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An efficient ruthenium-vanadium catalyst for selective hydrogenation of *ortho*-chloronitrobenzene

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ABSTRACT

An attempt has been made at obtaining a catalyst for hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) which would be both selective and active. Ruthenium has been used as the active phase since it is the most selective of all metals investigated in the above reaction. Catalyst precursors, $RuCl_3 \cdot 3H_2O$ and NH_4VO_3, were introduced onto an unconventional support – MgF_2 and reduced in hydrogen flow at 673 K. The catalysts obtained revealed unusually high activity and selectivity in the reaction of hydrogenation of *o*-CNB to *o*-CAN, both in the gas- and liquid phase. The structural study of the Ru-V/MgF_2 catalyst has shown that its high activity and selectivity were determined by the strong metal–support interactions and ruthenium–VO_x species electron interactions.

1. Introduction

Halogenated anilines are important intermediates in the manufacturing of a large variety of fine and specialty chemicals. The production of herbicides, fungicides, insecticides and animal repellents, pharmaceuticals, dyes and pigments strongly depends on their supply [1].

Platinum and nickel are the metals most widely used for the hydrogenation of halonitroaromatics. Metals with favourable selectivity patterns are ruthenium [2,3] rhodium [4], and iridium [5], but for economic reasons, their use is limited to special applications. Ruthenium was found to be the most selective catalyst [2], however, its activity for haloaromatic amine formation is low [6]. Therefore, attempts have been made at increasing the activity of ruthenium catalysts, while preserving their high selectivity. For a given hydrogenation reaction, the most important to catalyst activity are intrinsic activities of the metals. These activities, however, can be changed significantly by the use of modifiers (inhibitors, mediators, promoters) which control metal dispersion and metal–support interactions.

Taking into consideration the great effect of metal–support interactions on the activity and selectivity of supported metal catalysts, we have chosen magnesium fluoride as a support [7,8]. Thanks to high chemical resistance and almost neutral character of the surface, this support has proved to be excellent for ruthenium catalysts [9–12]. The activity of Ru/MgF_2 was several times higher than that of Ru/Al_2O_3 at the same almost 100% selectivity of *ortho*-chloronitrobenzene (*o*-CNB) reduction to *ortho*-chloroaniline (*o*-CAN).

In order to improve catalytic activity, a solution of ammonium vanadate and ruthenium(III) chloride was used for co-impregnation of the support to get ruthenium crystallites separated by vanadium atoms on the support surface. This procedure was expected to increase dispersion of Ru and to facilitate formation of new Ru^{n+} centres that could be engaged in the reduction of $-NO_2$ group. The ruthenium catalysts doped with vanadium showed over twice as high activity as that of monometallic ruthenium catalysts, while maintaining the same high selectivity.

2. Experimental

2.1. Preparation of support and catalysts

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 few days under stirring, dried at 353 K and calcined at 673 K for 4 h. After the calcination, MgF_2 was ground to

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obtain particles of 0.2–0.5 mm in size. The surface area of the MgF_2 obtained in this way was 34 $m^2 g^{-1}$.

Ruthenium and vanadium were deposited on MgF_2 by conventional co-impregnation using $RuCl_3 \cdot 3H_2O$ and NH_4VO_3 in methanolic solution. The samples were dried at 353 K and reduced at 673 K under hydrogen flow for 4 h. The Ru content was 1 wt.%, while that of vanadium 0.1, 0.5 and 1.0 wt.%. The catalysts were labelled as Ru1, Ru1-V01, Ru1-V05 and Ru1-V1.

2.2. Catalyst characterisation

The metal–support interactions were studied by FTIR using CO as a probe molecule. Experiments were carried out on a BIORAD spectrometer, model FTS 3000MX. MgF_2 wafers (4 mg cm^{-2}) were placed in a glass cell equipped with KRS-5 windows. Carbon monoxide was adsorbed at 10 Torr at 393 K.

2.3. Ortho-chloronitrobenzene hydrogenation

Hydrogenation of *o*-CNB was performed in two ways:

(a) in liquid-phase conditions – at 353 K and hydrogen pressure of 4.0 MPa in a 200 ml stainless-steel autoclave (0.1 g of catalyst; reaction time: 2 h),
(b) in gas-phase conditions – at 523 K under atmospheric pressure in the flow of reactants (0.1 g of catalyst; 0.1 M *o*-CNB in methanol; infusion rate 2.80 ml h^{-1}; hydrogen flow rate 30 ml min^{-1}). The conversion and selectivity are given after 2 h on stream.

Prior to the reaction, the catalysts were reduced *in situ* under hydrogen flow at 673 K for 2 h.

3. Results and discussion

Catalytic activity and selectivity in *o*-CNB hydrogenation to *o*-CAN depend on performing the reaction in gas or liquid phase, type of solvent, concentration of reactants, reaction temperature and hydrogen pressure [6]. The catalysts obtained in this study were tested in *o*-CNB hydrogenation in the gas phase under atmospheric pressure and in the liquid phase under increased pressure of hydrogen. The reaction conditions were optimised for the catalyst Ru1.

3.1. o-CNB hydrogenation in liquid phase

From among many factors influencing the activity and selectivity of the catalyst in hydrogenation of *o*-CNB to *o*-CAN in the liquid phase, the most important factors are the type of solvent, pressure and temperature.

The effect of the solvent used was significant: catalytic activity for the reaction carried out in methanol was 2–3 times greater than that obtained in diethyl ether. The type of solvent had practically no effect on the selectivity of the catalyst towards *o*-CAN. The effect of pressure was studied in the range 2–6 MPa and the maximum activity was found at 4 MPa. The effect of temperature was studied in the range 333–413 K and the conversion gradually increased from 10% at 333 K to 100% at 413 K. The selectivity remained at a level of 100% in the range 333–373 K, whereas above 373 K it gradually decreased reaching 90% at 413 K. The catalyst grain size and intensity of stirring were also optimised. The tests have shown that the only by-product of the reaction in the liquid phase was aniline.

The activities and selectivities of the Ru/MgF_2 and $Ru-V/MgF_2$ catalysts and, for the sake of comparison, those of commercial 0.5% Ru/Al_2O_3 catalyst made by Engelhard are given in Fig. 1A.

Thanks to the use of MgF_2 as a support, the final catalyst was about five times more active than the commercial one (Engelhard)- Fig. 1A. Interestingly enough, much higher activity of the Ru/MgF_2 catalyst was accompanied by 100% selectivity towards *o*-CAN. Further increase in the catalyst activity was achieved as a result of the introduction of vanadium. Irrespective of the amount of vanadium introduced (0.1, 0.5, 1.0 wt.%), the conversion was >98% and the selectivity >97% in the reaction carried out in the liquid phase (Fig. 1A). The only undesirable product was aniline. It is well-known that hydrodehalogenation on ruthenium concerns mainly haloanilines. On the other hand, on palladium both chloronitrobenzene and chloroaniline take part in the above reaction and this is why aniline is present and nitrobenzene absent in the post-reaction mixture.

3.2. o-CNB hydrogenation in gas phase

The optimum conditions of the reaction in the gas phase have been established on the basis of a number of tests performed on the

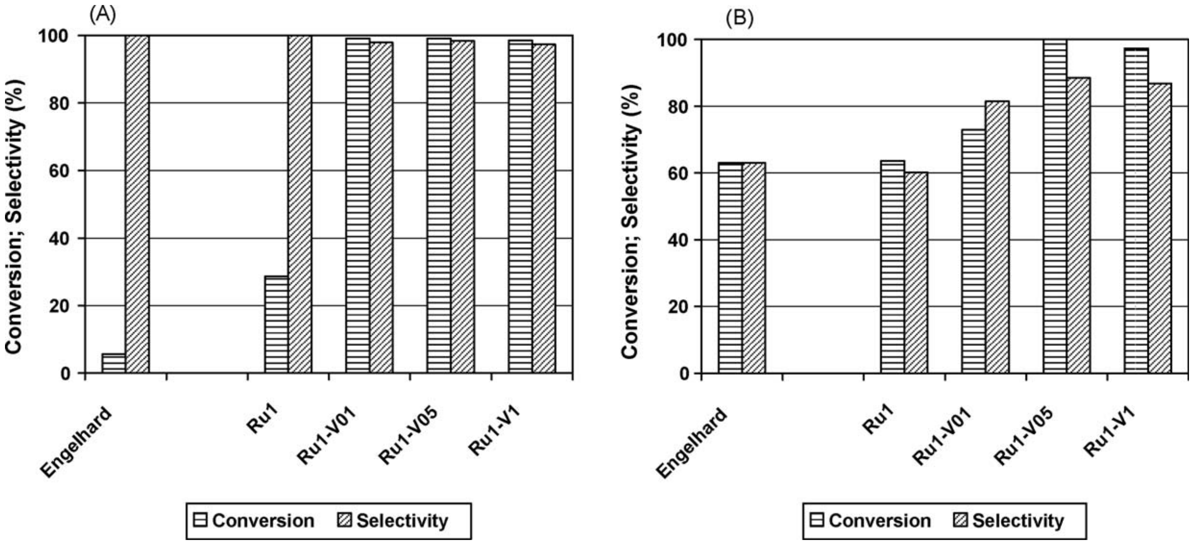

Fig. 1. Hydrogenation of *o*-CNB over ruthenium and ruthenium–vanadium catalysts. (A) Liquid-phase reaction 353 K, 4.0 MPa; (B) Gas-phase reaction 523 K, 0.1 MPa. In the case of 0.5% Ru/Al_2O_3 Engelhard catalyst twice as large portion of sample was used in order to obtain the same amount of ruthenium as in the case of Ru/MgF_2 and $Ru-V/MgF_2$ catalysts.

Ru1 sample. The optimum concentration of *o*-CNB for 0.1 g of the catalyst was 0.1 M in methanol, while the optimum rate of *o*-CNB dosing was 2.80 ml h^{-1}. Activity and selectivity increased gradually and reached the stable level after about 1.0–1.5 h, so all the results presented refer to the stable activity and selectivity after 2 h on stream. All the catalysts studied showed very high stability and did not undergo detectable deactivation even after 5 h of the process. The effect of partial pressure of hydrogen on the activity of the Ru1 was also studied. A reduction in hydrogen concentration from 100% H_2 to 50% H_2/He was found to have no effect on the activity and selectivity of the catalyst, however, further decrease in the H_2 concentration leads to a gradual decrease in the activity and a small increase in the selectivity towards *o*-CAN.

The activities and selectivities of the Ru/MgF_2 and Ru-V/MgF_2 catalysts, and for the sake of comparison, those of commercial 0.5% Ru/Al_2O_3 catalyst made by Engelhard are given in Fig. 1 B. The activity and selectivity of Ru1 in the reaction performed in the gas phase are comparable with those of commercial Engelhard catalyst.

Similarly as it was in the case of the reaction carried out in the liquid phase, the addition of vanadium increases catalytic activity. The highest activity (100% conversion) and selectivity (88.5%) were obtained over the Ru1-V05 catalyst. The selectivities of the catalysts tested were lower when the reaction proceeded in the gas phase compared to those obtained in the liquid phase. A possible reason for this fact can be relatively high temperature of the reaction (523 K) as it is known that selectivity deteriorates at higher temperatures.

3.3. Metal–support interaction

Results of our earlier studies have shown that both vanadium [13] and ruthenium [14] strongly interact with the MgF_2 surface. The interaction of ruthenium with strongly electronegative fluorine ions leads to the generation of a positive charge on Ru atoms which significantly inhibits chemisorption of hydrogen on ruthenium. VO_x species may have a similar effect on ruthenium (generation of a positive charge on ruthenium) which affects the chemisorption properties of ruthenium and the catalytic properties of Ru-V/MgF_2.

Important information on the state of ruthenium in the catalysts Ru/MgF_2 and Ru-V/MgF_2 was provided by the FTIR study of carbon monoxide adsorption. On the surface of metallic ruthenium, CO adsorbs in the linear form which gives in the FTIR spectrum an LF (low frequency) band at about 2000 ± 20 cm^{-1} [15–17]. In the spectra of the ruthenium catalysts also MF (middle frequency) band at ~2070 cm^{-1} and HF (high frequency) band at ~2140 cm^{-1} appear. They are assigned to the $Ru^{n+}(CO)_2$ complexes, where n = 1, 2 or 3 [16] and tricarbonyl complexes with ruthenium at the oxidation state of +II [15]. These bands can also originate from CO adsorbed on ruthenium atoms whose electronic state is disturbed by the neighbouring oxygen or chlorine atoms, water molecules or hydroxyl groups [18].

Fig. 2 presents the FTIR spectra recorded after CO adsorption on the Ru1 and Ru1-V05 catalysts. After CO adsorption on Ru1, an strong band is observed at 1971 cm^{-1} that is assigned to CO adsorbed in the linear form on metallic Ru^0. The spectra reveal also two bands at 2073 and 2140 cm^{-1} related to the presence of ruthenium at oxidation states of +I and/or +II. The centres of this type are generated by the interaction between ruthenium and strongly electronegative fluoride ions, as confirmed by our earlier EPR study in liquid helium [14].

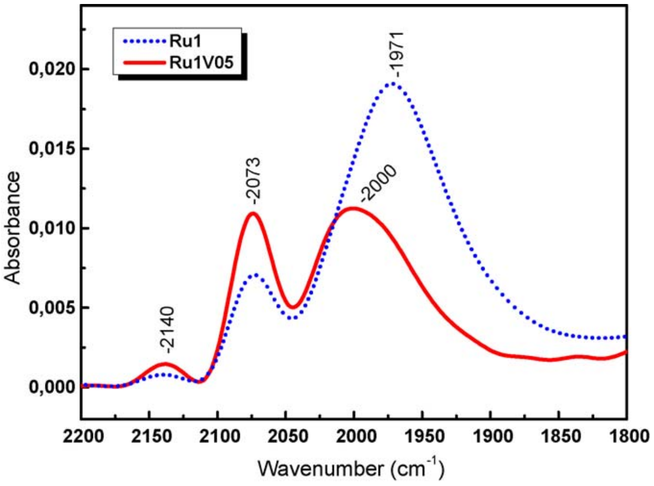

Fig. 2. FTIR spectra after CO adsorption on Ru1 and Ru1-V05 catalysts.

In the spectrum of Ru1-V05 the LF band appears at 2000 cm^{-1} and its intensity is much lower, which testifies to a lower number of Ru^0 centres on its surface. In the same spectrum the intensity of the MF and HF bands corresponding to the centres of Ru at higher oxidation state considerably increases. The changes in the band intensities should be attributed to the effect of electronic interactions of VO_x species and ruthenium leading to a decrease in the electron density on ruthenium atoms. The VO_x species [19], formed after reduction with hydrogen at 673 K, in which vanadium occurs as V^{4+} [20] and/or V^{3+} [21,22] cover the surface of ruthenium crystallites, modify their electronic properties and generate new Ru^{n+} sites active for *o*-CNB hydrogenation f[23]. This explains the observed increase in the activity of Ru-V/MgF_2 relative to that of Ru/MgF_2. A lower selectivity of the bimetallic catalysts can be explained by the presence of the V^{n+}sites having some hydrodechlorination activity [24].

4. Conclusions

The use of an untypical support of MgF_2 enabled to obtain a ruthenium catalyst that was characterised by very high activity and 100% selectivity in the reaction of hydrogenation of *o*-CNB to *o*-CAN in the liquid phase at 353 K under 4 MPa H_2. Several times higher activity of Ru/MgF_2 than that of the commercially available Ru/Al_2O_3 follows probably from a strong interaction of Ru with the surface of MgF_2 which leads to a decreased electron density on Ru atoms and generation of Ru^{n+} centres.

The high activity of Ru/MgF_2 was still enhanced by the addition of vanadium. This addition also resulted in a small decrease in the selectivity towards *o*-CAN. The increased activity was explained by the generation of new Ru^{n+} centres with ruthenium at higher oxidation states. The reduction in the selectivity was interpreted as a consequence of decreasing size of Ru crystallites, which are able to adsorb *o*-CAN more strongly making it more susceptible to hydrodechlorination.

References

[1] R.L. Augustine, Heterogeneous Catalysis for the Synthetic Chemist, Dekker, New York, 1996, 475–476.
[2] A. Tijani, B. Coq, F. Figueras, Appl. Catal. 76 (1991) 255.
[3] B.J. Zuo, Y. Wang, Q.L. Wang, J.L. Zhang, N.Z. Wu, L.D. Peng, L.L. Gui, X.D. Wang, R.M. Wang, D.P. Yu, J. Catal. 222 (2004) 493.
[4] J. Wrzyszcz, M. Zawadzki, A.M. Trzeciak, J.J. Ziolkowski, J. Mol. Catal. A: Chem. 189 (2002) 203.
[5] P. Baumeister, M.F. Studer, F. Roessler, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 5, VCH, Weinheim, 1997, pp. 2186–2209.
[6] X. Wang, M. Liang, J. Hang, Y. Wang, Curr. Org. Chem. 11 (2007) 299.
[7] M. Wojciechowska, B. Czajka, M. Pietrowski, M. Zieliński, Catal. Lett. 66 (2000) 147.

[8] M. Wojciechowska, M. Zieliński, M. Pietrowski, J. Fluorine Chem. 120 (2003) 1.
[9] M. Wojciechowska, M. Pietrowski, S. Łomnicki, J. Chem. Soc., Chem. Commun. 5 (1999) 463.
[10] M. Wojciechowska, M. Pietrowski, B. Czajka, Catal. Today 65 (2001) 349.
[11] M. Wojciechowska, M. Zieliński, M. Pietrowski, Catal. Today 90 (2004) 35.
[12] M. Wojciechowska, M. Zieliński, W. Przystajko, M. Pietrowski, Catal. Today 119 (2007) 44.
[13] M. Wojciechowska, J. Goslar, W. Kania, M. Pietrowski, J. Fluorine Chem. 91 (1998) 141.
[14] M. Pietrowski, M. Wojciechowska, J. Goslar, M. Zieliński, Mol. Phys. Rep. 37 (2003) 105.
[15] K. Hadjiivanov, J.-C. Lavalley, J. Lamotte, F. Maugé, J. Saint-Just, M. Che, J. Catal. 176 (1998) 415.
[16] E. Guglielminotti, A. Zecchina, A. Bossi, M. Camia, J. Catal. 74 (1982) 240.
[17] C. Crisafulli, S. Scirè, S. Minicò, R. Maggiore, S. Galvagno, Appl. Surf. Sci. 99 (1996) 401.
[18] V.P. Londhe, V.S. Kamble, N.M. Gupta, J. Mol. Catal. A 121 (1997) 33.
[19] S. Dźwigaj, I. Gressel, B. Grzybowska, K. Samson, Catal. Today 114 (2006) 237.
[20] G. Silversmit, J.A. van Bokhoven, H. Poelman, A.M.J. van der Eerden, G.B. Marin, M.F. Reyniers, R. De Gryse, Appl. Catal. A: Gen. 285 (2005) 151.
[21] G. Bond, S. Flamerz, J. Chem. Soc. Faraday Trans. 87 (1991) 767.
[22] A.E. Lewandowska, M.A. Banares, Catal. Today 118 (2006) 323.
[23] G.D. Zakumbayeva, L.B. Shapovalova, A.V. Gabdrakipov, V.Z. Gabdrakipov, Petrol. Chem. 37 (1997) 484.
[24] B. Coq, A. Tijani, F. Figueras, J. Mol. Catal. 68 (1991) 331.