EXPLOITING THE TUNABLE ACIDITY OF NB-KIT-6 CATALYSTS FOR ETHANOL DEHYDRATION: EXPERIMENTS AND KINETIC MODELING

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Abstract

Increasing demand for biomass-derived platform chemicals presents new opportunities for (earth abundant) metal-incorporated mesoporous silicates with tunable acidity. In this work, Nb-containing mesoporous silicates (KIT-6) are demonstrated to show exceptional activity for ethanol dehydration and selectivity towards ethylene that are comparable to those on an industrial γ-alumina sample. Intrinsic kinetics modeling shows favorable activation energy for ethylene production on Nb-KIT-6 (65.7±2.3 kJ/mol) compared to γ-alumina (95.6±8.9 kJ/mol) catalysts.

Introduction

Recently, it was shown that ethanol-rich mixed alcohol product can be produced from syngas derived from lignocellulosic biomass (Hensley et al., 2013). Catalytic dehydration of such mixed alcohol stream produces olefins. Predominantly Brønsted acidic catalysts such as HZSM-5 show excellent dehydration activity but lower olefin selectivity (Connor et al., 2015). In contrast, predominantly Lewis acidic catalysts (Zr-KIT-6) show relatively low dehydration activity but excellent olefin selectivity. This suggests the existence of an optimum acidity that maximizes the yield of olefins. We investigate such an optimum with metal-exchanged mesoporous silicates (W-KIT-6, and Nb-KIT-6) whose total acidity and the relative distribution of Lewis vs. Brønsted acid sites can be tuned with metal loading (Table 1) (Ramanathan et al., 2014).

Experimental

The performance of the various pelletized metal-incorporated catalysts was evaluated in a fixed-bed reactor as described elsewhere (Pan et al., 2013). Vaporized ethanol is mixed with heated diluent gas (N_2) and the vapor phase mixture is passed through the catalyst bed. The reactor effluent is analyzed online using a HP 5890 GC equipped with a FID. Conversion and product composition profiles were obtained in the 300 – 350 °C range at conditions that eliminated transport limitations. The C balance closure in all experiments is 100±2%, within experimental error.

Results and Discussion

Fig. 1 compares the best ethanol dehydration activities and product selectivities obtained with various metals (M = Zr, W or Nb) incorporated KIT-6 materials with an industrial γ-alumina sample. The values represent steady state values observed during 8 h runs. The Nb-KIT-6 (10.9 wt% Nb) catalyst clearly exhibited the best activity and ethylene selectivity among the M-KIT-6 catalysts. The Nb-KIT-6 catalyst with highest synthesized loading also

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showed comparable performance with the industrial γ-alumina sample operated at fourfold greater space velocity.

Table 1. Acidity distribution on Nb- and W-KIT-6

Nb wt%	Total Acidity[a]	L/B ratio[b]	W wt%	Total Acidity[a]	L/B ratio[b]
1.5	0.11	29.15	2.5	0.26	13.00
3.4	0.15	16.18	5.5	0.43	2.08
6.1	0.23	8.78	10.5	0.48	1.51
10.9	0.34	6.13	17.2	0.46	0.40

[a] Total acidity (mmol NH_3/g cat) via NH_3-TPD
[b] Lewis/Brønsted ratio via FT-IR of pyridine-adsorption
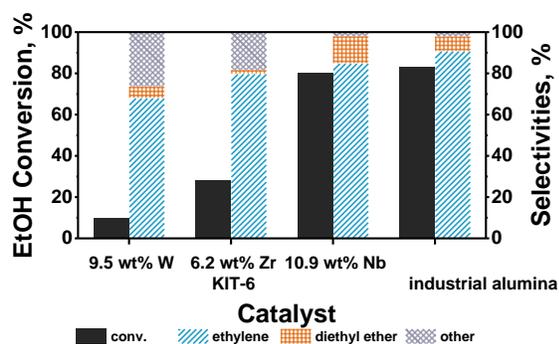

Figure 1. Comparison of ethanol dehydration activities and carbon selectivities on various catalysts. Conditions: T = 350 °C; EtOH WHSV = 2.36±0.01 g EtOH/g cat/h for KIT-6 materials, 9.48 g EtOH/g cat/h for alumina.

The KIT-6 material (10.9 wt% Nb) was further investigated to develop a kinetic model. Only the reactions producing ethylene and diethyl ether (DEE) (combined selectivity > 98%) were considered. Assuming plug flow and ideal gas behavior, the mass balances for product yields are derived (Eq. 1). Rate expressions (Eqs. 2 and 3) are derived based on recent literature (DeWilde et al., 2014) assuming that either unimolecular ethanol absorbed on single sites decomposes to produce ethylene, or bimolecular ethanol co-adsorbed on two adjacent sites decomposes to produce DEE.

$$\frac{d(Y_i)}{dm} = \frac{pT_0}{p_0T}\frac{1}{C_{EtOH,0}v_{total,0}}r_i(C_{EtOH}) \qquad (1)$$

$$r_{C_2H_4} = \frac{k_1K_1C_{EtOH}}{1+K_1C_{EtOH}} \qquad (2)$$

$$r_{DEE} = \frac{k_2K_1K_2C_{EtOH}^2}{1+K_1K_2C_{EtOH}^2} \qquad (3)$$

where $r_{C_2H_4}$ and r_{DEE} are the formation rates of ethylene and DEE, respectively; k_1 and k_2 are intrinsic rate constants; K_1 and K_2 are the equilibrium constants for

ethanol adsorption. The activation energies for ethylene and DEE production (65.7±2.3 and 175.9±6.3 kJ/mol, respectively) on Nb-KIT-6 are evaluated via nonlinear regression of experimental data using SciPy. The values are more favorable for ethylene production compared to those on γ-alumina (95.6±8.9 and 51.2±7.1 kJ/mol, respectively). As shown in the parity plot (Fig. 2), the predicted yields compare reasonably well with experimental values.
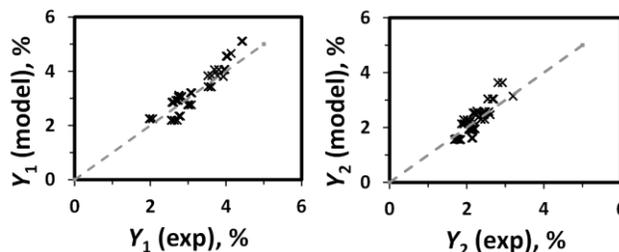

Figure 2. Predicted and experimental yields

Conclusions

Nb-KIT-6 shows outstanding activity and good olefin selectivity that are comparable to those obtained with an industrial alumina catalyst. Our results suggest that the activity of such metal-containing mesoporous materials (M-KIT-6) can be improved by tuning the Lewis and Brønsted acidities. Such optimization studies along with fundamental insights into catalyst acidity/activity/selectivity correlations will be presented.

Acknowledgments

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