

CATALYTIC DECOMPOSITION OF METHANOL IN AIR OVER DIFFERENT COMBINATIONS OF BIMETALLIC EXCHANGED H-BEA ZEOLITES WITH COBALT, CHROMIUM AND COPPER

Ahmad Zuhairi Abdullah*, Mohamad Zailani Abu Bakar
and Subhash Bhatia

School of Chemical Engineering
Engineering Campus, Universiti Sains Malaysia
Nibong Tebal, 14300 Seberang Prai Selatan
Penang.

*(azuhairi@yahoo.com)

RINGKASAN: Penguraian bermangkin metanol (MeOH) oleh zeolit Beta (H-BEA) tertukar ion dengan kobalt (Co), kromium (Cr) dan kuprum (Cu), samada secara tunggal atau gabungan dwilogam yang berlainan telah dikaji menggunakan reaktor bermangkin alas tetap dalam julat suhu antara 100°-500°C, kepekatan suap MeOH 11,500 ppmv dan GHSV 26,500 per jam. Aktiviti mangkin dwilogam tersebut dibandingkan dengan aktiviti mangkin dengan logam tunggal. Ketiga-tiga logam tersebut memberikan penukaran MeOH melebihi 90% bila suhu melewati 350°C. Penambahan 0.516% berat Cr ke dalam Co-BEA didapati dapat mempertingkatkan aktiviti. Sebaliknya, penambahan 0.446% berat Co ke dalam Cu-BEA tidak menunjukkan sebarang kesan positif. Pengurangan sebanyak 18.6% kandungan Cr dalam Cr-BEA tidak menunjukkan penurunan yang ketara dalam aktiviti mangkin, malah peningkatan hasil CO₂ dapat dicapai dengan cara penambahan 0.745% berat Cu ke dalam Cr-BEA. Penghasilan hasil penguraian tak lengkap methanol didapati begitu ketara di bawah suhu 450°C.

ABSTRACT: The catalytic decomposition of methanol (MeOH) over single and different bimetallic exchange combinations of cobalt (Co), chromium (Cr) and copper (Cu) and zeolite Beta (H-BEA) was studied using a fixed-bed catalytic reactor in the temperature range 100°C-500°C, at MeOH feed concentration of 11,500 ppmv and gas hourly space velocity (GHSV) of 26,500 hour⁻¹. The catalytic activity of each bimetallic catalyst was compared to that of catalyst with individual metal component. All the three metal-exchanged H-BEAs gave high MeOH conversions of above 90% when the reaction temperatures exceeded 350°C. Incorporation of 0.516% wt. of Cr into Co-BEA increased its catalytic activity. Conversely, the addition of 0.446% wt. Co into Cu-BEA showed no or little positive effect. A reduction of 18.6% Cr content of Cr-BEA did not result in significant loss in its catalytic activity but improved CO₂ yield could be materialised by inclusion of 0.745% wt. of Cu into Cr-BEA. The formation of products of incomplete decomposition of methanol was found to be significant below 450°C.

KEYWORDS: VOC, catalyst, catalytic decomposition, metal exchange, Beta zeolite, bimetal.

MATERIALS AND METHODS

Co, Cr and Cu exchanged zeolite Beta (H-BEA with $\text{SiO}_2/\text{Al}_2\text{O}_3=25$) were prepared in two separate steps. In the first step, NH_4^+ exchange of the zeolite was performed in 2.25 M of NH_4Cl solution for 12 hours. The metal exchange step was carried out in aqueous salt solution of intended metals (targeted at 3% metal loading) for 24 hours followed by filtration, drying, calcination at 500°C for 6 hours, pressed and sieved between 250 to $350\ \mu\text{m}$. For bimetallic exchanged zeolites, co-solutions of metals were used. All zeolite samples were characterised for BET surface area using Autosorb-1 surface analyser and final metal loading using Perkin Elmer 6650 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 make up the total flow rate, premixed and passed through the catalytic reactor previously heated at the intended reaction temperature. A thermocouple probe continuously in contact with the catalyst bed was used to measure the actual reaction temperature.

The total flow rate was fixed at 250 ml/min with corresponding GHSV of $26,500\ \text{hour}^{-1}$ while the concentration of methanol in the inlet stream was maintained at 11,500 ppmv. Throughout the experiment, the ratio of oxygen to MeOH was 3.6 : 1 (excess) and this was important to avoid oxygen limitation in the oxidation process. The inlet and outlet gas were analysed using an off-line GC equipped with Porapak-Q column for separation of organic components and carbon dioxide (CO_2) and Molecular Sieve 5A column for separation of carbon monoxide (CO) in the product gas.

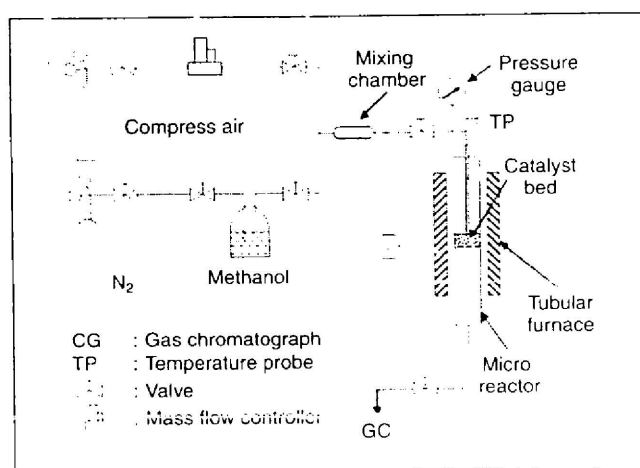


Figure 1. Experimental set up for catalyst activity testing

The catalytic activities of Co-, Cr- and CoCr-BEA for MeOH decomposition are depicted in Figure 2. The conversion increased with an increase in reaction temperature. All three catalysts were very active above 350°C. with conversions exceeding 90% and reaching total conversion above 450°C. Cr-BEA appeared to be the most active despite comparatively lower metal loading. Incorporation of 0.149% wt. of Co was found to weaken its activity, but, it was still better than that of Co-BEA.

It is clearly noted in Figure 3 that Co-BEA gave better conversion than Cu-BEA. Bimetallic catalyst of Co and Cu with 0.446% wt of Co and 0.715% wt. of Cu produced no positive effect as compared to Cu-BEA. No activity was observed for this catalyst at 200°C.

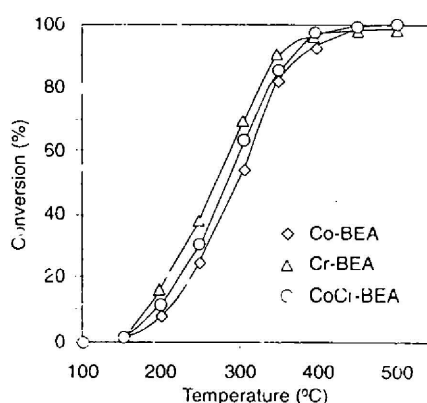


Figure 2. MeOH conversion over Co-, Cr- and CoCr-BEA (GHSV=26,500 hour⁻¹, MeOH feed = 11,500 ppmv)

Figure 4 shows that Cr-BEA demonstrated better activity than Cu-BEA and with that, it was the most active catalyst among the three single metal exchanged H-BEAs tested. Elimination of 18.6% Cr content and replacing it with 0.745% wt. Cu appeared to produce a comparable catalyst to Cr-BEA in terms of its catalytic activity.

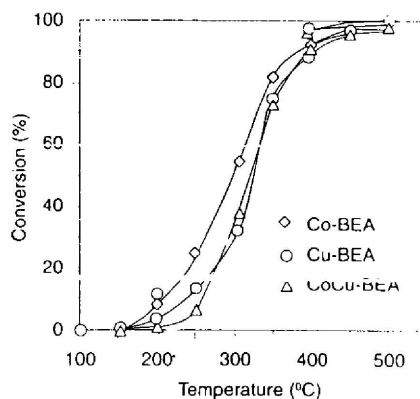


Figure 3. MeOH conversion over Co-, Cu- and CoCu-BEA (GHSV=26,500 hour⁻¹, MeOH feed = 11,500 ppmv)

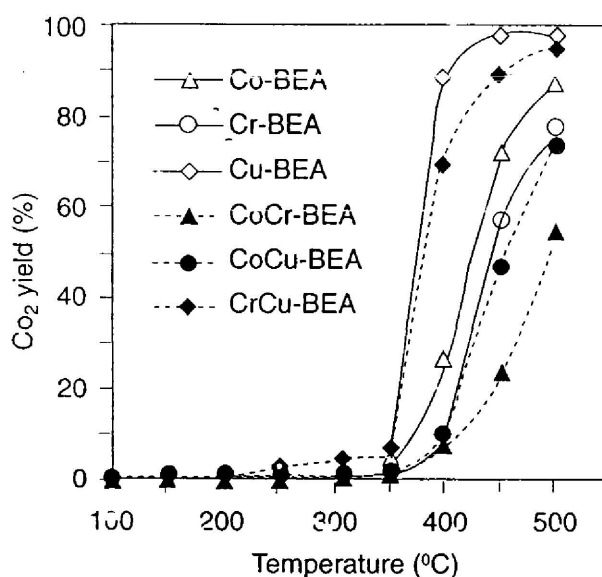


Figure 5. CO_2 yield for different metal exchanged H-BEA (GHSV=26,500 hour^{-1} , MeOH feed = 11,500 ppmv)

The combination of Cr and Cu into H-BEA seemed to produce a catalyst with high MeOH conversion and high CO_2 yield. Significant CO_2 yield was noted below 300°C and at 500°C, a yield of about 93% was demonstrated by this catalyst.

It has been postulated that oxidative decomposition of VOC in metal exchanged zeolite catalysts occurs through reduction-oxidation (redox) reactions of exchanged cation with extra-lattice oxygen. The type and location of the cation largely determined the catalytic activity of the site. The Cr ion could be oxidised to higher valence states (Cr^{3+} to Cr^{5+} to Cr^{6+}) by attachment to extra-lattice oxygen atoms (Chintawar and Greene, 1997). The same mode of oxidation also occurs for Cu (Cu^+ to Cu^{2+}) and 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.

Product of incomplete decomposition

The formation of products of incomplete decomposition was significant at reaction temperatures between 200°C to 450°C as evident in Figure 6. Below 350°C, significant concentrations of formic acid (HCOOH) and formaldehyde (HCHO) were detected in the product gas. These two components were gradually eliminated in favour of CO and subsequently CO_2 as the temperature increased to 450°C. At higher temperatures, CO_2 was present as almost the sole carbon containing compound.

Technology and Environment Malaysia (MOSTE) through the National Science Fellowship (NSF) is also greatly appreciated by one of the authors (Ahmad Zuhairi Abdullah).

REFERENCES

- Atwood, G.A., Greene, H. L., Chintawar, P., Rachapudi, R., Ramachandran, B. and Vogel, C. A. (1998). Trichloroethylene sorption and oxidation using a dual function sorbent/catalyst in a falling furnace reactor. *Appl. Catal. B: Environ.*, **18**, pp. 51-61.
- Becker, Lutz and Förster, Hurst (1998). Oxidative decomposition of benzene and its methyl derivatives catalysed by copper and palladium ion-exchanged Y-type zeolites. *Appl. Catal. B: Environ.*, **17**, pp. 43-49.
- Chen, N. Y., Degnan, Thomas F. and Smith, C Morris (1994). *Molecular transport and reaction in zeolites*, VCH, New York.
- Chintawar, Prashant S. and Greene, Howard L. (1997). Decomposition characteristics of chlorinated ethylenes on metal-loaded zeolite Y and γ -Al₂O₃. *Appl. Catal. B: Environ.*, **13**, pp. 81-92.
- Cordi, Eric M. and Falconer, John L. (1996). Oxidation of volatile organic compounds on Al₂O₃, Pd/Al₂O₃ and PdO/Al₂O₃ catalysts. *J. Catal.*, **162**, pp. 104-117.
- Dégé, Ph., Pinard, L., Magnoux, P. and Guisnet, M. (2000). Catalytic oxidation of volatile organic compounds II: Influence of the physicochemical characteristics of Pd/HFAU catalysts on the oxidation of o-xylene. *Appl. Catal. B: Environ.*, **27**, pp. 17-26.
- Kühl, Günter H. (1999). Modification of zeolites. In: *Catalysis and zeolites : Fundamentals and applications*, Weitkamp, J and Puppe, L., Springer (ed.), Berlin, pp. 81-197.
- Niu, Guoxing, Huang, Yao, Chen, Xiaoyin, He, Jianming, Liu, Yong and He, Adi (1999). Thermal and hydrothermal stability of siliceous Y-zeolites and its application to high-temperature catalytic combustion. *Appl. Catal. B: Environ.*, **21**, pp. 63-70.