Hydrodeoxygenation of guaiacol over ion-exchanged ruthenium ZSM-5 and BEA zeolites

Penghui Yan,[a] **Eric Kennedy,**[a] **Michael Stockenhuber** [a,*]
[a] *Chemical Engineering, School of Engineering, The University of Newcastle, Callaghan, NSW, 2308, Australia*
**Corresponding author: michael.stockenhuber@newcastle.edu.au*

Abstract: Ru-MFI and Ru-BEA catalysts, prepared by ion exchange of Ru^{3+} ions with extra framework NH_{4+} cations in zeolites, are examined to catalyse the hydrodeoxygenation (HDO) of guaiacol. The results indicate Ru ion-exchanged zeolites with extremely low Ru loading (0.2 wt.%) have high intrinsic HDO activity. Based on the TEM, SEM, Chemisorption and NH_3-TPD analysis results, the NH_{4+} was substituted by Ru and the metal was finely dispersed when compared to catalysts with similar metal loading that were prepared using incipient wetness technique.

Keywords: hydrodeoxygenation, ion-exchanged, Ru, guaiacol.

1. Introduction

The commercial production of liquid fuels from the pyrolysis and liquefaction of biomass is inhibited by the high residual oxygen content of the biocrude intermediate [1]. The oxygen content of biocrude oil can be reduced by hydrodeoxygenation (HDO) over a suitable catalyst. HDO catalysts are often prepared by incipient wetness impregnation, which usually results in low dispersion of the metal due to significant levels of aggregation of the metal on the external surface of the zeolite support. This has the disadvantage that metals active towards the HDO of biocrude oil such as Ru require a high loading on metal in order to be effective, thus significantly adding to the cost of the catalyst. In an effort to improve the metal dispersion, and thus reduce the required loading, this work considers the use of an ion-exchange method for preparing Ru HDO catalysts.

2. Experimental

Ion exchanged (IX) Ru-ZSM-5 and Ru-Beta samples were prepared as follows. 8 g NH_4^+ form of ZSM-5 (Si/Al=15) and β (Si/Al=12.5) was added to 200 ml of 0.3 g ruthenium (III) acetylacetonate solution with constant stirring at 80 °C. After 24 h, the catalyst was filtered and washed with deionized water. The catalyst samples were then dried at 110 °C in air for 8 h, and calcined at 550 °C for 6 h. For comparison, samples with the same metal loading (0.2 wt%) were prepared by incipient wetness (IW) impregnation.

3. Results and discussion

The TEM and EDS mapping images of fresh ion-exchange Ru-ZSM-5 and Ru-ZSM-5 catalysts are displayed in Figure 1. These indicate that the Ru particles were finely dispersed over the surface of both supports, with particle size lower than 2 nm. Unlike catalysts prepared by incipient wetness impregnation, the ion-exchanged Ru-ZSM-5 (Si/Al=15) catalyst large metal crystal phase appear to be absent.

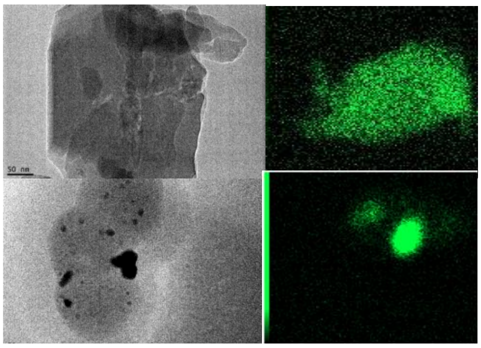

Figure 1. TEM and EDS mapping images of ion-IX-Ru-ZSM-5 and IW-Ru-ZSM-5

This assertion is supported by the SEM images presented in Figure 2.

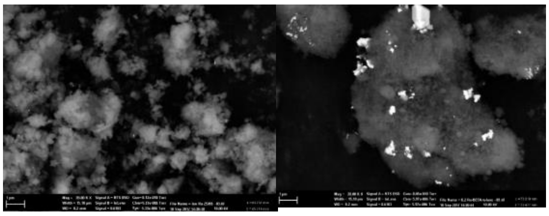

Figure 2. SEM images of IX-Ru-ZSM-5 and IW-Ru-ZSM-5

NH_3-TPD profiles of both supports, and IX-Ru-ZSM-5 and IX-Ru-β are shown in Figure 3. Both supports display three peaks at 250 °C, 350 °C and 550 °C. The low temperature peak can be attributed to weak Lewis acid sites while the high temperature peak corresponds to the Brønsted acid sites [2]. However, the IX-Ru catalysts display a dramatic decrease in medium and strong acid sites, suggesting that the original Brønsted acid H^+ in HZSM-5 and Hβ was substituted by Ru [3].

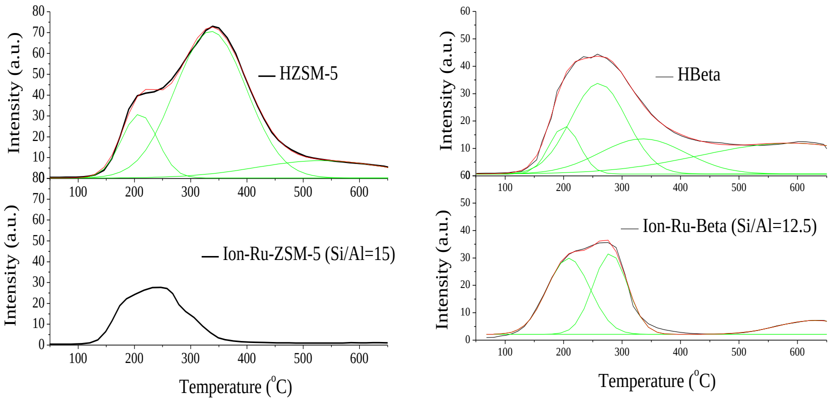

Figure 3. NH_3-TPD profiles for ion-exchange samples, m/z=16, the black line-original trace, the red line-the composite sum of fitted peaks, and the green line- fitted peaks

HDO of guaiacol was carried out over IX-Ru-zeolites and IW-Ru-β in batch and flow reactors. The results for the batch reactor are summarized in Table 1, which indicate that ion-exchanged catalysts display higher HDO activity compared to the incipient wetness catalyst, with high yield of cyclohexane and 2-methoxycyclohexanol. It is likely that this is due to the higher metal dispersion and number of active sites found in the catalysts prepared by ion exchange (Figure 4).

Table 1 Result for HDO of guaiacol in batch reactor (X-Conversion, Y-Yield)

Catalysts	X-guaiacol (%)	Y-cyclohexane (%)	Y-1,1'-bicyclohexyl (%)	Y-2-methoxycyclohexane (%)
IX-Ru-ZSM-5	90.6	77.4	1.5	0.5
IX-Ru-β	94.4	49.5	4.0	24.9
IW- Ru-β	94.9	10.2	0.8	0

0.4 g guaiacol, 0.2 g catalyst, initial H_2 pressure 4.0 MPa, reaction temperature, 250 °C.

The results for HDO of guaiacol in flow reactor is shown in Table 2. The R is reaction rate, namely, moles of product produced in 1 minute and 1 g catalyst. These results reflect those seen in the batch reactor.

Table 2 Results for HDO of guaiacol in flow reactor

Catalysts	X-guaiacol (%)	R-cyclohexane (10^{-5}·Mol·min^{-1}·g^{-1})	R-2-methoxycyclohexanol (10^{-5}·Mol·min^{-1}·g^{-1})
IX-Ru-ZSM-5	11.0	1.42	4.16
IX-Ru-β	16.9	1.84	1.10
IW-Ru-β	7.8	0	0

H_2 pressure 4.0 MPa, reaction temperature, 200 °C, WHSV: 0.0084 min^{-1}

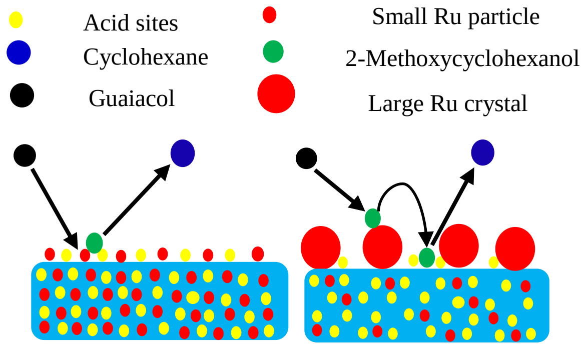

Figure 4a. IX-Ru zeolite **Figure 4b**. IW-Ru-zeolite

4. Conclusions

This work has demonstrated that ion-exchanged Ru catalysts achieve high metal dispersion and high HDO conversion compared with traditionally prepared catalysts, where the H^+ in HZSM-5 and Hβ is substituted by Ru. This form of catalyst thus makes more efficient use of rare, catalytically active metals through a synergistic effect between the acid sites and metal sites.

References

1. P. M. Moetensen, J. D. G., P. A. Jensen, K. G. Knudsen, A. D. Jensen, Appl. Catal. A 407 (2011) 1
2. K.Na, S.A., R. Ye, G. A. Somorjai, J.Am. Chem. Soc. 136 (2014) 17207
3. C. X. Lu, T. Z. L., Q. L. Shi, Q. Li, Y. Xin, L. Zheng, Z. L. Zhang, Sci. Rep. 3300 (2017) 7