CATALYTIC DECOMPOSITION OF SHORT-CHAIN ALCOHOLS IN AIR ON BIMETALLIC ION-EXCHANGED H-BEA ZEOLITES

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ABSTRACT

The catalytic decomposition of methanol (MeOH) over different bimetallic exchange combinations of Co, Cr and Cu and zeolite Beta (HBEA) was studied using a fixed-bed catalytic reactor in the temperature range of 150°-450°C, at partial pressure of 1.2 % and GHSV of 26,500 hour^{-1}. The catalytic activity of each catalyst was compared to that of catalyst with individual metal component. All of the three metals give high MeOH conversion of above 90 % when the reaction temperatures exceed 300°C. Incorporation of 0.116 % wt. of Cr into Co-BEA can increase the its catalytic activity. Conversely, the addition of 0.526 % wt. Co into Cu-BEA shows no positive effect. A reduction of 7 % of Cr content of Cr-BEA without significant loss in its catalytic activity but improved CO_2 selectivity can be materialized by inclusion of 0.745 % wt. of Cu in Cr-BEA.

INTRODUCTION

Volatile organic compounds (VOCs) are emitted in dilute concentrations from many industrial processes. Catalytic decomposition is a viable method of controlling emissions of (VOCs) (Cordi and Falconer, 1996). Beside noble metals (Pt and Pd), Cr, Co and Cu are among the most active catalysts to achieve deep oxidative decomposition of VOCs in air. Despite being most active among the three (Atwood *et al.*, 1998 ; Chintawar and Greene, 1997), Cr is also a problematic substance to the environment and research on finding the replacement or reducing its content is a worthwhile effort.

Zeolites, which have been used widely as catalysts, supports or adsorbents in chemical industry, are also given close attention in VOC catalytic decomposition in recent year (Niu *et al.*, 1999 ; Chintawar and Greene, 1997). Compared to alumina supported catalysts, metal exchanged zeolites always show higher and more durable activity in low-catalytic decomposition of some VOCs.

EXPERIMENTAL

Co-, Cr- and Cu-exchanged zeolite Beta (H-BEA with SiO_2/Al_2O_3=25) were prepared in two discernible steps. In the first step, NH_4^+ exchange of the zeolite was performed in NH_4Cl solution for 12 hours. The metal exchange step was done using aqueous salt solution of corresponding metals (targeted at 3 % metal loading) for 24 hours followed by filtration, drying and calcination at 500°C for 6 hours. For bimetallic zeolites, co-solutions of metals were used. All zeolite samples were analyzed for BET surface area using Autosorb-1 surface analyzer and final metal loading using atomic absorption spectroscopy (AAS).

The catalytic activity test was performed in a 12 mm i.d. glass reactor charged with 0.2 gram of catalysts (Figure 1). A methanol-laden air stream was obtained by bubbling N_2 through liquid methanol and another air flow was used to mark up the total flow rate.

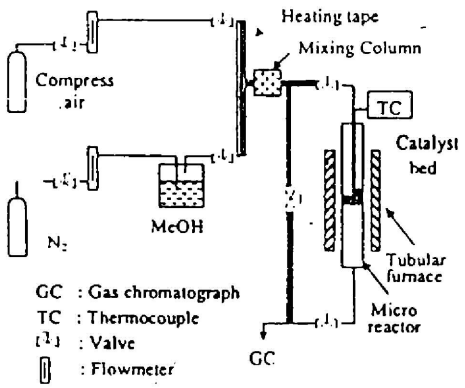

Figure 1 : Experimental set up for catalyst activity testing.

The total flow rate was fixed at 250 ml/min with a corresponding GHSV of 26,500 hour^{-1} while the partial pressure of methanol in the inlet gas was targeted at 1.2 %.The inlet and outlet gas were analyzed using an off-line GC equipped with Porapak-Q and Molecular Sieve 5A columns.

RESULTS & DISCUSSION

The characteristics of zeolites obtained by ion exchange procedures is as summarized in Table 1. For all of the metal exchanged catalysts, the BET surface area is maintained above 400 m^2/g. A reduction in surface area can be attributed to bigger cations being incorporated into zeolite lattice structure in place of smaller H^+ cation and thermal treatment during metal exchange procedure.

Table 1 : Characteristic of the catalysts used.

Sample	BET surface area (m^2/g)	Metal loading (% wt.)			
		Co	Cr	Cu	Total
H-BEA	500	-	-	-	-
Co-BEA	497	0.546	-	-	0.546
Cr-BEA	416	-	0.125	-	0.125
Cu-BEA	487	-	-	0.982	0.982
CoCr-BEA	490	0.528	0.116	-	0.644
CoCu-BEA	406	0.526	-	0.715	1.241
CrCu-BEA	457	-	0.116	0.745	0.861

The catalytic activities for MeOH decomposition are depicted in Figure 2. All three catalysts are active at above 300°C with conversions exceed 90 % and reaching total conversion at above 400°C. Cr-BEA appears to be the most active catalyst despite very low metal loading. Incorporation of 0.528 % wt. of Co, however, found to weaken its activity, but, it is still better than that of Co-BEA. With these three catalysts, no CO is observed among the products, even at low MeOH conversions. At lower temperature, formaldehyde was detected but with increasing temperature, it was further oxidized to CO and subsequently to CO_2.

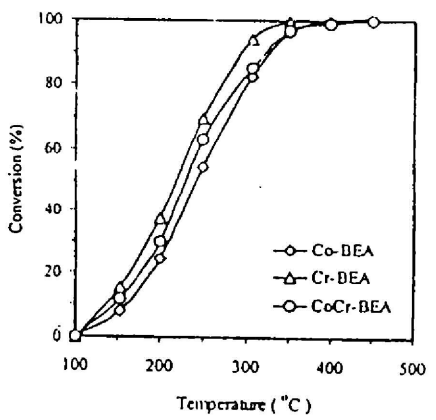

Figure 2: MeOH conversion over Co-, Cr- and CoCr-BEA (GHSV=26,500 h^{-1}, P_{MeOH}=1.2).

It is clearly noted in Figure 3 that Co-BEA gives better conversion than Cu-BEA. Bimetallic catalyst of Co and Cu with 0.526 % wt of Co and 0.715 % wt. of Cu produces no positive effect as compared to Cu-BEA. No activity, for instance, has been observed for this catalyst at 150°C.

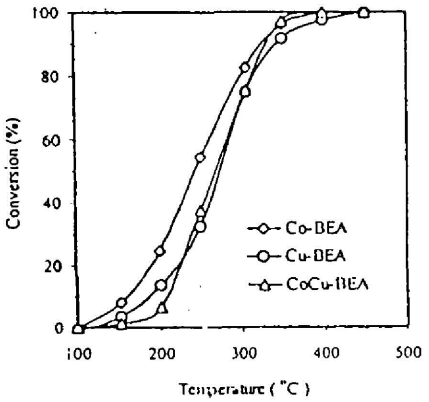

Figure 3: MeOH conversion over Co-, Cu- and CoCu-BEA (GHSV=26,500 h^{-1}, P_{MeOH}=1.2).

Figure 4 shows that Cr-BEA shows better activity than Cu-BEA and with that, it is the most active catalyst among the three single metal exchange H-BEAs tested. Elimination of 7 % of Cr content and replacing it with 0.745 % wt. of Cu is seen to produce comparable catalyst to Cr-BEA in terms of its catalytic activity.

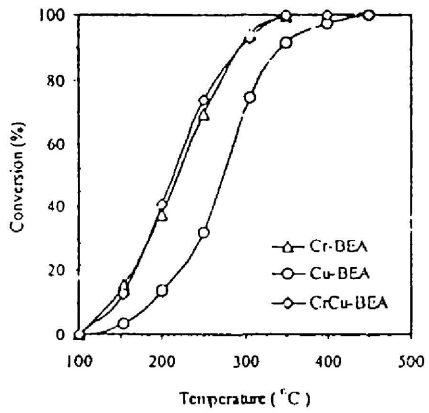

Figure 4: MeOH conversion over Cr-, Cu- and CrCu-BEA (GHSV=26,500 h^{-1}, F_{MeOH}=1.2).

The profile of CO_2 selectivity for metal exchanged H-BEAs is as depicted in Figure 5. The selectivity toward this deep oxidation product appears to show marked increase after 300°C. As might be expected, the CO_2 selectivity increases with temperature. Cu-BEA is no doubt gives the best CO_2 selectivity while, Cr-BEA, despite giving highest MeOH conversion, only shows mild selectivity toward this product.

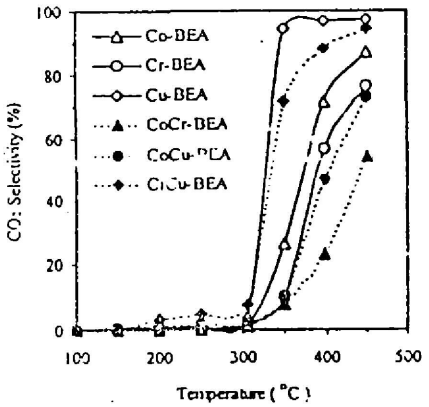

Figure 5: CO_2 selectivity for different metal exchanged H-BEA (GHSV=26,500 h^{-1}, P_{MeOH}=1.2).

The incorporation of a combination of Cr and Cu into H-BEA seems to produce a catalyst with high MeOH conversion and high selectivity toward CO_2. Below 300°C, significant CO_2 selectivity has been noted and at 450°C, a selectivity of about 93 % was demonstrated by the catalyst.

It is well accepted that cations in zeolite determine the catalytic activity as they can influence the acidity and O_2 adsorption capacity. For H-BEA, the O_2 adsorption capacity is believed to increase with the highest available oxidation state change. The Cr ion could be oxidized to a valence state (Cr^{3+} to Cr^{5+} to Cr^{6+}) by attachment to extralattice oxygen atoms (Chintawar and Greene, 1997), higher than that of Cu (Cu^{+} to Cu^{2+}) or Co (Co^{+2} to Co^{+3}). With an increase in the oxidation state, the electron acceptor ability of the Cr cation is expected to increase, thereby making the

higher oxidation states highly susceptible to reduction.

CONCLUSION

Among the three metals studied, Cr exchanged HBEA shows highest catalytic activity followed by Co- and Cu-BEA. By incorporating 0.745 % wt of Cu into Cr-BEA, a catalyst with activity comparable to 0.125 % wt. Cr-BEA is produced but with a reduction of 7 % of Cr content. Cu is also shown to improve selectivity toward CO_2 of the resulting catalyst.

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