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Heterogeneous Catalysis

Ruthenium-Catalyzed Selective Hydrogenation of Benzene to Cyclohexene in the Presence of an Ionic Liquid**

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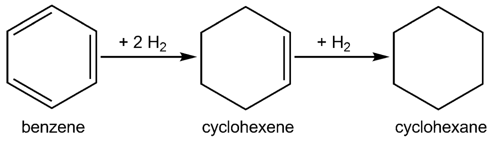
The hydrogenation of benzene is a frequently used model reaction for determining the activity of hydrogenation catalysts which usually very rapidly produce cyclohexane (CHA) in an organic phase and with standard heterogeneous catalyst systems (upon which the industrial CHA synthesis is based). Under these conditions, the possible intermediates of stepwise hydrogenation (1,3-cyclohexadiene, cyclohexene), which are linked to the reaction's lack of selectivity, are not formed even at low conversions, owing to the free standard reaction enthalpies (benzene→cyclohexene: $-23\ \mathrm{kJ\,mol^{-1}}$, cyclohexene→cyclohexane: $-75\ \mathrm{kJ\,mol^{-1}}$, Scheme 1) and the high reactivity of cyclohexene. New calculations for Ru(0001) surfaces based on density functional theory confirm that at high hydrogen coverage, the activation energy required for the second hydrogenation step is much lower than that of the partial hydrogenation leading to cyclohexene.[1]



Scheme 1. Benzene hydrogenation as a simple consecutive reaction.

The selective hydrogenation of benzene to cyclohexene is also of considerable industrial interest because the cost-efficient synthesis of this intermediate facilitates subsequent syntheses such as hydration to cyclohexanol and further to adipic acid and ε-caprolactam.[2] Until now, intermediate steps—the complete hydrogenation of benzene to cyclohexane followed by oxidation to a cyclohexanol/cyclohexanone mixture—have been necessary and are carried out at low conversion of about 10%. With the selective hydrogenation of benzene to cyclohexene, which could be easily hydrated to cyclohexanol, the cyclohexane oxidation step can be eliminated.

The established reaction systems for the selective hydrogenation of benzene to cyclohexene are very complex four-phase systems comprising an organic phase and an aqueous phase, as well as hydrogen and a solid catalyst. The latter is frequently based on an oxide carrier (Al_2O_3, ZrO_2, ZnO) loaded with ruthenium and a second metal. Also large amounts of inorganic salts are dissolved in the aqueous phase which should increase, just like H_2O, the hydrophilicity of the Ru catalyst. Zinc salts in particular are used, without which no cyclohexene is formed. In many cases NaOH is also added. In the aqueous phase the inherently hydrophobic catalyst is surrounded by a hydrate shell in which the solubility of cyclohexene is lower than that of benzene (factor of 6 at 150 °C, 50 bar);[3] this impedes the re-adsorption of the cycloalkene and protects it against subsequent hydrogenation. Typical reaction conditions are 140 to 150 °C at a pressure of 40 to 60 bar H_2. An unsupported Ru–Zn catalyst dispersed by ZrO_2 in the aqueous phase, which additionally contains $ZnSO_4$, has reached industrial maturity. However, with a cyclohexene selectivity of 80% (maximum yield 56%),[4] the salt load in the reactor is substantial, amounting to 50 times the amount of Ru used.

In recent studies, a number of second metals (Mn, La) as well as other additives in the aqueous phase, including toxic cadmium sulfate, have been evaluated.[5,6] Under the aqueous alkaline reaction conditions, leaching is expected, by which ZnO and ZrO_2 enter the liquid phase and then act as additives.[7] Because the use of even larger amounts of Ru catalyst and the high salt load[5] is associated with considerable corrosion problems in the reactor and additional separation steps, the use of such catalyst systems is problematic. Therefore, more research is required.

The very simple catalyst system we present herein comprises only supported ruthenium in water with the addition of very small amounts (in the ppm range) of ionic liquids (ILs); there is no need for added salts and second metals. Nevertheless, cyclohexene is formed with high selectivity. The ILs used (Scheme 2) must be water-soluble so as not to produce any fifth phase in the suspension, and they must not decompose on the Ru catalyst in the presence of water or the reactants.[8]

The properties of ILs have been comprehensively described. Ionic liquids have numerous important applications, such as solvents in organic synthesis, as stabilizers for nanoparticles,[9] and as constituents of SILP (supported ionic liquid phase) catalysts[10] and SCILL (solid catalyst with an ionic liquid layer) systems.[11]

As shown in Table 1, the ILs first used in the screening affect both the activity of the catalyst Ru/Al_2O_3-41 (mean Ru particle size $d_{Ru} = 4.1$ nm) and the cyclohexene selectivity. In

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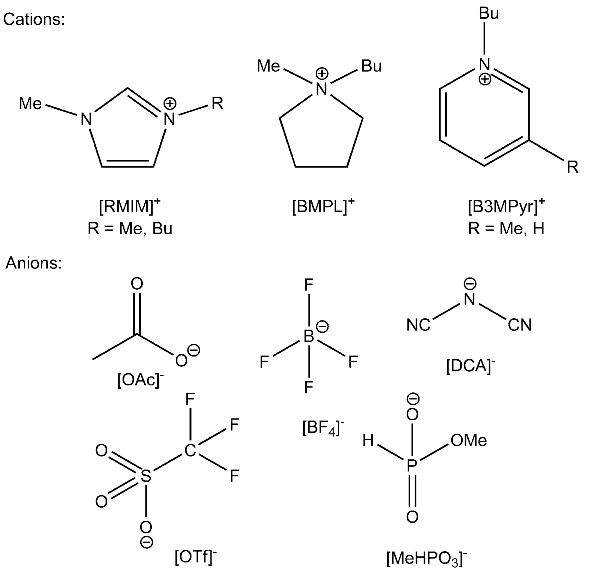

Scheme 2. Structures of cations and anions of the ionic liquids used.

Table 1: Comparison of ionic liquids.[a]

Entry	Ionic liquid	m(IL) [mg]	t[b] [min]	X(benzene) [%]	S(cyclohexene) [%][c]
1	–	0	110	100	0
2	[BPyr][BF4]	50	60	42	4
3	[BMPL][OTf]	50	240	100	0
4	[MMIM][MeHPO3]	50	120	18	13
5	[BMIM][BF4]	50	180	39	7
6	[BMIM][OAc]	50	180	32	8
7	[BMIM][DCA]	50	300	12	18
8	[B3MPyr][DCA]	50	120	17	30
9	[BMPL][DCA]	50	180	31	14

[a] Conditions: m(Ru/Al$_2$O$_3$-41) = 1 g, V(H$_2$O) = 100 mL, V(benzene) = 50 mL, p = 20 bar H$_2$, T = 100 °C). X(benzene) = conversion; S(cyclohexene) = selectivity. [b] Time of the highest yield. [c] S(cyclohexane) = 100 % − S(cyclohexene).

the reference test without IL (entry 1) only cyclohexane was produced in the entire range of conversion, as expected.[12] In comparsion, with added ILs the activity of the Ru catalyst was decreased. Some of the reaction times became considerably longer. The formation of cyclohexene was then observed with the addition of the ILs (exception: [BMPL][OTf]); the ILs increased the selectivity for cyclohexene, but to differing extents.

The ILs based on [BF$_4$] and [OAc] anions achieved cyclohexene selectivities below 10 %, even at low conversions (entries 2, 5, and 6). The greatest effect was observed by adding small amounts[13] of the ILs based on [MeHPO$_3$] and [DCA] anions (entries 4 and 7–9). Specifically with the latter, selectivities for cyclohexene of up to 30 % were achieved.

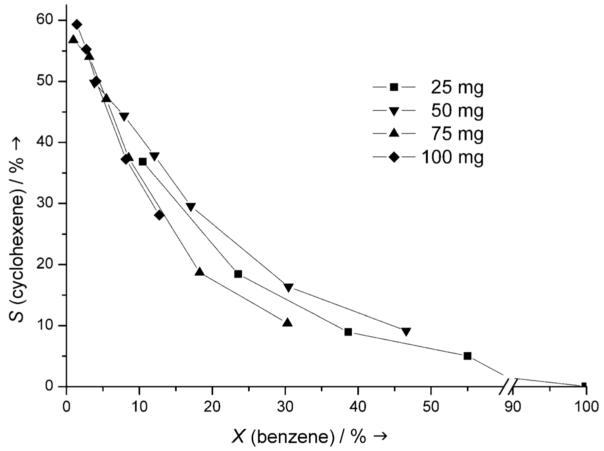

Figure 1. Effect of the amount of [B3MPyr][DCA] on the selectivity–conversion curve. Conditions: m(Ru/Al$_2$O$_3$-41) = 1 g, V(H$_2$O) = 100 mL, V(benzene) = 50 mL, p = 20 bar H$_2$, T = 100 °C.

Systematic tests were performed with [B3MPyr][DCA] using varying amounts of IL and the Ru catalyst (for the effect of the benzene/water ratio, see Figure S1 in the Supporting Information). Note, that because of the consecutive steps of benzene hydrogenation the cyclohexene selectivities must be always compared at constant benzene conversion (selectivity–conversion diagrams). Figure 1 shows the cyclohexene selectivity as a function of conversion with various amounts of IL. The test conditions were changed only by varying the amount of IL used (between 25 and 100 mg).

These results indicate that selective hydrogenation of benzene is achieved; in other words, now cyclohexene is the main product of the reaction at low conversions ($S_{\text{cyclohexene,max}} = 60\,\%$). The amount of IL mainly affects the catalyst activity. With increasing amounts of IL in the range of 25–100 mg, the conversion decreases from 100 % to 13 % at a constant reaction time (t = 240 min). All of the initial cyclohexene selectivities range between 50 % and 60 %.

The formation of the intermediate at the expense of catalyst activity, which is already sharply decreased in the lower concentration range of the added IL ($< 7.5 \times 10^{-4}$ mol L^{-1} (< 170 ppm); Figure 2) is typical for intervention in the kinetics of a consecutive reaction and is otherwise caused in heterogeneous catalysis, for example, by the presence of an ensemble effect or a ligand effect of a second metal.[14]

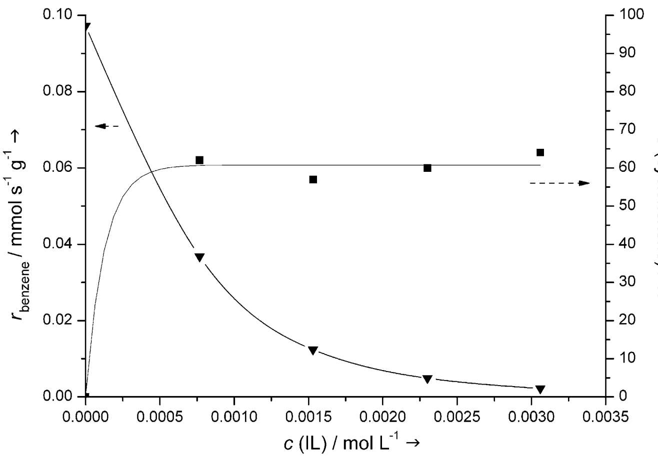

Figure 2. Dependence of the initial reaction rate of benzene consumption and cyclohexene selectivity on the concentration of [B3MPyr][DCA]. See Figure 1 for reaction conditions.

The decrease in activity with the increase of the IL amount indicates that the IL interacts with the Ru catalyst. To examine this further, we analyzed the surface of the Ru/Al_2O_3 catalyst applied in the hydrogenation experiment by means of photoelectron spectroscopy (XPS) (Ru 3d and N 1s spectra: Figures S2–S5 in the Supporting Information). The N 1s spectra confirm the presence of nitrogen, which can originate only from the IL because the IL is the only nitrogen source in the reaction system. These findings unequivocally indicate that the IL is chemisorbed on the catalyst. The ratio of the surface (s) atoms of nitrogen to ruthenium is $(N/Ru)_s = 0.22$, which is distinctly lower than the ratio resulting from the chosen hydrogenation batch in the liquid phase (v) $(N/Ru)_v = 3.5$. If one considers that the only binding energy detected in the N 1s spectra is at 398.0 eV and keeping in mind the XPS results measured with catalysts in which the IL is present as a thin film on the supported noble metal (SCILL systems),[11b] a preferred binding of the dicyanamide anion to the Ru surface and its modification can be deduced. In contrast to Pd catalysts (SCILL type), there are no indications of a significant change in the electronic state of the ruthenium in Ru/Al_2O_3 after benzene hydrogenation in the presence of the IL. These findings suggest that catalyst activity is instead reduced by an ensemble effect; that is, the geometric arrangement or the number of Ru atoms catalyzing the benzene hydrogenation is reduced ("diluted") by the anion of the IL.

If the IL modifies the Ru surface in this way, the selective hydrogenation of benzene to cyclohexene in the presence of the IL should also respond to a change in Ru dispersion, in other words, the Ru particle size (determined by H_2 chemisorption, Table S1 in the Supporting Information). Figure 3 shows that this is precisely the case. In the case of highly nanodisperse Ru particles in the catalyst $RuAl_2O_3$-14 ($d_{Ru} = 1.4$ nm), cyclohexene selectivity was higher over a wide range of conversion than that with the catalyst having a mean Ru particle size of 4.1 nm, so that higher yields of cyclohexene ($Y_{\text{cyclohexene,max}} = 11\,\%$) were obtained.

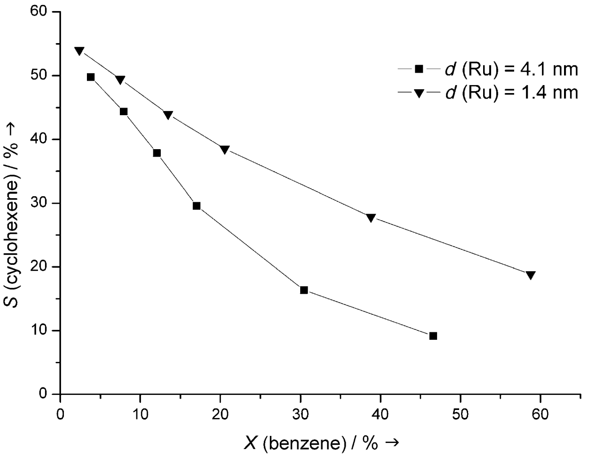

Figure 3. Effect of Ru particle size on the selectivity–conversion curve, $n(IL)/n(Ru\text{-}41) = 2.9$, $n(IL)/n(Ru\text{-}14) = 3.5$. See Figure 1 for reaction conditions.

This is evidence that the IL adsorbs in situ to strongly binding Ru centers through its $N(CN)_2$ anion, and these ensembles block the consecutive hydrogenation to cyclohexane. We also observed this "cocatalytic" effect of IL in citral hydrogenation with an ex situ prepared thin IL film on supported nanoparticles, and ascribed it to a new kind of ligand effect,[11b] expressed by a decrease of the adsorption enthalpy of H_2.

Because usually the adsorption enthalpy of H_2O on ruthenium in the presence of H_2 is roughly half of that of a surface coated only with water,[3] the hydrogen coverage which is now decreased by the presence of the IL a) improves the hydrophilic character of the Ru catalyst and b) diminishes over-hydrogenation.

Of course, the different solubilities of the starting material, intermediate, and product in ILs must also be considered (physical solvent effect). Thus, the excess values of molar free enthalpies of mixing for mixtures of benzene, cyclohexene, or cyclohexane with $[EMIM][NTf_2]$ increase in the order mentioned[15] and their solubilities decrease correspondingly. This has also been established for a number of other ILs.[16] Consequently, in presence of an IL during the selective hydrogenation of benzene, the cyclohexene, which is formed but less soluble in the IL, is withdrawn faster from catalyst surface, so that the further hydrogenation to cyclohexane is reduced. This is also associated with the considerably lower solubility of cyclohexene in water relative to that of benzene. Cyclohexene is formed as the main product in the initial phase of the reaction (Figures 1 and 2), and water and IL impede its renewed adsorption. If the degree of coverage of benzene and cyclohexene on the Ru surface are comparable as the reaction advances, and their adsorption competes with that of water, the hydrophilicity of the catalyst surface no longer suffices for fast desorption of cyclohexene, and more cyclohexane is formed.

Analysis of the aqueous phase after the reaction using ICP-OES revealed no ruthenium, indicating that leaching and the formation of a homogeneous catalyst did not occur during the reaction.

In summary, with the simple catalyst system described here the extremely difficult selective hydrogenation of benzene to cyclohexene in water as a solvent in the presence of an IL has been successfully carried out. Cyclohexene is the main product of the reaction in the presence of ruthenium on $Al_2O_3/H_2O/[B3MPyr][DCA]$ under moderate reaction conditions with a high selectivity of 60% at low conversions. Using small amounts (ppm range) of an IL based on DCA, the addition of inorganic salts and NaOH is not necessary, substantially simplifying the reaction and eliminating the expensive purification of the reaction medium. These advantages over the ordinary multicomponent reaction mixtures and catalysts—along with the associated saving of costly materials—make catalyst optimization attractive. Future work should be focused on SCILL systems and an appropriate catalytic reaction engineering, for example in a continuous-flow reactor, similar to SILP catalysis.[17]

Experimental Section

Example of a hydrogenation experiment: The catalyst (1 g), the aqueous IL solution (50 mg IL in 100 mL H_2O), and benzene were placed in the reactor (300 mL autoclave, PARR, stirring speed 1000 rpm), and the mixture was flushed twice with 10 bar Ar (Linde, 5.0). The mixture was then heated under 2 bar Ar to 100 °C. The addition of 20 bar H_2 (Linde, 5.0) defined the start of the reaction. Samples were removed at defined intervals and analyzed by gas chromatography (HP 6890, FID, capillary column Agilent DB-Wax, $l = 30$ m, $d_i = 0.25$ mm, $t_i = 0.25$ μm). Further experimental details are provided in the Supporting Information.

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