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ARTICLE TYPE

Simple selective hydrogenation of benzene to cyclohexene in presence of sodium dicyanamide

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A new catalyst system was used in the liquid phase hydrogenation of benzene to cyclohexene containing only an aqueous solution of Ru/La₂O₃ and a very small quantity of sodium dicyanamide (NaDCA). This additive considerably improves the catalyst performance compared to DCA based ionic liquids. The effects of the amount of NaDCA and metal loading of the catalyst were investigated and a high initial ¹⁰ selectivity to cyclohexene of 70 % was reached.

1. Introduction

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The hydrogenation of benzene is of both industrial and academic interest, i.e. for the production of cyclohexane (CHA) and cyclohexene (CHE) and as benchmark test for the performance of ¹⁵ hydrogenation catalysts. Under industrial conditions, the intermediates of this consecutive hydrogenation, cyclohexene, is not formed with usual hydrogenation catalysts, even at low degrees of conversion, which could be easily explained regarding the free standard reaction enthalpies (formation of cyclohexene: -²⁰ 23 kJ / mol, formation of cyclohexane: -98 kJ / mol, ¹ Scheme 1)

and by kinetic reasons (high reactivity of cyclohexene).



Scheme 1 Benzene hydrogenation as a consecutive reaction.

- 25 The hydrogenation of benzene to cyclohexene is of considerable industrial interest, as a cheap synthesis of this intermediate would be an attractive alternative route to synthesize products like adipic acid or ε-caprolactam (monomeres of polyamides). The state-of-the-art process for the synthesis of ε-30 caprolactam consists of the complete hydrogenation of benzene to
- cyclohexane with a subsequent oxidation to a cyclohexanol/cyclohexanone mixture. However, this oxidation step can only be performed at a conversion level of 5 to 10 % to reach high selectivities.² If the challenging task, namely a selective
- ³⁵ hydrogenation of benzene to cyclohexene, could be achieved, the latter can easily be hydrated to cyclohexanol. This indicates a significant improve to the existing process as the disadvantages of the process would be eliminated and the production of εcaprolactam would be both energetically more efficient and ⁴⁰ resource saving.

The reaction system of the selective hydrogenation of benzene described in literature is a very complex tetra-phase system,

consisting of an organic and an aqueous phase, hydrogen and the solid catalyst. The latter is always based on ruthenium and a ⁴⁵ second metal. In addition, large amounts of inorganic salts are dissolved in the aqueous phase which increase the hydrophilicity of the Ru catalyst. For this purpose, especially zinc salts are commonly used. NaOH is often added as well to increase the selectivity to cyclohexene. It is believed that a hydrate shell is ⁵⁰ formed around the inherently hydrophobic catalyst by the aqueous phase. Because of the lower solubility of cyclohexene in water compared to benzene in H₂O (factor 6 at 150 °C, 50 bar)³ the re-adsorption of cyclohexene and the consecutive hydrogenation to cyclohexane is impeded.

After initial attempts of gas and liquid phase hydrogenation of benzene to cyclohexene resulting in yields < 1 %⁴ Drinkhard introduced an aqueous phase with salts and NaOH reaching yields of 32 % for the first time.⁵ Based on these experiments ASAHI Chem. Corp. developed a catalyst system which was used of in a pilot plant with an annual production of 60,000 tons of cyclohexene in 1988.⁶ In this reaction system an unsupported Ru-Zn catalyst was suspended with zirconia in the aqueous phase. In addition, zinc sulfate was dissolved. The catalyst system used reached a cyclohexene selectivity of 80 % (maximum yield: 56 65 %). However, the salt loading in the reactor was significantly high, about approximately 50 times of the amount of Ru.⁷

Recent studies included a variety of second metals, various support materials and new additives in the aqueous phase.⁸ Using a lanthanum doped Ru/SBA-15 catalyst Liu et al. achieved a ⁷⁰ yield of 56 %.⁹ In addition to zinc sulfate as additive, toxic cadmium sulfate was used as well. According to the authors the latter should provide a direct modification of the catalyst surface, while zinc sulfate should stabilize the cyclohexene in the aqueous phase and thus preventing its re-adsorption (and the complete ⁷⁵ hydrogenation). A catalyst without additives in the aqueous phase was used by Liu et al¹⁰ reaching a yield of 56 %. Still, the solid catalyst consists of all parts which are used in the aforementioned catalyst systems. It is described in the form of Ru/ZnO-ZrO_x(OH)_y. NaOH was also added in the production process via

precipitation. The reduction with sodium borohydride is mentionable whereby the catalyst could be contaminated with boron. The leaching behavior was not investigated by which ZrO₂ and ZnO reached the liquid phase and then could act as the 5 aforementioned additives. Sun et al.¹¹ reached a maximum yield of cyclohexene of 64 % by increasing the ruthenium content and adding small amounts of diethanolamine.

The state-of-the-art can thus be characterized as a complicated multi-phase system containing benzene, hydrogen, Ru catalyst, 10 water and other additives. It has to be noted that without the latter no cyclohexene formation is observed. Due to the high precious metal content of the catalyst (up to 95 wt. %) and the large amounts of salt additives and NaOH in the aqueous phase the systems described are neither environmentally nor economically 15 viable. So there is still need for further research.

Recently, we presented a simple catalyst system, consisting of only supported ruthenium in water with very low quantities (ppm range) of the ionic liquids [B3MPyr][DCA]. The need of salt additives and second metals is completely eliminated. 20 Nevertheless, the formation of cyclohexene occurs with high selectivity.¹² This catalyst system is in good agreement with the 12 principles of green chemistry.¹³ The needed amounts of active metal and ionic liquid could be reduced dramatically as well as separation and corrosion problems could be avoided.

In the present work this system is further improved by the 25 usage of a very small quantity of sodium dicyanamide (NaDCA) in presence of lanthanum oxide supported ruthenium. The catalyst performance is compared to three ionic liquids comprising the DCA anion and [BMIM], [BMPL] or [B3MPyr] 30 in the cationic part of the molecule (Scheme 2). Ionic liquids have received by now a very wide range of applications in chemical research, including such as solvents in organic syntheses or in the SILP and SCILL concepts in catalysis research.¹⁴ The dicyanamide based ionic liquids (IL) used here have to be water 35 soluble to avoid any fifth phase in the reaction system and must decompose neither on the surface of the Ru catalyst nor in the presence of water or reactants.¹⁵



40 Scheme 2 Structures of the DCA based ionic liquids (IL)

2. Experimental

2.1 Catalyst Preparation

The Ru/La₂O₃ catalysts were prepared by impregnation following a protocol described elsewhere.¹⁶ A certain amount of ruthenium 45 chloride hydrate was dissolved in 500 mL of water to create a 0.01 wt. % solution. The corresponding amount of lanthanum oxide was suspended in the solution. The black solution changed its color to green. After 3 h of stirring at room temperature the catalyst was filtered off and dried under air for 15 h at 333 K. The 50 catalyst (5 g) was reduced in a hydrogen flow (87 mL/min) at 673

K ($\beta = 5$ K/min, 3 h isotherm, passive cooling).

2.2 Catalyst Testing

The catalyst (0.5 g), the aqueous NaDCA solution (100 mL) and the benzene phase (50 mL) were introduced into the autoclave 55 (300 mL, Parr Instruments, r = 1000 rpm) and were flushed twice with argon (10 bar). The reactor was heated to 373 K under argon (2 bar). The introduction of hydrogen defined the start of the reaction. In defined intervals samples were taken for gas chromatography analysis (HP 6890, FID, capillary column 60 Agilent DB-Wax, l=30 m, d_i=0.25 mm, t_i=0.25 μm).

2.3 Characterization

The catalyst was analyzed by X-ray photoelectron spectroscopy (VG ESCALAB 220 iXL with an Al Ka radiation source under ambient conditions) to determine the oxidation state of ruthenium 65 and to prove the existence of ingredients of the additive on the catalyst surface.

3. Results and Discussion

The catalytic behavior of 1Ru/La2O3 in the selective 70 hydrogenation of benzene was investigated with different DCA based ILs as additives. They were used in equimolar concentration. The high initial selectivities of the experiments with ILs were of about 60 %. However, with sodium dicyanamide (NaDCA) as additive an initial selectivity of 66 % was reached 75 and cyclohexene was the main product at conversions below 15 %. This catalyst system is more selective over the whole conversion range than these containing ILs which clearly demonstrates a further improvement of the [B3MPyr][DCA] based alumina supported catalyst system.

- In comparison with NaDCA as additive the ILs had an inhibiting influence on the performance of the catalyst. The selectivity to cyclohexene was decreased in all experiments. The imidazolium and pyridinium cations lowered the conversion from 45 % to 34 % and 13 %, respectively, after 240 min. Maybe,
- st there is a competitive adsorption of the aromatic educt benzene and these aromatic cations on the active sites of the catalyst.



Fig. 1 Effect of the cations of DCA based ILs, conditions: m (1Ru/La₂O₃) = 0.5 g, n ([DCA]⁻) = 110 μ mol, T = 373 K, p (H₂) = 20 bar, V (H₂O)/V 90 (BEN) = 2:1

NaDCA is a cheap alternative to DCA based ionic liquids.





Fig. 2 Effect of the amount of NaDCA, conditions: $m (1Ru/La_2O_3) = 0.5 \text{ g}$, add.: NaDCA, T = 373 K, $p (H_2) = 20 \text{ bar}$, $V (H_2O)/V (BEN) = 2:1$.

Because of the large gain in selectivity in comparison with the 5 ILs (up to 20 % at same conversion) the amount of the additive was varied to analyze its influence on the reaction (Fig. 2). There was only a small range of DCA addition in which the NaDCA had a positive effect on the performance of the catalyst. In comparison with the experiment without IL the selectivity to 10 cyclohexene was increased to 40 % by adding only 60 µmol NaDCA in combination with an increase of the reaction time from 60 to 240 min. A further addition of NaDCA (110 and 170 μ mol) decreased the activity of the catalyst from 94 % to 42 % and 28 %, respectively. The selectivities in these experiments 15 were increased further more and an excellent initial selectivity to cyclohexene of about 70 % was achieved. It should be noted that the addition of very small amounts of the additive has a tremendous influence on the selectivity in the hydrogenation of benzene. This is a similar effect as it was described before for the 20 influence of the IL [B3MPyr][DCA] in the catalyst system with alumina as support.12



Fig. 3 Effect of metal loading, conditions: m (Ru/La₂O₃) = 0.5 g, n (DCA)/n (Ru) = 2.3, T = 373 K, p (H₂) = 20 bar, V (H₂O)/V (BEN) = 2:1.

25 The selectivity-conversion plot obtained for three lanthanum oxide supported ruthenium catalysts with different metal loading (1, 2 and 5 wt.% Ru) showed a similar behavior up to conversion

degrees of ca. 25 % with an initial selectivity (S_{CHE,max}) around 65-70 %. This implies a similar Ru dispersion of the catalysts. ³⁰ Chemisorption experiments with hydrogen gave low and comparable values of 1.9, 2.7 and 2.8 µmol H₂/g_{cat}, respectively, from which large Ru particle sizes can be calculated. However, the presence of Ru particles could not be affirmed in control experiments by TEM analysis. Keeping in mind the preparation ³⁵ protocol of the catalysts which were reduced at 673 K, it must be assumed that the ruthenium surface is covered with partially reduced lanthanum oxide due to well-known SMSI effect (Strong Metal Support Interaction).¹⁷ Only at higher conversions the SRu/La₂O₃ catalyst was more selective than the other two with ⁴⁰ lower Ru loading.



Fig. 4 N1s spectra of $1Ru/La_2O_3$ before and after reaction (BE of N1s = 398 eV).

From the decreasing conversion with increasing NaDCA 45 amount (Fig. 2) it can be assumed that the additive interacts with the surface of the ruthenium catalyst. To provide evidence for the interaction of ruthenium active sites and NaDCA the 1Ru/La₂O₃ catalyst was analyzed by X-ray photoelectron spectroscopy 50 (XPS) before and after the reaction. The N1s spectra (Fig. 4) show that nitrogen could be observed on the surface of the catalyst after the reaction in which the NaDCA was used. In addition, it has to be noted that sodium was not detectable. Therefore, it can be concluded that the DCA anions adsorb on the 55 surface of the catalyst because the anion is the only origin for nitrogen in this reaction system. From analyzing the surface composition the ratio of surface atoms (s) of nitrogen to ruthenium can be calculated to $(N/Ru)_s = 0.18$ which is distinctly lower than the ratio deduced from the chosen feed composition in the liquid phase (l) $(N/Ru)_l = 2.3$. It is evident that a part of the DCA concentration in the batch reactor is adsorbed on the catalyst surface whereby the most active Ru sites are poisoned leading to a strong decrease of the second hydrogenation step s CHE \rightarrow CHA.

Finally, the leaching behavior was investigated by ICP-OES and mass spectroscopy. The analysis of the aqueous phase showed neither ruthenium nor lanthanum to a detection limit of 0.2 ppm. In the mass spectrum of the organic phase no indication of a Ru

¹⁰ complex were found. The absence of the typical isotope distribution of ruthenium is evidence for no leaching of ruthenium to the organic phase.

4. Conclusions

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The selective hydrogenation of benzene to cyclohexene was achieved with this catalyst system (Ru/La₂O₃ + NaDCA) with excellent initial selectivities of 70 %. At conversions below 15 % cyclohexene is the main product and a maximum yield of 14 % is reached. This is a further improvement of our presented catalyst system towards a greener route to produce cyclohexene. ²⁰ Compared to other catalyst systems based on Ru-Zn type catalysts together with ZrO₂ and ZnSO₄ as additives, the amounts of the expensive ruthenium and NaDCA, used in presented approach, are about two orders of magnitude smaller. The DCA anion has the most important influence on the activity and ²⁵ selectivity of the catalyst. From XPS analysis, it is evident that the DCA anion is adsorbed on the catalyst surface whereby the most active Ru sites are poisoned so that the undesired total hydrogenation to cyclohexane is inhibited.

Notes and references

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