

Comparative performance of ZSM-5 and activated carbon supports in alcohol conversion over Fe, Zn and Ni based catalysts

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Abstract

Alcohol transformation to benzene, toluene, ethylbenzene and xylene (BTEX) aromatic compounds over transition metals supported on zeolite (HZSM-5 (50)) and activated carbon (AC) was studied at 400 °C and 1 atm. Product distribution and selectivity was compared based on the performance of catalytic supports and metal types. Other than BTEX hydrocarbons, paraffins, indane, naphthalene were also among product. HZSM-5 support performed better in conversion and BTEX production as compared to activated carbon due to presence of Lewis and Bronsted acid sites available in zeolite support. Generally, promotion of HZSM-5 with Zn, Ni and Fe enhanced the production of paraffins and naphthalene, while HZSM-5 alone favoured the production of BTEX. Promotion of AC with Zn, Ni and Fe favoured the production of paraffins and BTEX.

Keywords: Catalyst supports, ZSM-5, Activated carbon, Alcohols and Transition metals

INTRODUCTION

In numerous chemical reactions, transition metals and other metal compounds have shown catalytic activity; in conversion of ethanol and butanol obtained through fermentation of lignocellulose biomass is no exception [1]. The catalytic activity is due to metals' ability to demonstrate multiple oxidation states and formation of complexes [2]. These metals have been found to possess low dispersion, low porosity and are associated with high prices, thus they have been considered better if supported on certain materials to overcome these problems [3]. Materials with high surface area and porosity such as zeolites, activated carbons, ceramics and oxides have been used as supports for metal. Catalysts supported metals are used in chemical industries especially for enhancement of reactions for conversions of different organic compounds to selective products.

For maximum activity with minimal metal loading, metal dispersion is of importance, which is achievable using supports. Supports are able to create high atomic metal dispersion due to their structures and pores. Metal particles become stabilized by the supports lattice inside pores. Active supports like zeolite become bifunctional catalyst with a metal function and acid Bronsted sites function, apart from everything, they are very stable in reaction conditions and acquire high surface area [3]. On the other hand, carbons are employed as inert supports to facilitate the formation and the stability of well dispersed active

sites since metals interact weakly or does not interact with activated carbon supports [4].

Catalytic supports have been found to play different and crucial role in conversion, product distribution and selectivity depending on the designated reactions. [5] studied various zeolite supports (H- Beta, HZSM-5 USY and H-mordenite) during the conversion of ethanol over various metals. It was reported that H-Beta, USY and H-mordenite formed no or little BTX and were found to produce heavy deposit of carbon. HZSM-5 was reported to produce high yield of BTX and it exhibited moderate deposit of carbon [5]. [6] studied the effect of platinum supported on molecular sieves (ZSM-5, ZSM-22, SAPO-11, Al-MCM-41, H-Y and H-Beta) for n-hexadecane hydro-isomerization. ZSM-5, H-Beta and ZSM-22 were found to have high conversion when compared to H-Y, SAPO-11 and Al-MCM-41 supported catalysts. Catalyst supported on SAPO-11 and Al-MCM-41 showed high isomerization (branched isohexadecanes) selectivity, and in this case, Al-MCM-41 was found to be the good candidate for dewaxing catalysts [6]. [7] employed cobalt oxide supported catalysts for conversion of ethanol. Other than hydrogen, it was observed that acetone can be obtained from ethanol conversion over catalysts supported on cobalt oxide. [7] also reported that the conversion of ethanol and its selectivity are influenced by the nature of the support. Other than zeolite class supports, [8] studied the conversion of ethanol over catalysts supported on carbon. Catalyst supported on carbon was found to promote dehydration of ethanol to form ethane and diethyl-ether.

In this study, comparison between zeolites and activated carbon as supports iron, zinc and nickel has been evaluated in the conversion of ethanol and butanol.

EXPERIMENTAL

Catalyst Preparation

ZSM-5 zeolite in ammonium form (CBV 5524G with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) obtained from Zeolyst International was calcined in a muffle furnace at 600 °C in atmospheric environment for 5 hours to directs the ammonia to leave the zeolite framework which turns into zeolite transformation to protonic. HZSM-5 and activated carbon obtained from Donau Carbon were used as supports. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ obtained from Sigma-Aldrich were used as a precursor for iron, zinc and nickel metal respectively for preparation of catalyst systems supported on HZSM-5 and activated carbon. Catalyst systems were prepared

using incipient wetness impregnation technique ($M = 5$ wt. %). The samples were oven dried at $110\text{ }^{\circ}\text{C}$ overnight for removal of water and calcined at $550\text{ }^{\circ}\text{C}$ for 6 hours to get rid of organic impurities. Samples obtained were designated as Fe/HZSM-5, Zn/HZSM-5, Ni/HZSM-5, Fe/AC, Zn/AC and Ni/AC.

Catalyst characterization

XRD measurements of catalyst was performed on BRUKER AXS D8 Advance XRD machine powder diffraction system. Copper radiation source was used and the x- ray generator settings for scans were conducted with 40 KV and 40 mA with a scanning range of 0.5° to 90° .

Catalyst Activity

The catalyst activity was studied in a fixed bed down flow reactor made from $\frac{1}{2}$ in stainless steel tube. The reactor was packed with 0.5 grams of catalyst supported on quartz wool for each experiment. Heating was applied through an external tube furnace. The relay receiver input from PID temperature controller measuring the temperature of the reactor was through a thermocouple inserted at the centre of the furnace. Ethanol and butanol as a feed stock were fed by HPLC pump into the reactor. All experiments were carried out at a weight hourly space velocity (WHSV) of 2.5 h^{-1} . The reactor was operated at $400\text{ }^{\circ}\text{C}$ and atmospheric pressure. Before the experiment start, catalyst was preheated for activation. Feed stock was charged over the catalyst in a reactor and the product was sent to a collecting vessel with gas outlet. Liquid samples were then sent for analysis. The Liquid products were analysed using offline gas chromatograph mass spectroscopy (GCM-SQP-2010 Ultra), equipped with DB5MS and FID detector.

RESULTS AND DISCUSSION

Catalyst characterization

Figure 1 shows XRD pattern of HZSM-5 and activated carbon doped with zinc, iron and nickel metals. Catalysts supported on ZSM-5 were found to exhibit major peaks at 7.96° and 23.28° corresponding to zeolite crystals. Catalysts supported on activated carbon showed several number of major peaks, which are not corresponding to that of zeolite. Major peak detected at 2θ of 26.5° was found to correspond with carbon. Further diffraction peaks appearing at 2θ of 43° for Ni/HZSM-5 suggests that Ni existed in the form of NiO in HZSM-5. No peaks of Zn and Fe detected in Zn/HZSM-5 and Fe/HZSM-5 respectively suggesting that these metals were available at high dispersion. The sharp peak in activated carbon and catalysts supported on activated carbon represents the presence of carbon at 2θ of 26.5° . Zinc and nickel in the form of ZnO and NiO crystalline phase were detected at 2θ values of 37° , 43° and 63° , and 32° , 36° , 56.5° and 67° respectively. Iron in Fe/AC was found to be finely dispersed in activated carbon suggested by the absence of iron peaks from XRD pattern.

Further with XRD pattern assistance, it was confirmed that metal impregnation does not change the crystalline structure of

zeolite catalyst. Relative crystallinity calculations showed that impregnation reduces the relative crystallinity of the catalysts supported on ZSM-5. The crystallinity of all impregnated catalysts were reduced to 75%, 70% and 80% for Fe/HZSM-5, Zn/HZSM-5 and Ni/HZSM-5 with respect to HZSM-5 catalyst. Metal impregnation with zinc and nickel decreased the particle size of the crystallite at 2θ of 23° from 29.46 nm to 16.75 nm and 16.36 nm respectively, while on the other hand, impregnation with iron metal increased particle size of the crystallite to 49.75 nm. Crystal system studies deduced that all samples exhibited similar crystal systems of monoclinic nature except for Zn/HZSM-5 which exhibited both monoclinic and orthorhombic.

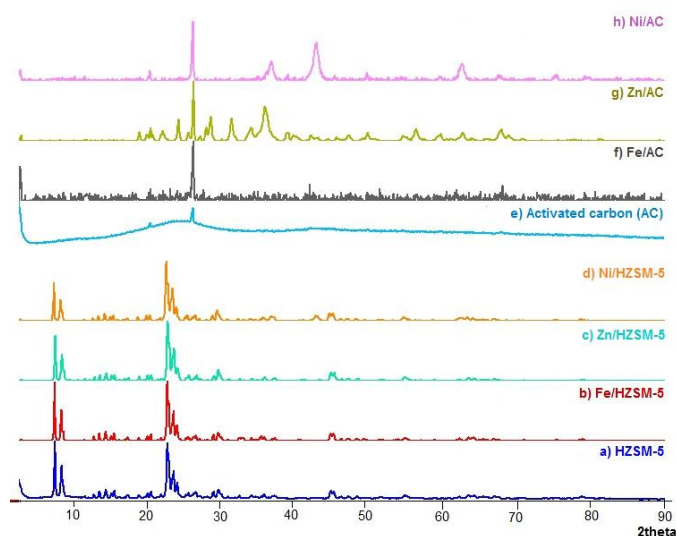


Figure 1. Powder XRD Spectra of a) HZSM-5, b) Fe/HZSM-5, c) Zn/HZSM-5, d) Ni/HZSM-5, e) Activated carbon, f) Fe/AC, g) Zn/AC and h) Ni/AC

Catalyst studies

Table 1 shows comparison between the conversion and product distributions obtained over Fe/HZSM-5, Zn/HZSM-5, Ni/HZSM-5, Fe.AC, Zn/AC and Ni/AC under the same reaction conditions. More than 93% ethanol conversion was achieved with catalysts supported on HZSM-5 and not more than 21.8% of conversion was achieved with catalysts supported on activated carbon. The yield of liquid hydrocarbons produced from catalysts supported on ZSM-5 ranged from 15.1% to 42.95%, and that from catalysts supported on activated carbon ranged from 9.4% to 21.8%. Catalysts supported on HZSM-5 produced paraffins, BTEX, indane and naphthalene. Catalysts with activated carbon support did not produce compounds such as ethylbenzene, xylene, indane and naphthalene while paraffins, benzene and toluene were produced. When ethanol was substituted with butanol, 100 % conversion was achieved in all catalysts supported on HZSM-5 and not more than 46% butanol conversion was achieved in catalysts supported on activated carbon. Between 17.5% to 52.2% liquid hydrocarbons yield was obtained from catalysts supported on HZSM-5, and 9.6% to 20.4% yield was obtained from catalyst supported on activated carbon. Paraffins, BTEX, indane and naphthalene were generated from catalyst supported on HZSM-5. Catalyst

supported on activated carbon did not produce ethylbenzene, xylene, indene and naphthalene.

During ethanol conversion, 61.22% BTEX was generated over HZSM-5 catalyst. When HZSM-5 was promoted with Fe, Zn and Ni compounds, the selectivity was reduced to 38.21%, 51.76% and 40.51% respectively. The BTEX selectivity was as follows: HZSM-5 > Zn/HZSM-5 > Ni/HZSM-5 > Fe/HZSM-5 > Fe/AC > Zn/AC. When ethanol was substituted with butanol, 67.3% BTEX was generated over HZSM-5 catalyst. Promotion of ZSM-5 with Fe, Zn and Ni compounds reduced the selectivity to 54.17%, 61.53% and 61.31% respectively. BTEX selectivity was as follows: HZSM-5 > Zn/HZSM-5 > Ni/HZSM-5 > Fe/HZSM-5 > Ni/AC > Fe/AC > Zn/AC.

Owing that ZSM-5 supports are active in conversion of alcohols, it was deduced that the formation of high liquid

hydrocarbons such as benzene, toluene, ethylbenzene, toluene and xylene (BTEX) were due to the activity of ZSM-5. Unlike activated carbon, ZSM-5 poses Lewis and Bronsted acid sites, whereas Lewis acid sites are sufficient for formation of high liquid hydrocarbons (BTEX) and Bronsted acid sites catalyses dehydration of alcohols. Further, these acid sites allows the possible reactions to take place inside the frame work of the zeolite. On the other hand activated carbon was observed as inert supports, the production of hydrocarbons over catalysts supported on activated carbons were due to metals doped on activated carbon support. The reaction took place on the sites of metals; it is also suggested that the formation of liquid hydrocarbons is due to metal dispersion on activated carbon since there was no interactions between activated carbon and metals in terms of increasing or reducing the metal sites.

Table 1. Product distribution of alcohol conversion over various catalysts at 400 °C, 1 atm. and WHSV of 2.5 h-1

Catalysts Types	Conversion (%)	Product distribution (wt. %)				
		Paraffins	BTEX*	Indane	Naphthalene	Other hydrocarbons
Ethanol						
HZSM-5	99.45	-	61.22	7.66	2.95	27.84
Fe/HZSM-5	99.86	0.20	38.21	0.40	3.11	57.97
Zn/HZSM-5	98.50	0.02	51.76	0.51	0.91	46.57
Ni/HZSM-5	93.12	0.32	40.51	0.38	6.56	51.60
Fe/AC	21.80	18.85	29.50	-	-	51.65
Zn/AC	16.00	37.00	4.19	-	-	58.81
Ni/AC	10.10	-	-	-	-	10.10
Butanol						
HZSM-5	100	0.22	67.30	6.30	0.36	25.82
Fe/HZSM-5	100	0.18	54.17	2.83	2.40	54.17
Zn/HZSM-5	100	0.36	61.53	3.89	7.09	61.53
Ni/HZSM-5	100	0.45	61.31	-	8.90	61.31
Fe/AC	35.90	2.79	18.43	-	-	18.43
Zn/AC	46.00	43.50	16.77	-	-	16.77
Ni/AC	34.90	27.36	19.24	-	-	19.24

*Benzene, Toluene, Ethylbenzene and Xylene

In all cases, promotion of HZSM-5 with Zn, Ni and Fe enhanced the production of paraffins and. HZSM-5 catalyst showed better results for generation of BTEX hydrocarbons. High amount of BTEX produced by HZSM-5 catalyst was contributed by the amount of xylenes, in other words HZSM-5 catalyst had high selectivity to xylene. Promotion with metals enhanced the production of benzene, and zinc showed high selectivity to benzene amongst all metals in both ethanol and butanol conversion. In some cases, metals like zinc and iron enhanced the production of toluene. In overall, the formation of aromatics hydrocarbons were suppressed when HZSM-5 was impregnated.

This observation may be due to the reduction of HZSM-5 acidity caused by metal doping on HZSM-5. Impregnation with metals is followed by calcination at high temperature, this

may also decrease the amount of acid sites of HZSM-5 through ion-exchange of framework aluminium of ZSM-5 with the introduced metal cation [9], and also this limits the diffusion of the alcohol and the reaction products in zeolite. Reduction of acid sites inhibits the secondary reaction to generate high liquid hydrocarbons. Other factors such as the location of metals in HZSM-5 channel and physical blocking of the channel structure itself may also influence these observations.

CONCLUSION

Ethanol and butanol alcohols were successfully converted to hydrocarbons over catalysts supported on ZSM-5 and activated carbon. ZSM-5 support performed better compared to activated carbon. BTEX production was high on catalysts supported on

ZSM-5 compared to those supported on activated carbon. The active components were found to perform differently on conversion and product distribution.

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