An exceptionally rapid and selective hydrogenation of 2-cyclohexen-1-one in supercritical carbon dioxide[†]

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Selective hydrogenation of 2-cyclohexen-1-one over Pt–MCM-41 proceeds at a very high rate and produces cyclohexanone with selectivity of 100% in a batch reactor; a marked increase in the reaction rate (TOF) from 2283 min⁻¹ to 5051 min⁻¹ is observed on increasing the pressure from 7 MPa to 14 MPa at 40 °C.

Supercritical carbon dioxide (scCO₂) is considered a most promising reaction medium for rapid and selective hydrogenation promoted by homogeneous and heterogeneous catalysts.¹ A particularly significant advantage of hydrogenation in scCO₂ is the high miscibility of the reacting hydrogen gas and its high diffusivity. In particular, chemoselective hydrogenation driven by heterogeneous catalysts has attracted considerable attention because of the faster reaction rate, high product selectivity and clean product separation.² Besides this, scCO₂ is a non-flammable, non-toxic and efficient reaction medium. In this communication, we would like to describe the very fast hydrogenation of 2-cyclohexen-1-one over Pt–MCM-41 (1 wt% Pt containing mesoporous material) catalyst producing cyclohexanone with 100% selectivity within 10 min.

The liquid phase hydrogenation of 2-cyclohexen-1-one is generally carried out over Rh/SiO₂ (turnover frequency TOF = $1.9 \times 10^{-5} \text{ min}^{-1}$),³ Pt/B (TOF = 1.37 min^{-1})⁴ or a homogeneous Ru/Os complex⁵ catalyst in a conventional organic solvent. It has been found that the reaction is slow and a mixture of cyclohexanone and cyclohexanol is formed as the product. However, the utilization of scCO₂ causes a significant enhancement in the reaction rate compared to the conventional organic solvent and gives excellent selectivity for cyclohexanone. Scheme 1 shows the probable reaction path under the studied reaction conditions (T = 40 °C, t = 10 min, $P_{H_2} = 2$ MPa, $P_{CO_2} = 7$ –14 MPa).

First, we carried out the hydrogenation reaction over commercially available different noble metal catalysts at 40 $^{\circ}$ C in scCO₂ (12 MPa) with 2 MPa of hydrogen for 10 min and the results are shown in Table 1. The reaction goes smoothly over Pd/C, Pt/C (5 wt% of the respective metal; Entries 1 and 2) but the selectivity of **II** is low at 51.2% and 85%, respectively whereas the Rh/C and Ru/C catalysts gave unsatisfactory

results for conversion (Table 1; Entries 3, 4). However, compared to the other catalysts, the promotion of the reaction by 1% Pt–MCM-41 (mesoporous; ESI†) provides very high conversion of > 99% and the complete selectivity to **II**. Thus, depending on the performance, Pt-MCM-41 is selected as an effective catalyst for selective hydrogenation of **I** and used to check the effect of different reaction parameters.

Fig. 1 exhibits the variation in TOF and selectivity of the reaction with CO2 pressure. Notably a dramatic TOF augmentation is observed, suggesting a marked increase in reaction rate with increasing CO₂ pressure. A visual inspection of the phase behavior of the reaction mixture (CO₂ + H_2 + substrate; Fig. 2; the detailed method has been described elsewhere⁶) confirmed the formation of a single phase at 10 MPa, which seems to be a crucial factor in determining the activity and selectivity of the reaction. Considering the % yield of **II**, it has been found that the yield increases with increasing CO₂ pressure and reaches a maximum at 10 MPa and then remains constant. At lower CO₂ pressure (7 MPa; Fig. 2a; biphasic conditions) the yield of II is $\sim 41\%$ and the subsequent increase in CO₂ pressure to 10 MPa leads to 100% yield of the product II as the system proceeds towards a single phase. Hence, the significant increase in reaction rate with the transition of the reaction mixture from biphasic to a single phase mirrors the reduction of mass transfer resistance. To get an insight into the role of CO₂, an experiment was performed without CO₂ under the same reaction conditions (Table 1; Entry 8). The result shows that the conversion and selectivity of II decrease significantly. On the other hand when comparing with the conventional organic solvent medium under the same reaction conditions (Table 1; Entries 9, 10), as the medium changes the reaction rate becomes slow as compared to $scCO_2$ (TOF = 5051 min⁻¹), which is confirmed by the TOF of the reaction carried out in the corresponding medium (hexane = 483 min^{-1} ; 2-propanol = 498 min^{-1}).



Scheme 1 Selective hydrogenation of I in supercritical carbon dioxide. Conditions: $P_{CO_2} = 7-14$ MPa, $P_{H_2} = 2$ MPa; catalyst = 0.05 g (1 wt% Pt); substrate = 2 g; T = 40 °C; t = 10 min; 50 ml batch reactor.

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| | | | | | Selectivity (%) | | |
|-------|-----------------------|-------------------------|-----------------------|----------------|-----------------|--------------|---------------------|
| Entry | Substrate | Catalyst | Medium/Pressure (MPa) | Conversion (%) | Cyclohexanone | Cyclohexanol | TOF $(\min^{-1})^d$ |
| 1 | 2-Cyclohexen-1-one | 5% Pd/C | $scCO_2/12$ | 65.4 | 51.2 | 48.8 | 777 |
| 2 | | 5% Pt/C | $scCO_2/12$ | 75.6 | 85.0 | 15.0 | 964 |
| 3 | | 5% Rh/C | $scCO_2/12$ | 25.1 | 100.0 | 0.0 | 270 |
| 4 | | 5% Ru/C | $scCO_2/12$ | 13.0 | 56.2 | 43.8 | 128 |
| 5 | | 5% Rh/ SiO ₂ | $scCO_2/12$ | 48.8 | 89.8 | 10.2 | 232 |
| 6 | | 1% Pt/SiO ₂ | $scCO_2/12$ | 81.3 | 90.0 | 10.0 | 2433 |
| 7 | | 1% Pt-MCM-41 | $scCO_2/12$ | 100.0 | 100.0 | 0.0 | 5051 |
| 8 | | 1% Pt-MCM-41 | No solvent | 15.4 | 87 | 13 | 483 |
| 9 | | 1% Pt-MCM-41 | Hexane | 16.6 | 49.7 | 50.3 | 498 |
| 10 | | 1% Pt-MCM-41 | 2-Propanol | 10.2 | 90.1 | 9.9 | 352 |
| 11 | | 1% Pt-MCM-41 | $scCO_2/12^b$ | 100.0 | 100.0 | 0.0 | 5049 |
| 12 | 3-Methylcyclohexenone | 1% Pt-MCM-41 | $scCO_2/12$ | 97.4 | 100.0^{c} | 0.0 | 4603 |
| 13 | 3-Ethoxycyclohexenone | 1% Pt-MCM-41 | $scCO_2/12$ | 75.9 | 100.0^{c} | 0.0 | 2816 |
| 14 | Mesityl oxide | 1% Pt-MCM-41 | $scCO_2/12$ | 95.5 | 100.0^{c} | 0.0 | 5020 |

Table 1 Selective hydrogenation of 2-cyclohexen-1-one (I) over various noble metal catalysts in scCO₂ and in different organic solvent⁴

^{*a*} Conditions: catalyst = 0.05 g; T = 40 °C; t = 10 min; $P_{H_2} = 2$ MPa; organic solvent = 5 ml. ^{*b*} After 3 times recycle. ^{*c*} Corresponding hexanone. ^{*d*} Turnover frequency (TOF) = number of moles reacted/moles of metal × time; 2-cyclohexen-1-one is used as substrate from Entries 1–11; catalysts from entries 1 to 6 are commercial catalysts (1–4 and 6 are from Aldrich; 5 is from Johnson Matthey, incipient wetness impregnation); Pt–MCM-41 is obtained by the hydrothermal method.¹²



Fig. 1 Effect of CO₂ pressure on the rate and the selectivity of the reaction. Conditions: $P_{H_2} = 2$ MPa; catalyst = 0.05 g (1 wt% Pt); substrate = 2 g; T = 40 °C; t = 10 min; 50 ml batch reactor.



Fig. 2 Snapshots of reaction mixture $(CO_2 + H_2 + 2$ -cyclohexen-1-one) (a) 7 MPa, (b) 10 MPa.

Therefore, the higher reaction rate in $scCO_2$, in contrast with the other solvent or solventless conditions, can be attributed to the enhanced solubility and high diffusivity of the reactant gases, which eliminates or reduces the effect of gas/liquid mass transfer. It has to be mentioned that in each case, the selectivity of **II** decreased with the formation of **III** by the hydrogenation of both C=C and C=O in the absence of CO₂ (Table 1; Entries 8–10) and this implies that CO₂ might preferentially cover the active site for the hydrogenation of C=O,⁸ resulting in a significant increase in activity and selectivity of **II**. To confirm the inhibition of the hydrogenation of C=O by CO₂ the reaction was continued for 10 min to 24 h in scCO₂, and no change in the selectivity of **II** was observed.

It has to be mentioned that the properties of $scCO_2$ are strongly influenced by changes in pressure and temperature. Thus, fine tuning of the temperature can also change the density of the medium and consequently the solvent strength, which have a strong impact on the phase behavior as well as the chemical equilibrium and reaction rates.⁹ To explore the effect of temperature, the reaction was conducted at 30, 35, 40, 45 and 50 °C. Conversion increased with temperature and reached a plateau at 40 °C but the selectivity remained unaltered (Fig. 3). Supercritical carbon dioxide is a compressed liquid and for example a change in temperature from 35 to 45 °C at a fixed pressure of 10 MPa can easily change the density¹⁰ from 0.714 to 0.502 g mL⁻¹ and also the solubility of the reactant. Therefore it is difficult to explain the change in activity with temperature.¹¹ Hence, the effect of temperature was checked at fixed fluid density rather than at a specified constant pressure. At a fixed density of ~ 0.7 g mL⁻¹



Fig. 3 Effect of reaction temperature on conversion. Conditions: $P_{CO_2} = 12$ MPa, $P_{H_2} = 2$ MPa; catalyst = 0.05 g (1 wt% Pt); substrate = 2 g; t = 10 min; 50 ml batch reactor.

 $(35 \,^{\circ}C, 10 \,\text{MPa}, 0.714 \,\text{g mL}^{-1}; 40 \,^{\circ}C, 12 \,\text{MPa}, 0.719 \,\text{g mL}^{-1};$ $45 \,^{\circ}\text{C}$, 14 MPa, 0.721 g mL⁻¹),¹⁰ the hydrogenation of I exhibits the same conversion and selectivity, but contrasts with the effect of temperature at fixed pressure on conversion and selectivity (Fig. 3). For instance, the system at 35 °C and 10 MPa exhibits better conversion and selectivity compared to 35 °C and 12 MPa (Fig. 3) and these remain unaltered as the pressure changes from 10 to 12 MPa at 40 °C and 12 to 14 MPa at 45 °C, which is difficult to explain. So in this case it is better to suggest that the temperature has a straightforward effect on the conversion and selectivity at a fixed pressure. It is obvious that the solubility of hydrogen has prime significance for hydrogenation in scCO₂. Considering the hydrogen pressure (fixed $P_{CO_2} = 12$ MPa; T = 40 °C; t = 10 min), the conversion changes from 13.1% to 100% as the pressure increases from 0.2 to 2.0 MPa keeping the selectivity of II unchanged. The change in hydrogen pressure can alter the phase behavior of the reaction mixture, which can affect the reaction rate. An optimum hydrogen pressure of 2 MPa is necessary to maintain the high reaction rate under the studied reaction conditions.

Recycling of the catalyst is an important aspect in the heterogeneous catalysis system. The most significant advantages of the method described are that the reaction is conducted at very low temperature and the reaction time is short. Therefore, the chance of deactivation of the catalyst is low and no leaching of Pt has been observed. To check the activity of the used catalyst, it was recycled at least three times and the activity and selectivity for **II** (Table 1; Entry 11) remained the same.

We have extended the process to the hydrogenation of methyl and ethoxy substituted cyclohexenone and also an acyclic ketone, and the results are shown in Table 1 (Entries 12, 13, 14). In each case excellent selectivity of the corresponding C=C hydrogenated product is obtained. The results show a reasonable reaction rate but it is still lower compared to I as observed from the TOF (reaction rate). A decrease in TOF from 4603 min⁻¹ to 2816 min⁻¹ as the substitution changes from methyl to ethoxy is evident. This may be attributed to the bulkiness of the substrate, which prevents easy access of the substrate molecule to the active sites of the mesoporous channel and consequently the rate of the reaction decreases. However, the acyclic ketone shows a comparable TOF to that of the cyclohexenone (5020 min⁻¹). In conclusion, the present study shows that it is possible to achieved an exceptionally high reaction rate (TOF = 5051 m^{-1}) at very low temperature of 40 °C for the hydrogenation of I in scCO₂. This unusually high reaction rate might be due to the enhanced diffusion of the reactants and also the mass transfer reduction as the reaction occurs under conditions of a single phase scCO₂, hydrogen and the substrate. Of particular note, we find that the density of the medium, which is related to the solubility of reactant, plays an important role in increasing the reaction rate and also the substrate does not change the selectivity but a slight decrease in the reaction rate has been observed depending on the size of the substrate.

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