Ni-modified Ir/SiO_2 catalyst for selective C=C hydrogenation of styrene

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Abstract: The modification of noble metal with another metal was one strategy to improve the activity for selective C=C hydrogenation of styrene to ethylbenzene. We found that Ni-modified Ir/SiO_2 ($IrNi/SiO_2$) showed significantly high activity in comparison with that of Ir/SiO_2, and the high TOF of 747 h^{-1} was obtained over $IrNi/SiO_2$ with the Ni/Ir molar ratio of 1, which was more than 7 times than that over Ir/SiO_2. XRD analysis indicated that $IrNi/SiO_2$ was composed of the IrNi alloy and Ni phase. Activity test suggested that IrNi alloy played an important role in the hydrogenation of styrene.

Keywords: Iridium, Styrene hydrogenation, Ni-modification.

1. Introduction

The hydrogenation of the C=C double bond was interesting and useful for the practical production of petrochemicals, fine chemicals and so on. The reduction of olefinic group was easy to realize, however, selective hydrogenation of C=C double bond with a minimum loss of the functional groups was still a challenge. Styrene, which was composed of olefinic group and benzene, was usually employed as a model reaction for selective hydrogenation of C=C double bond. Some noble metals such as Pd, Rh, Ru, Ir and Pt supported heterogeneous catalyst showed good catalytic performance for this reaction. However, their application is limited by their global reserve scarcity and high price. Therefore, developing the suitable method to fabricate highly active and stable catalytic species is important. The modification of noble metal with another metal can not only decrease the amount of noble metal, but also enhance the catalytic performance because of the special electronic and geometric effect.

Herein, we report that Ni-modified Ir/SiO_2 catalyst showed outstanding catalytic performance for C=C hydrogenation of styrene, and the corresponding TOF is 747 min^{-1} at the Ni/Ir molar ratio of 1, which is larger than that over Ir/SiO_2 by a factor of 7.

2. Experimental

All the catalysts were prepared by impregnation method. $IrNi/SiO_2$ (Ir: 4wt%) was prepared by impregnating SiO_2 with Ir and Ni species in sequence. Firstly, Ir/SiO_2 was synthesized by impregnating SiO_2 with H_2IrCl_6 aqueous solution, then it was dried in oven at 373 K overnight after water evaporation, subsequently, Ni was loaded on the Ir/SiO_2 by impregnating Ir/SiO_2 with aqueous $Ni(NO_3)_2$ solution in the same method. Finally, the $IrNi/SiO_2$ was calcined at 773 K for 3 h in muffle furnace. Monometallic Ni/SiO_2 (Ni: 1.2wt%) was prepared by impregnating SiO_2 with $Ni(NO_3)_2$ aqueous solution in the same method. IrM/SiO_2 (Ir 4wt%, M=Fe, Cu, Mn, Cr, Zn and Co, M/Ir=1) was prepared by the same method as described above for the synthesis of $IrNi/SiO_2$, but using corresponding nitrate in place of $Ni(NO_3)_2$. The catalyst was reduced under H_2 flow (30 ml/min) at 773 K for 1 h before activity test. The standard reaction conditions were presented as follows: catalyst: 20 mg (Ir: 4wt%, Ni/Ir=1), styrene 21.0 g (200 mmol), methanol 30 g, H_2 8 MPa, stirring speed 500 rpm, reaction temperature 303 K, reaction time 0.5 h. TOF (min^{-1}) = (Amount of produced ethylbenzene (mmol))/(Total Ir amount (mmol))/(Time(min))

X-ray diffraction (XRD) patterns were recorded by a diffractometer (MiniFlex600; Rigaku). Cu $K\alpha$ (λ = 0.154 nm, 45 kV, 40 mA) radiation was used as an X-ray source. The sample was mixed with Si powder for XRD measurement, and the pattern was calibrated with Si(111) of 28.42°. Field emission scanning transmission electron microscope (FE-STEM) images was obtained on a Hitachi spherical aberration corrected STEM/SEM HD-2700 instrument operated at 200 kV. After the reduction, the samples were dispersed in ethanol and placed on Cu grids under air atmosphere.

3. Results and discussion

First, the addition of 2nd metal (M=Fe, Cu, Mn, Cr, Zn, Co, Ni) to Ir/SiO_2 was investigated, and the result is shown in Figure 1. All the catalysts exhibited 99.9% selectivity to ethylbenzene. Among the IrM/SiO_2 catalysts tested, IrNi/SiO_2 exhibited the best catalytic performance for the reaction with TOF of 747 min^{-1}, which was more than 7 times than that over Ir/SiO_2. Co species also provided the positive effect on the hydrogenation of styrene with TOF of 246 min^{-1}. However, Fe, Cu, Mn, Cr and Zn species decreased the catalytic performance of Ir/SiO_2.

Furthermore, the effect of Ni/Ir molar ratio of IrNi/SiO_2 in hydrogenation of styrene was shown in Figure 2. Introduction of Ni to Ir/SiO_2 gave an obvious enhancement of styrene conversion when the molar ratio increased at the range from 0.01 to 1. The conversion reached 47.8% at the molar ratio of 1, and then it gradually increased with molar ratio range from 2 to 8. At higher molar ratio, then the conversion gradually decreased to 30.4%. Compared to Ir/SiO_2, the selectivity was also promoted from 98.5% to 99.9% with the Ni/Ir molar range from 0.05 to 32. The modification of Ni not only significantly enhanced the conversion, but also improved the selectivity to ethylbenzene.

XRD analysis was used to investigate the structure of IrNi/SiO_2. Compared to Ir/SiO_2, the Ir peak of IrNi/SiO_2 shifted to a higher angle at the Ni/Ir molar ratio range from 0.01 to 1, indicating the formation of the IrNi alloy. Then, the peak position of Ir was not changed with the molar ratio between 1 and 8, meantime, the intensity of Ni peaks gradually increased with the increase of Ni/Ir molar ratio, indicating that catalyst had a mixture of IrNi alloy and Ni phase. TEM was also conducted to evaluate the particle size. Most of metal nanoparticle was uniformly dispersed on the SiO_2 surface for IrNi/SiO_2 (Ir: 4wt%, Ni/Ir=1) with average particle of 5 nm. The outstanding catalytic performance of IrNi/SiO_2 could be attributed to the IrNi alloy species.

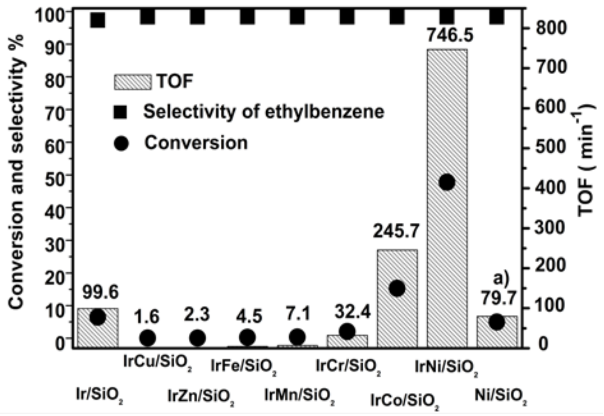

Figure 1. The effect of second metals of IrM/SiO_2 (M=Fe, Cu, Mn, Cr, Zn, Co, Ni) in hydrogenation of styrene. Conditions: catalyst 20 mg (Ir 4wt%, M/Ir=1), styrene 21.0 g (200 mmol), H_2 8 MPa, 303 K, 30 min.
a) TOF based on total Ni amount.

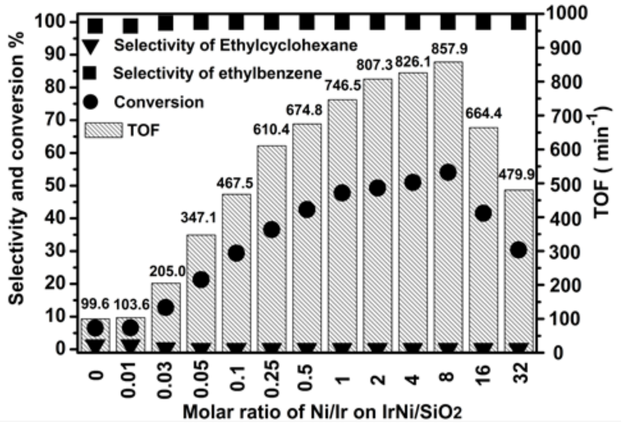

Figure 2. The effect of Ni/Ir molar ratio of IrNi/SiO_2 in hydrogenation of styrene. Conditions: catalyst 20 mg (Ir 4wt%), styrene, 21.0 g (200 mmol), H_2 8 MPa, 303 K, 30 min.

4. Conclusions

The IrNi/SiO_2 catalyst showed significantly high catalytic performance for C=C hydrogenation of styrene in comparison with Ir/SiO_2. The TOF was 747 min^{-1} at the Ni/Ir molar ratio of 1, which was larger than that over Ir/SiO_2 by a factor of 7. Based on XRD and TEM characterization, it is suggested that the IrNi alloy species play an important role for the hydrogenation of styrene.

References

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