Letter

Benzene-selective hydrogenation to cyclohexene over supported ruthenium boride catalysts prepared by a novel method

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Supported amorphous ruthenium boride catalysts, prepared by a novel method that does not require any modifiers in the reaction system, are able to convert benzene to cyclohexene with high yields when the partial hydrogenation of benzene is carried out in the liquid phase.

The partial hydrogenation of benzene to cyclohexene is of great synthetic and industrial interest. It has been found that high yields of cyclohexene can be obtained when the partial hydrogenation of benzene is carried out in aqueous solution by using ruthenium catalysts together with large amounts of modifiers (strongly acidic inorganic salts) in the reaction system of benzene and water.[1–3] However, these modifiers cause corrosion of reactors and hasten the deactivation of catalysts under reaction conditions.[4] Metal boride catalysts obtained from the reduction of metal salts with borohydride, due to the combination of their ultrafine size and amorphous structure,[5] are expected to have different catalytic properties. Recently, we have shown that ruthenium boride (RuB) catalysts are highly selective for reducing benzene to cyclohexene.[6] We report here a new method for the preparation of the supported ruthenium boride catalysts, which are able to convert benzene to a high yield of cyclohexene without the presence of any modifiers in the reaction system.

These catalysts were prepared by the following chemical mixing and reducing procedure (CMR). Aqueous solutions of NH_3(aq) (6 M, 20 ml) and KBH_4 (0.2 M, 10 ml) were concurrently added dropwise to 150 ml of a mixed aqueous solution of $RuCl_3$ (5.8×10^{-3} M) and $ZrOCl_2$ (5.5×10^{-2} M) with stirring, leading to a precipitate. The precipitate was kept in liquor solution overnight and then washed thoroughly with a large amount of distilled water. The catalysts containing zinc together with ruthenium were prepared in a similiar manner, by dissolving their chlorides in the same aqueous solution. The unsupported (US) and impregnated (IP) RuB catalysts were also prepared for comparison, using procedures described elsewhere.[6]

The X-ray diffraction (XRD) patterns were collected on a Rigaku Dmax-3C powder diffractometer using Ni-filtered Cu-Kα radiation (0.15418 nm). The X-ray tube was operated at 35 kV and 20 mA.

The selective hydrogenation of benzene over amorphous RuB powders was carried out in a 500 ml stainless steel autoclave equipped with a magnetic stirrer. The as-prepared RuB powder, 100 ml distilled water and 50 ml of benzene were introduced into the reactor. Then the autoclave was sealed and filled with H_2 several times to exclude air. The final reaction conditions were 433 K, 5.0 M Pa of hydrogen pressure, and 1000 rpm stirring rate to exclude diffusion effects. The reaction process was monitored by taking small amounts of the reaction mixture at intervals, followed by gas chromatographic analysis on an instrument equipped with a TCD detector.

As shown in Fig. 1 (traces c–e), the XRD patterns of the unsupported and impregnated catalysts indicate that a typical amorphous state of ruthenium boride alloy is present in these catalysts, as evidenced by a very broad peak around $2\theta = 43°$.[6] However, no diffraction peaks related to ruthenium were observed in the XRD patterns of the chemically mixed catalysts (traces a and b), suggesting that the RuB alloy is highly dispersed in the catalysts prepared by the CMR method. It can also be seen from the XRD patterns that the ZrO_2-supported RuB catalyst (trace e), in addition to the broad peak at $2\theta = 43°$, shows several diffraction peaks that are characteristic of monoclinic ZrO_2. The hydrous zirconia ($ZrO_2 \cdot xH_2O$) support is amorphous with no diffraction peaks detected (traces a, b and d).

Table 1 shows the highest cyclohexene yields, the corresponding reaction time and the concomitant benzene conversions as well as selectivities for cyclohexene observed in the reactions catalyzed by ruthenium boride catalysts prepared with different methods. It can be clearly seen that the chemically mixed and reduced catalyst is much more effective for cyclohexene formation than the impregnated and unsupported catalysts if hydrogenation is performed without any modifiers in the reaction mixture of benzene and water (compare Run 1 with Runs 5, 7 and 8). For the unsupported amorphous RuB catalysts, the coexistence of a large amount of zinc sulfate in the reaction mixture is essential for the cyclohexene yield to be comparable with that obtained the chemically mixed and reduced catalyst (Run 9). On the other hand, in the case of the impregnated catalysts, although the addition of $ZnSO_4$

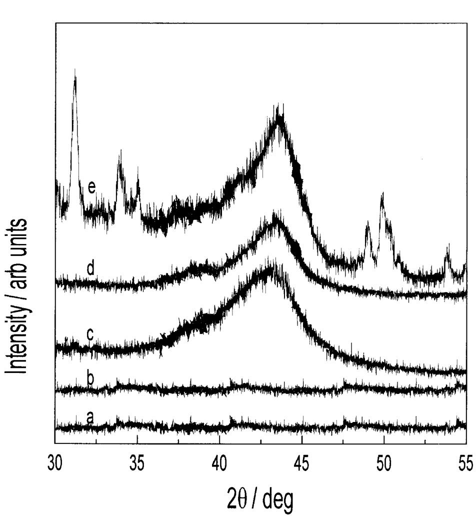

Fig. 1 XRD patterns of amorphous RuB catalysts prepared by different methods. (*a*) 9 wt.% RuB/$ZrO_2 \cdot xH_2O$ (CMR), (*b*) 9 wt.% RuB–2.5 wt.% Zn/$ZrO_2 \cdot xH_2O$ (CMR), (*c*) RuB (US), (*d*) 9 wt.% RuB/$ZrO_2 \cdot xH_2O$ (IP), (*e*) 9 wt.% RuB/ZrO_2 (IP).

Table 1 Partial hydrogenation of benzene catalyzed by different ruthenium boride catalysts[a]

Run	Catalyst	Preparation procedure[b]	Yield[c] of cyclohexene/ mol%	Conversion of benzene/ mol%	Selectivity for cyclohexene/ %	Reaction time/ min
1	9 wt.% RuB/$ZrO_2 \cdot xH_2O$	CMR	33.2	66.8	49.7	30
2	9 wt.% RuB–1 wt.% Zn/$ZrO_2 \cdot xH_2O$	CMR	35.8	67.3	53.2	40
3	9 wt.% RuB–2.5 wt.% Zn/$ZrO_2 \cdot xH_2O$	CMR	45.6	73.1	62.3	55
4	9 wt.% RuB–4 wt.% Zn/$ZrO_2 \cdot xH_2O$	CMR	38.6	63.0	61.3	50
5	9 wt.% RuB/$ZrO_2 \cdot xH_2O$	IP	9.5	47.1	20.2	30
6	9 wt.% RuB/$ZrO_2 \cdot xH_2O$[d]	IP	18.4	51.7	35.6	90
7	9 wt.% RuB/ZrO_2	IP	5.2	35.6	14.6	25
8	RuB	US	12.2	44.3	27.5	45
9	RuB[d]	US	31.3	55.9	55.9	110

[a] Reaction conditions: benzene (50 ml), water (100 ml), catalyst (1 g), reaction temperature 433 K, reaction pressure 5 MPa. [b] CMR = chemical mixing and reducing, IP = impregnation, US = unsupported. [c] The highest cyclohexene yield in each run. [d] For Runs 6 and 9, 4.5 g of $ZnSO_4 \cdot 7H_2O$ was added to the mixture of benzene and water.

to the reaction mixture of benzene and water can enhance the selectivity for cyclohexene and its yield (Run 6), they still are incomparable with the chemically mixed catalysts. In contrast to the US and IP catalysts, the addition of zinc sulfate to the reaction system using CMR gives rise to no positive effects on the cyclohexene yield. Thus, remarkable differences are found between the properties of the chemically mixed and the other two kinds of amorphous RuB catalysts. The CMR method ensures an intimate mixing of RuB particles and the hydrous zirconia support. It seems that the hydrophilicity of the support together with its close contact with active sites may affect the selectivity of the reaction in an analogous way as when using modifiers that can change the hydrophilicity of ruthenium. Most likely the hydrophilic support prepared by the CMR procedure causes a stagnant water layer that expels cyclohexene formed on the catalyst surface by competitive adsorption with cyclohexene,[7] and so results in an increase in cyclohexene yield.[8]

As observed from Runs 2, 3 and 4 in Table 1, the addition of small amounts of zinc to the chemically mixed and reduced catalyst can effectively promote cyclohexene formation. The reaction catalyzed by a CMR catalyst containing 2.5 wt.% zinc gives a cyclohexene yield of 45.6 mol% at a benzene conversion of *ca.* 73% (Run 3). However, a further increase of zinc content to 4 wt.% in the catalyst results in a decrease in the cyclohexene yield. The role of zinc is probably best interpreted as a stabilization of the hydrogenated intermediate and suppression of further hydrogenation to cyclohexane.[9]

Furthermore, the hydrogenation of benzene with the same CMR catalyst (Run 3) was repeated 5 times by extracting the oil phase after completion of the hydrogenation and charging fresh benzene into the reaction system. The cyclohexene yield in all 5 cycles was no less than 42 mol%, and no deactivation of the catalyst was observed.

In conclusion, the supported RuB catalysts prepared using the CMR method can effectively convert benzene to cyclohexene with high yield, and the addition of a small amount of zinc to the as-prepared catalyst can enhance the yield of cyclohexene and its selectivity.

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References

1 H. Nagahara and M. Konishi, Eur. Pat. 220525, 1986.
2 K. Yamashita, H. Obana and I. Katsuta, Eur. Pat. 552809, 1993.
3 H. Nagahara, M. Konishi and Y. Fukuoka, *Appl. Surf. Sci.*, 1997, **121/122**, 448.
4 R. Remirez, *Chem. Eng.*, 1979, **24**, 80.
5 S. Linderoth and S. Morup, *J. Appl. Phys.*, 1991, **69**, 5256.
6 S. Xie, M. Qiao, H. Li, W. Wang and J. F. Deng, *Appl. Catal., A*, 1999, **176**, 129.
7 T. Lopez, L. Herrera, R. Gomez, W. Zou, K. Robinson and R. D. Gonzales, *J. Catal.*, 1992, **136**, 621.
8 J. Struijk, M. d'Angremond, W. J. M. Lucas-de-Regt and J. J. F. Scholten, *Appl. Catal., A*, 1992, **83**, 263.
9 P. Kluson and L. Cerveny, *Appl. Catal., A*, 1995, **128**, 13.

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