79.2
C_3	0.2	trace	trace
C_3=	1.8	0.2	0.3
C_4=	0.3	0.3	0.3
C_4-C_5	0.1	trace	trace
% Conversion	100	100	100
% Coke	1.8	1.5	1.6

IMP = impregnation.

Reaction pathways

The product distribution pattern from the ethanol conversion is similar to that obtained with methanol. In general, for methanol conversion, it has been observed that reduction of contact time, low acidity, water dilution and modification of catalyst with suitable promoters, enhanced the selectivity to light olefins [28]. Ethylene is the major product in the reaction. As can be seen, ethanol dehydration to diethyl ether was not observed in this work as this reaction is extremely fast [31]. It is widely accepted that, similarly to the transformation of methanol (MTG process), the mechanism for the transformation of ethanol into ethylene (as the primary product) occurs via oxonium ions as intermediate products [32].

4. Conclusions

The catalysts prepared in this work can be utilized for the conversion of ethanol derived from biomass. Ethylene is the main product obtained. Water in the ethanol competes with light alkenes for the Bronsted and Lewis acid sites. The adsorption of water reduces their strength and concentration. As a consequence, the conversion of light alkenes into higher hydrocarbons decreases. By modification of dealuminated mordenite with some metals, more efficient catalysts were obtained. The incorporation of single metal or mixed metals led to selective catalysts to ethylene. The amount of coke deposited on the catalysts was low.

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