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Selective Reduction of Chloronitrobenzene to Chloroaniline on Ru/MgF_2 Catalysts

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Abstract The use of magnesium fluoride as a support for ruthenium has enabled to obtain a catalyst of high activity and selectivity for hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) in the liquid-phase at 353 K under 4 MPa of hydrogen pressure. The introduction of water to methanolic medium of the reaction (volume ratio of water to methanol equal to 1:2) has resulted in almost five-fold increase in catalytic activity, while selectivity towards *o*-CAN remained on the level close to 100%. The nature of ruthenium precursor and catalyst activation conditions appeared to have a clear influence on metallic phase dispersion that was reflected by the activity of Ru/MgF_2 catalysts. The catalysts of poorer dispersion were more active in *o*-CNB hydrogenation, however, their selectivity to *o*-CAN was slight lower.

Keywords Chloronitrobenzene hydrogenation · Ruthenium catalyst · Magnesium fluoride · MgF_2

1 Introduction

The catalytic hydrogenation of organic functional groups is probably the most common application of heterogeneous catalysis to the synthesis of organic compounds. The selective hydrogenation of nitrocompounds is commonly used to the manufacture amines that are important intermediates in the manufacture of agrochemicals, pharmaceuticals, dyes and pigments on commercial scale.

Platinum [1–5] and nickel [6–10] are the metals most widely used for catalytic hydrogenation of halonitroaromatics. Metals with favourable selectivity patterns but, for economic reasons used only to a limited extent, are rhodium [11], iridium [12], palladium [13] and gold [14]. The most selective catalyst is ruthenium [7, 8, 15, 16] however, it exhibits low activity for haloaromatic amine formation [8]. That is why attempts are made at increasing activity of ruthenium catalysts, while maintaining their high selectivity. For a particular hydrogenation reaction, the intrinsic catalytic properties of the metals have the greatest influence on the catalysts activity. Their activity, however, can be changed significantly by the use of suitable supports and modifiers (inhibitors, mediators and promoters) that control metal particle dispersion and metal-support interactions. Modification of electronic state and/or morphology of ruthenium crystals through metal-support interaction creates a chance of obtaining a catalyst of unique catalytic properties.

Taking into consideration the importance of the effect of the metal-support interactions [15, 17–19] on catalyst activity and selectivity, we have applied magnesium fluoride [20, 21] as a support. This support has proved to be excellent for ruthenium catalysts [22, 23].

Catalytic properties of metal-support systems can be modified by applying suitable precursors of active phase [17]. The precursor influences dispersion of active component and modifies its electronic interactions with a support. Therefore, we have used in our study two precursors of ruthenium phase: trirutheniumdodecacarbonyl and ruthenium chloride trihydrate.

Recent reports [24] on advantageous effect of water addition to ethanolic solution of *ortho*-chloronitrobenzene

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on selectivity and activity of ruthenium catalysts have encouraged us to perform similar studies in the case of Ru/MgF_2 catalyst.

2 Experimental

2.1 Support and Catalysts Preparation

Magnesium fluoride was obtained by adding small portions of $MgCO_3 \cdot 2H_2O$ to an aqueous solution of hydrofluoric acid until neutralisation, and acidifying it by introducing a few additional drops of the acid. The precipitate was then aged at room temperature for a couple of days under stirring, dried at 353 K and calcined at 673 K for 4 h. After the calcination, MgF_2 was ground to particles size at the range of 0.2–0.5 mm.

Ruthenium was deposited on MgF_2 by conventional impregnation using methanolic solution of $RuCl_3 \cdot 3H_2O$ (denoted as Cl), and $Ru_3(CO)_{12}$ (denoted as CO). The content of Ru was 1 wt%. The catalysts were dried at 353 K and reduced at 673 K under hydrogen flow. Reduced catalysts were labelled Cl-r, and CO-r, respectively. The catalysts were dried, pre-oxidised in air at 673 K for 2 h and then reduced as described above. The specimens were denoted as Cl-or and CO-or, respectively.

2.2 Activity Test

Hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) was performed in liquid-phase at 353 K for 2 h at 4.0 MPa of hydrogen pressure in a 200 mL stainless steel autoclave with a magnetic stirrer. The autoclave was loaded with 0.05 g of catalyst and 50 mL of 0.1 M methanolic solution of *o*-CNB. Then the autoclave was flushed several times with helium followed by flushing with hydrogen in order to remove air. In each case, the reaction time was 2 h. The reaction products were analysed on a gas chromatograph equipped with a capillary column RESTEK MXT-5.

Catalytic activity was expressed as turnover number (TON) in moles of *o*-CNB reacted per mole of surface Ru atoms (The latter value was determined by hydrogen chemisorption). To make possible the presentation of TON and selectivity results on the same plot, the selectivity was expressed in degrees of selectivity, where 100% selectivity = 1° of selectivity.

2.3 Hydrogen Chemisorption

Prior to hydrogen chemisorption, samples were pretreated in situ to remove adsorbed molecules from the surface of ruthenium. Samples were evacuated for 15 min at room temperature and next at 673 K for 60 min, followed by reduction in hydrogen flow (40 cm^3 min^{-1}) at 673 K and evacuated again for 120 min at 673 K.

The dispersion (D), defined as the ratio of the number of Ru atoms on the surface (N_s), to the total number of Ru atoms in the catalyst (N_T) was calculated from the formula:

$$D = \frac{\frac{V \cdot n}{22414 \cdot m}}{\frac{wt}{100 \cdot M}} = \frac{100 \cdot V \cdot n \cdot M}{22414 \cdot m \cdot wt}$$

where, V: H_2 adsorbed volume [cm^3 STP]; n: stoichiometry of hydrogen chemisorption (=2); 22,414: molar volume of gas [cm^3/mol]; m: weight of the catalysts [g]; wt: Ru loading in the catalyst [wt%]; M: molar mass of ruthenium (101.07 g/mol).

All chemisorption experiments were performed on an ASAP 2010C sorptometer. Hydrogen chemisorption measurements were carried out at 373 K.

2.4 Surface Area Measurements

The low-temperature adsorption of nitrogen was performed on a Micromeritics ASAP 2010 sorptometer. Specific surface area was determined by using the BET method.

3 Results and Discussion

3.1 Optimisation of Reaction Conditions

Selective hydrogenation of *ortho*-chloronitrobenzene to *ortho*-chloroaniline was carried out in a steel autoclave at 353 K for 2 h under 4 MPa of hydrogen pressure, that was loaded with 50 mL of 0.1 M methanolic solution of *o*-CNB and 25 mL of distilled water. The above conditions were established on the base of results of preliminary studies that were oriented towards optimisation of reaction conditions. All preliminary catalytic tests were performed on Cl-r catalyst.

In Fig. 1, the effect of water-to-methanol volume ratio on the activity of Cl-r catalyst was shown. As water was added, the activity increased: turnover number was 0.077 s^{-1} when the reaction was carried out in the absence of water, whereas TON = 0.352 s^{-1} for the ratio of H_2O:MeOH = 0.5. When the amount of water exceeded the above ratio, a small decrease in catalytic activity was observed. No noticeable effect of water on catalyst selectivity was observed; the latter was always ~97%. All further experiments were performed at volume ratio of H_2O:MeOH = 0.5.

In our opinion the increased catalytic activity after water addition was a consequence of the competition between water and ethanol on surface adsorption and hydrogen bonds between *o*-CAN and water in the solvent.

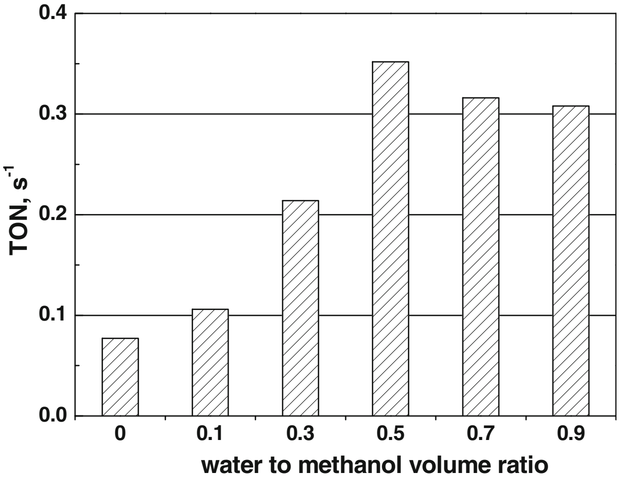

Fig. 1 Liquid-phase hydrogenation of *o*-CNB to *o*-CAN on Cl-r catalyst—the effect of water to methanol volume ratio on catalyst activity at 353 K. Selectivity was ~97% for all solvent compositions

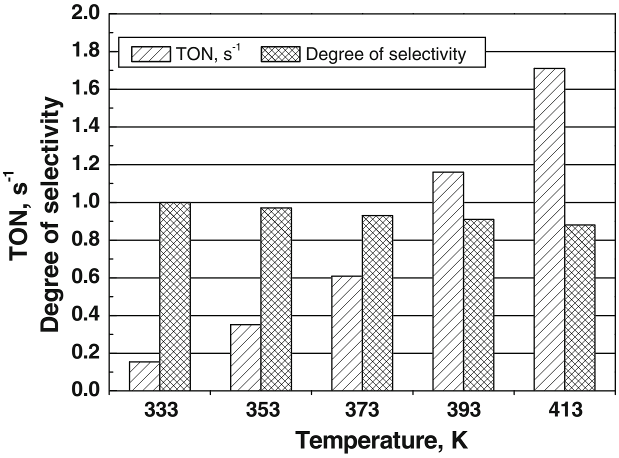

Fig. 3 Liquid-phase hydrogenation of *o*-CNB to *o*-CAN on Cl-e catalyst—the effect of reaction temperature on activity and selectivity. Solvent: 25 cm^3 H_2O + 50 cm^3 MeOH

In the liquid-phase hydrogenation, of great importance is hydrogen pressure. Results of our experiments show that the activity of Cl-r catalyst increases with a rise in H_2 pressure and reaches its maximum at 4 MPa, while the selectivity towards *o*-CAN remains all the time on the level of about 97% (Fig. 2). Further increase of pressure has resulted in a decrease both in catalytic activity and selectivity. Thus the pressure of 4 MPa can be regarded as the optimum one.

The last parameter to be optimised was the reaction temperature. In Fig. 3, the effect of temperature on the activity and selectivity of Cl-r catalyst was presented. Almost linear increase in catalytic activity with increasing temperature was found and, at the same time, the selectivity was decreasing almost linearly as well. The selectivity at 333 K was equal to 100%, however, the catalytic activity at 333 K was two times lower compared to that at 353 K. That has prompted us to performed further investigation at 353 K. Such a choice has enabled to see more clearly the differences in activity and selectivity between catalysts studied.

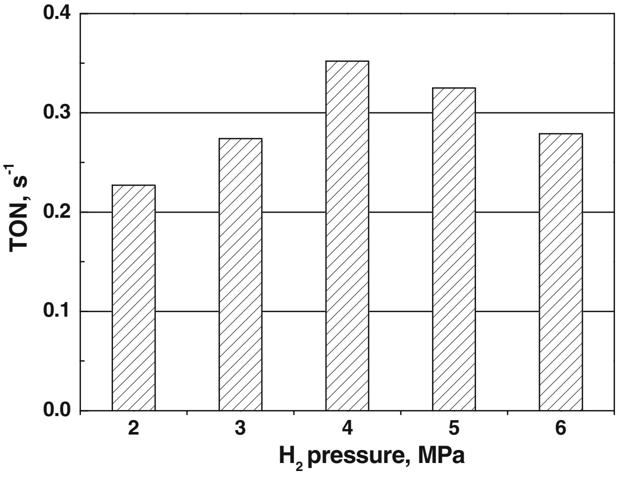

Fig. 2 Liquid-phase hydrogenation of *o*-CNB to *o*-CAN on Cl-r catalyst—the effect of hydrogen pressure on catalyst activity at 353 K. Solvent: 25 cm^3 H_2O + 50 cm^3 MeOH

3.2 The Influence of Ruthenium Precursor and Ruthenium Dispersion on Activity and Selectivity of Ru/MgF_2 Catalysts in *o*-CNB Hydrogenation to *o*-CAN

Ruthenium was deposited on MgF_2 by conventional impregnation using $RuCl_3 \cdot 3H_2O$ and $Ru_3(CO)_{12}$ in methanolic solution. The ruthenium content was 1 wt%. Catalysts, after drying, were subjected to thermal treatment according to two procedures. One group of catalyst samples was reduced in flowing hydrogen directly after drying, while the other was pre-oxidised at 673 K in air and then reduced.

In Table 1, all investigated catalysts were listed and their surface areas and ruthenium dispersions were given. Surface areas of catalysts are only slightly different from those of magnesium fluoride support (52 m^2 g^{-1}). A small reduction in surface areas results, most likely, from sintering of the narrowest pores, which was observed in the case of MgF_2 alone [20, 21].

Ru/MgF_2 catalysts prepared from both precursors are characterised by relatively low dispersion of metallic phase. The highest dispersion (16.5%) was observed in the case of CO-r catalyst, which results from specific adsorption of $Ru_3(CO)_{12}$ on MgF_2 surface [25]. The specimen prepared from ruthenium trichloride has twice lower ruthenium dispersion (8.2%) compared to that of CO-r. On the other hand, pre-oxidation of ruthenium chloride-originated

Table 1 Catalyst characterization—codes, precursors, pretreatment, surface areas and ruthenium dispersion

Catalyst code	Ruthenium precursor	Pretreatment	BET surface area ($m^2\ g^{-1}$)	Ru dispersion (%)
CO-r	$Ru_3(CO)_{12}$	reduction	51.7	16.5
Cl-r	$RuCl_3 \cdot 3H_2O$	reduction	46.7	8.2
CO-or	$Ru_3(CO)_{12}$	oxidation + reduction	48.3	5.6
Cl-or	$RuCl_3 \cdot 3H_2O$	oxidation + reduction	44.4	8.5

catalyst (Cl-or) does not result in dispersion change compared to the directly reduced catalyst (Cl-r).

In Fig. 4, results of measurements of catalytic activity and selectivity in the reaction of *o*-CNB hydrogenation are shown. The most active was CO-or and the least active CO-r. On the other hand, the highest selectivity was observed for Cl-r (97%), and the lowest for CO-or (80%). The relationship between catalytic activity (TON) and selectivity of Ru/MgF_2 and ruthenium dispersion was presented in Fig. 5, which proves the existence of a clear dependence of both activity and selectivity on metallic phase dispersion. The higher ruthenium dispersion the higher selectivity to *o*-CAN. At the same time no significant influence of ruthenium dispersion in the Ru/MgF_2 catalysts on their selectivity in the hydrogenation of *o*-CNB to *o*-CAN reaction has been observed. A reduction in catalytic activity for chloronitrobenzene hydrogenation with increase in ruthenium dispersion was observed earlier [16]. However, it is worth to add that differences in selectivities between the catalysts are small, whereas those in catalytic activity—considerable. It permits to nurse a hope that further studies will result in the preparation of Ru/MgF_2 catalyst of both high activity and high selectivity.

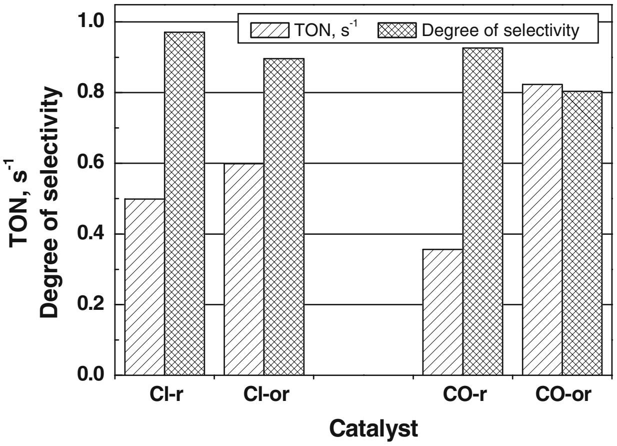

Fig. 4 Liquid-phase hydrogenation of *o*-CNB to *o*-CAN on Ru/MgF_2 catalysts at 353 K. Solvent: 25 cm^3 H_2O + 50 cm^3 MeOH

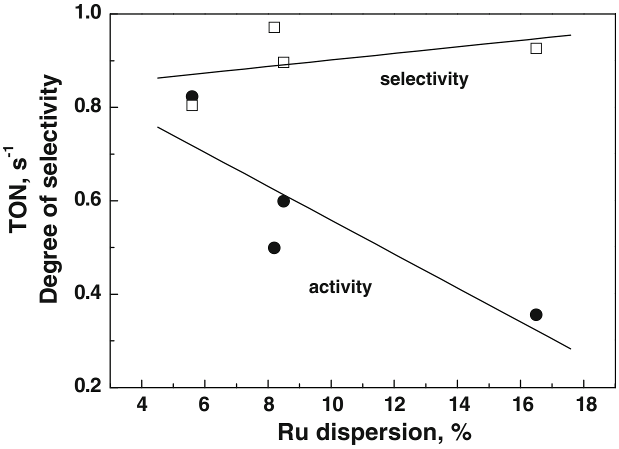

Fig. 5 The effect of ruthenium dispersion on activity and selectivity of Ru/MgF_2 catalysts in hydrogenation of *o*-CNB to *o*-CAN

4 Conclusions

Due to the application of magnesium fluoride as a support for ruthenium, it was possible to prepare a catalyst of high activity and selectivity in the reaction of *o*-CNB hydrogenation to *o*-CAN in liquid-phase at 353 K under 4 MPe of hydrogen pressure. It was established that the addition of water to methanolic medium of the reaction results in almost fivefold increase in catalytic activity, while selectivity is maintained practically unchanged (97%). Ru/MgF_2 catalysts prepared from different ruthenium precursors are characterised by different dispersion of metallic phase. The latter show, in turn, a decisive influence on the activity of catalysts for *o*-CNB hydrogenation (the activity increases with a reduction in dispersion) as well as on the selectivity to *o*-CAN, although to a smaller extent (the selectivity increases with the rise in Ru dispersion). At the same time no significant influence of ruthenium dispersion in the Ru/MgF_2 catalysts on their selectivity in the hydrogenation of *o*-CNB to *o*-CAN reaction has been observed.

References

1. Coq B, Tijani A, Figueras F (1991) J Mol Catal 68:331
2. Yang XL, Liu HF (1997) Appl Catal A: Gen 164:197
3. Yang XL, Deng ZL, Liu HF (1999) J Mol Catal A: Chem 144:123
4. Maity P, Basu S, Bhaduri S, Lahiri GK (2007) Adv Synth Catal 349:1955
5. Liang M, Wang X, Liu H, Liu H, Wang Y (2008) J Catal 255:335
6. Chen YZ, Chen YC (1994) Appl Catal A: Gen 115:45
7. Xiong J, Chen J, Zhang J (2007) Catal Commun 8:345

8. Wang X, Liang M, Zhang J, Wang Y (2007) Curr Org Chem 11:299
9. Wang C, Qiu J, Liang C, Xing L, Yang X (2008) Catal Commun 9(8):1749–1753
10. Li H, Zhao Q, Li H, Mol J (2008) Catal A 285:29–35
11. Wrzyszcz J, Zawadzki M, Trzeciak AM, Ziolkowski JJ (2002) J Mol Catal A: Chem 189:203
12. Baumeister P, Studer M, Roessler F (1997) In: Erlt G, Knözinger H, Weitkamp J (eds) Handbook of heterogeneous catalysis, vol 5. VCH, Weinheim, pp 2186–2209
13. Vishwanathan V, Jayasri V, Mahaboob Basha P, Mahata N, Sikhwivhilu L, Coville NJ (2008) Catal Commun 9(3):453–458
14. Cárdenas-Lizana F, Gómez-Quero s, Keane MA (2008) Catal Commun 9(3):475–481
15. Zuo BJ, Wang Y, Wang QL, Zhang JL, Wu NZ, Peng LD, Gui LL, Wang XD, Wang RM, Yu DP (2004) J Catal 222:493
16. Tijani A, Coq B, Figueras F (1991) Appl Catal 76:255
17. Coq B, Tijani A, Dutartre R, Figueras F (1993) J Mol Catal 79:253
18. Han XX, Zhou RX, Lai GH, Zheng XM (2004) Catal Today 93–95:433
19. Zhang JL, Wang Y, Ji H, Wei YG, Wu NZ, Zuo BJ, Wang QL (2005) J Catal 229:114
20. Wojciechowska M, Czajka B, Pietrowski M, Zieliński M (2000) Catal Lett 66:147
21. Wojciechowska M, Zieliński M, Pietrowski M (2003) J Fluorine Chem 120:1
22. Wojciechowska M, Pietrowski M, Łomnicki S (1999) J Chem Soc Chem Commun 5:463
23. Wojciechowska M, Pietrowski M, Czajka B (2001) Catal Today 65:349
24. Ning J, Xu J, Liu J, Miao H, Ma H, Chen C, Li X, Zhou L, Yu W (2007) Catal Commun 8:1763
25. Pietrowski M, Wojciechowska M, Goslar J, Zieliński M (2003) Mol Phys Rep 37:105