Catalysis Letters
https://doi.org/10.1007/s10562-018-2406-4

# Poisoning and Reuse of Supported Precious Metal Catalysts in the Hydrogenation of *N*-Heterocycles Part I: Ruthenium-Catalysed Hydrogenation of 1-Methylpyrrole

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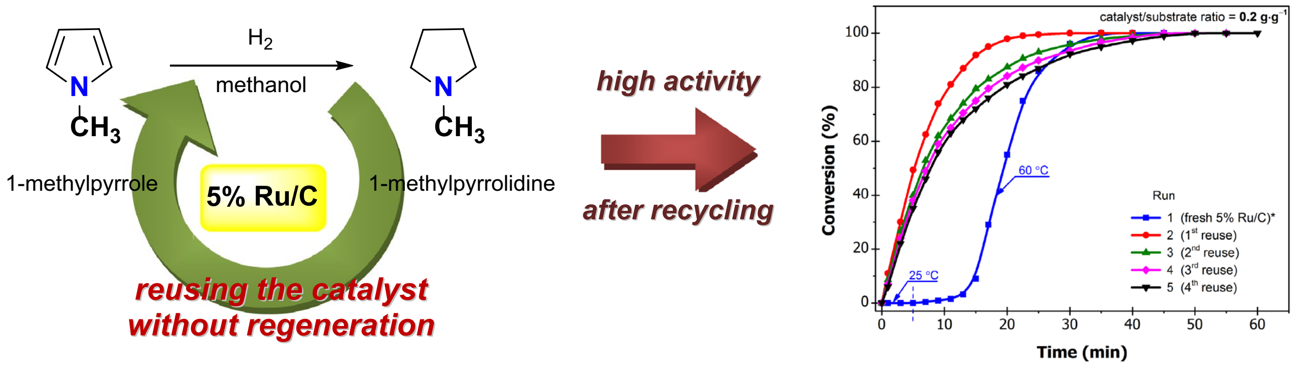
Received: 8 January 2018 / Accepted: 3 May 2018

## Abstract

Poisoning phenomena of heterogeneous, supported precious metal catalysts caused by nitrogen were investigated in the liquid-phase hydrogenation of 1-methylpyrrole (MP) to 1-methylpyrrolidine (MPD) over ruthenium on carbon, in non-acidic medium (methanol), at 10 bar and 25–60 °C. Reusing a spent, unregenerated 5% Ru/C catalyst, it was found that the activity of catalyst and the conversion of model substrate were strongly dependent on the amount of catalyst and the number of recycling, respectively. During the first reuse of this ruthenium catalyst, surprisingly, it showed high activity already at room temperature contrary to the fresh catalyst which worked at only 60 °C. This unexpected catalytic behaviour was studied by XRD and XPS methods which revealed the existence of a fine $RuO_2$ layer on the surface of the catalytic metal in the fresh catalyst.

### Graphical Abstract



**Keywords** Hydrogenation · Poisoning · Reusing · Ruthenium · Pyrroles · Spent catalyst

## 1 Introduction

Among the different types of catalyst deactivation, such as poisoning, fouling, thermal degradation, vapour–solid and/or solid–solid reactions, attrition/crushing, poisoning is a chemical interaction where the strong chemisorption of species (reactants, products or impurities) on catalytic sites blocks the surface chemical reaction [1–4]. As it has long been known [5–11], compounds containing basic nitrogen have inhibiting effects on the catalysts used for

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Dedicated to the memory of Dr. Tibor Máthé, an excellent researcher and inventor, who passed away 17 years ago.

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10562-018-2406-4) contains supplementary material, which is available to authorized users.

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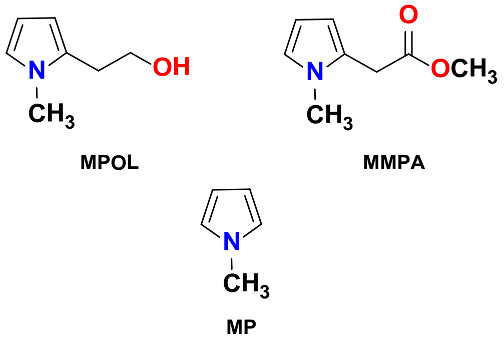
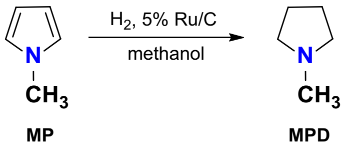


**Fig. 1** Structures of pyrrole derivatives hydrogenated previously



**Scheme 1** Ruthenium-catalysed hydrogenation of 1-methylpyrrole (MP) to 1-methylpyrrolidine (MPD)

hydrogenation due to their unshared pair of electrons. This effect can be neutralized by conversion of these reactants to a form in which the nitrogen atom is shielded, for instance, by adding protic acids [7]. However, this method cannot be applied if a substrate is sensitive to acids, i.e. a side-reaction (e.g. polymerisation) takes place in the presence of them [12].

Previously we reported the liquid-phase heterogeneous catalytic hydrogenations of several pyrrole derivatives, such as 1-methyl-2-pyrroleethanol (MPOL), methyl 1-methyl-2-pyrroleacetate (MMPA) and 1-methylpyrrole (MP) (Fig. 1), over different, supported precious metal catalysts (Pd/C, Ru/C, Rh/C, Rh/$Al_2O_3$, Pt/C, Ir/C), in non-acidic medium [13–16]. The corresponding pyrrolidines, which are important and valuable pharmaceutical intermediates [17–19], were prepared in good yields (80–90%). In these reductions the light platinum metals (Rh, Ru, Pd) proved to be the most active catalysts. Although these hydrogenations took place relatively easily under mild reaction conditions (25–80 °C, 6 bar) with complete conversion and high selectivity, poisoning of the catalysts was observed below some catalyst/substrate ratios. The values of these ratio limits ranged from 0.03 to 0.2, and they were dependent on the substrates, catalytic metals and solvents. Furthermore, the poison sensitivity of these precious metals referring to nitrogen was also determined which decreased in the following sequence: Pd > Ru > > Rh. This order was attributed to electronic factors [20].

In this work the poisoning phenomena of heterogeneous, supported precious metal catalysts caused by nitrogen and their reusing without regeneration were investigated in detail. Based on our previous experience [16], the liquid-phase hydrogenation of 1-methylpyrrole (MP) to 1-methylpyrrolidine (MPD) over ruthenium on carbon, in non-acidic medium (methanol) was chosen as a model reaction (Scheme 1).

Apart from our previous investigations [14–16, 20], ruthenium was very rarely used in the heterogeneous catalytic hydrogenation of pyrroles [21–23], moreover it acted at relatively high pressures (25–35 bar) and temperatures (130–150 °C). Thus, 2,5-dimethylpyrrole was converted to *cis*-2,5-dimethylpyrrolidine over 5% Ru/$Al_2O_3$ [21] or unsupported $RuO_2$ [22], in water, at 130 °C and 28–35 bar with 85–98% conversion and high *cis*-selectivity (> 90%). Most recently, 5% Ru/$TiO_2$ or 5% Ru/$TiO_{2-x}$ catalysts have been applied in the hydrogenation of MP to MPD in tetrahydrofuran, at 90–100 °C and 30 bar obtaining 80–95% conversion [23].

However, handling the spent catalysts formed during the hydrogenations is also an important technological aspect of the heterogeneous catalytic processes in the chemical industry [24–32]. Both precious [25] and base metals [26] on different supports or in unsupported forms are usually fully regenerated before their reusing, but the applied regeneration methods (e.g. incineration or pyrometallurgical processes) are typically energy-intensive and expensive. In pharmaceutical industry, where carbon supported precious metal catalysts (e.g. Pd/C, Ru/C) are mostly used, the usual method is applying the completely regenerated spent catalysts due to the very strict rules of quality assurance (e.g. GMP—*Good Manufacturing Practices* [33]). Since their reusing without regeneration has not solved up to now, an easy and less expensive catalyst recycling process for the heterogenous catalytic hydrogenations could afford to produce pharmaceuticals more economical.

In this paper the effect of reusing the spent, unregenerated, carbon supported ruthenium (5% Ru/C) on its activity and conversion of MP is discussed. An unexpected behaviour of this catalyst was examined by X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) surface analytical methods.

## 2 Experimental

### 2.1 Materials

1-Methylpyrrole (99%) was supplied by Merck-Schuchardt (Hochenbrunn, Germany), while methanol (p. a.) was purchased from Merck (Darmstadt, Germany).

The 5% Ru/C catalyst was received from Aldrich (Milwaukee, USA), whilst anhydrous ruthenium(IV) oxide (99.9%) was supplied by Alfa Aesar (Karlsruhe, Germany).

## 2.2 Hydrogenations

The hydrogenation reactions were carried out in a 250 $cm^3$ stainless steel autoclave (Technoclave, Budapest, Hungary) equipped with a magnetic stirrer (stirring speed: 1100 rpm), and electric heating system, at 10 bar and 25–60 °C.

Typically, the reactor containing MP (2.0 g), 5% Ru/C catalyst (0.4 g) and methanol (50 $cm^3$) was flushed with nitrogen and hydrogen, then charged with hydrogen to the specified pressure and heated up to the given temperature, if necessary. After finishing the hydrogen uptake, the catalyst was filtered off and a sample was taken from the filtrate. It was analysed by GC–MS and the conversion value was calculated from the hydrogen pressure drop and the gas-chromatographic data. The initial rate ($v_0$) was determined from the conversion curves.

1-Methylpyrrolidine (MPD), when the conversion was complete, was prepared in the same way as described in [16]. The MS data of the starting material and the product are the following: MP *m/z* (rel%) 81(100), 55(15), 53(26), 42(24), 39(23); MPD *m/z* (rel%) 85(55), 84(97), 57(90), 42(100), 32(8). These analytical results are in agreement with the literary data [34].

## 2.3 Catalyst Recycling

After filtering the spent catalyst, it was washed with distilled water (2×5 $cm^3$) and collected carefully to store for the next reaction, in that wet form. No regenerative processes were applied prior to its reusing.

When an acidic treatment of the used catalyst was implemented, the procedure was as follows. The spent catalyst was filtered, and subsequently suspended in 5% acetic acid (2×5 $cm^3$), then washed with distilled water (2×10 $cm^3$) to pH 7. Finally, it was also collected carefully to store for the next reaction, in that wet form.

## 2.4 Catalyst Pretreatment

The prehydrogenation of 5% Ru/C catalyst was carried out in the absence of substrate (MP), in methanol, at 10 bar and 25 or 60 °C for 30 or 90 min. After this pretreatment, the starting material was added to the reaction mixture at 25 °C, and its hydrogenation was performed at this temperature.

## 2.5 Catalyst Characterisation

The phase composition of the fresh or spent catalysts was determined by X-ray powder diffraction (XRD) measurements. The XRD patterns were obtained with a Philips PW 3710 diffractometer based PW 1050 Bragg–Brentano parafocusing goniometer using Cu *K*α radiation ($\lambda = 0.15418$ nm), graphite monochromator and proportional counter. Crystallite size of ruthenium was calculated from reflection line broadening using the Scherrer equation:

$$\Delta_{+}(2\theta)[\mathrm{deg}] = \frac{180}{\pi}\frac{0.9\lambda}{d\ \cos\theta}, \quad \Delta(2\theta) = \Delta_0 + \Delta_{+}(2\theta) \tag{1}$$

where $d$ is the diameter of the crystallite, $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg angle (in degrees), $\Delta(2\theta)$ denotes the full width (FWHM) of the diffraction peak associated with the scattering angle $2\theta$, and $\Delta_0 = 0.11$ deg accounts for instrumental broadening.

Surface compositions of the fresh and spent catalysts, as well as pure $RuO_2$ were determined by X-ray photoelectron spectroscopy (XPS) performed by a KRATOS XSAM 800 XPS machine. Mg *K*α X-ray line, 40 eV pass energy (energy steps 0.2 eV) and FAT mode were applied for recording the XPS lines of Ru 3*p*, Ru 3*d*, O 1*s*, N 1*s* and C 1*s* were applying. For charge compensation the C 1*s* binding energy at 284.8 eV was used as a reference. The surface concentrations of the elements were calculated from the integral intensities of the XPS lines using sensitivity factors given by the manufacturer.

Dispersion of the catalyst ($D_{5\%\ \mathrm{Ru/C}} = 0.43$) was determined by $H_2$-, $O_2$- and CO-chemisorption measurements using an atmospheric flow system [35, 36]. Prior to the first adsorption of $O_2$, the catalyst sample was treated with $H_2$ in argon at 90 °C for 4 h. $(Ru–H)_s$ was titrated with $O_2$ injections *via* a calibrated loop (0.1 $cm^3$ each) at 25 °C. Next $(Ru–O)_s$ was titrated with $H_2$ in the same way. CO-chemisorption was also measured after treating in hydrogen (80 °C, 4.5 h). The stoichiometry of the calculations was the following:

- for titration with $O_2$

$$(\mathrm{Ru-H})_s + 0.75\mathrm{O}_2 = (\mathrm{Ru-O})_s + 0.5\mathrm{H_2O} \tag{2}$$

- for titration with $H_2$

$$(\mathrm{Ru-O})_s + 1.5\mathrm{H}_2 = (\mathrm{Ru-H})_s + \mathrm{H_2O} \tag{3}$$

- for CO adsorption

$$(\mathrm{Ru-H})_s + \mathrm{CO}{=}(\mathrm{Ru-CO})_s + 0.5\mathrm{H}_2 \tag{4}$$

## 2.6 Analysis

The components of reaction mixtures were analysed and identified by GC–MS. The analyses were carried out with a Finnigan Mat/Automass II GC/MS spectrometer using a Zebron ZB-5 ms capillary column (30 m × 0.25 mm ID, 0.25 μm film). The temperature program was the following: 45 °C (2 min) to 300 °C at 10 °C $min^{-1}$, then to 350 °C at 25 °C $min^{-1}$.

## 3 Results and Discussion

### 3.1 Special Behaviour of Ruthenium

Conversion of MP over 5% Ru/C, depending on the number of reusing the catalyst, at 0.2 g $g^{-1}$ catalyst/substrate ratio, in methanol is shown in Fig. 2, while the initial rates ($v_0$) and the reaction time in the hydrogenation of MP are summarized in Table 1.

As seen, the fresh ruthenium on carbon proved to be a very efficient catalyst for this reduction, because the hydrogenation of MP was fast and complete after 30 min. Whereas, no $H_2$-uptake was observed at 25 °C, therefore it was necessary to increase the temperature to 60 °C, at least (run 1). Saturation of the pyrrole ring, in each reuse of the catalyst, was achieved with 100% conversion, even if the initial rates of the hydrogenation ($v_0$) were slightly lower (5.37–4.43 nL $H_2$ $g_{Ru}{}^{-1}$ $min^{-1}$) than that of the original reaction (5.53 nL $H_2$ $g_{Ru}{}^{-1}$ $min^{-1}$), i.e. the complete conversion of MP required a hardly longer reaction time (45–50 min) in the repeated hydrogenations (runs 2–5). Surprisingly, it was found that the reduction of MP took place completely already at room temperature, during the second use of 5% Ru/C (run 2), after the same time (30 min). Similar behaviour was observed in all reusing the catalyst, i.e. complete conversions were obtained over ruthenium on carbon, without heating, already at 25 °C.

Presumably, this phenomenon was caused by a fine $RuO_2$ layer formed on the surface of the catalytically active ruthenium particles, which can rapidly be transformed to pure metal around at 60–80 °C [37, 38]. This layer can avoid the process of catalytic hydrogenation, but after its reduction, the reaction can readily take place on the renewed and active surface of catalyst. Furthermore, the formed metallic ruthenium can remain stable for a longer time, therefore only a slight decrease in its activity can be observed in this hydrogenation (Table 1). To confirm our hypothesis, X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were performed on both fresh and used catalysts, which will be discussed in Sect. 3.3.

**Table 1** Effect of reusing the catalyst (5% Ru/C) on the initial rate ($v_0$) and the reaction time in the hydrogenation of 1-methylpyrrole (MP)

| Run | Reusing the catalyst | Reaction time for complete conversion (min) | $v_0$ (nL $H_2$ $g_{Ru}{}^{-1}$ $min^{-1}$) |
|---|---|---|---|
| 1* | – (fresh) | 30 | 5.53 |
| 2 | 1st | 30 | 5.37 |
| 3 | 2nd | 45 | 4.99 |
| 4 | 3rd | 45 | 4.71 |
| 5 | 4th | 50 | 4.43 |

Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 0.4 g catalyst, 25 °C, *25–60 °C, 10 bar

### 3.2 Effect of Catalyst Pretreatment

The influence of catalyst prehydrogenation and the number of reuse on the conversion of MP over 5% ruthenium on carbon, at 0.2 g $g^{-1}$ catalyst/substrate ratio, in methanol is depicted in Fig. 3.

As seen, pretreatment of the fresh catalyst at room temperature (10 bar $H_2$, 30 min) resulted in complete conversion of MP already at 25 °C (run 1), but this required a

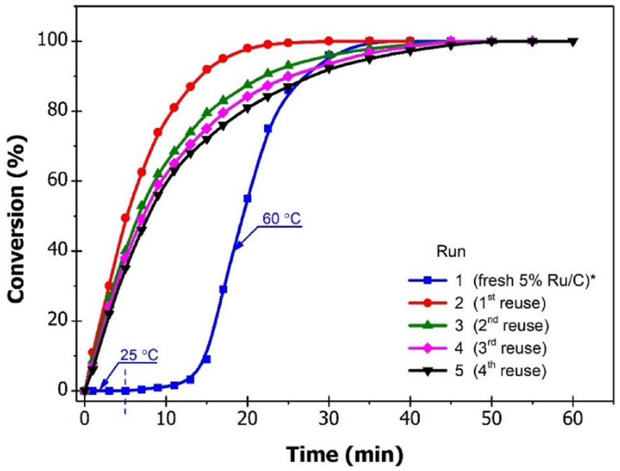


**Fig. 2** Reusing 5% ruthenium on carbon in the hydrogenation of 1-methylpyrrole (MP). Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 0.4 g catalyst, 25 °C, *25–60 °C, 10 bar

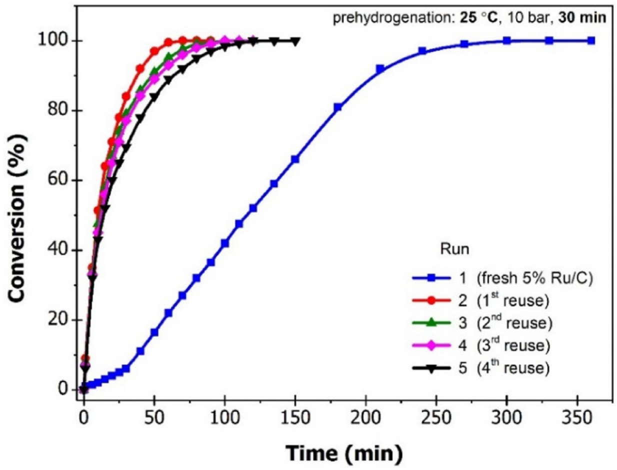


**Fig. 3** Conversion of 1-methylpyrrole (MP) vs. time over 5% Ru/C prehydrogenated at 25 °C. Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 0.4 g catalyst, 25 °C, 10 bar; pretreatment: 30 $cm^3$ methanol, 25 °C, 10 bar, 30 min

**Table 2** Effect of reusing the prehydrogenated catalyst (5% Ru/C) on the initial rates ($v_0$) and the reaction time in the hydrogenation of 1-methylpyrrole (MP)

| Run | Reusing the catalyst | Reaction time for complete conversion (min) | $v_0$ (nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$) |
|---|---|---|---|
| 1 | – (fresh) | 300 | 0.11 (0.55[a]) |
| 2 | 1st | 70 | 5.03 |
| 3 | 2nd | 100 | 4.43 |
| 4 | 3rd | 110 | 3.87 |
| 5 | 4th | 120 | 3.32 |

Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 0.4 g catalyst, 25 °C, 10 bar; pretreatment: 30 $cm^3$ methanol, 25 °C, 10 bar, 30 min

[a] After a transient period (30 min)

significantly longer reaction time (300 min). Behaviour of the recycled and prehydrogenated catalyst, however, was practically the same in this series as it was found in the previous one (Sect. 3.1), i.e. hydrogenation of the pyrrole ring, in each reusing the catalyst, was obtained with 100% conversion (runs 2–5). Although the reaction times were longer (70–120 min) in these cases (Table 2), the initial rate values ($v_0 = 5.03$–$3.32$ nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$) were very similar to those ones achieved earlier (Table 1). Whereas, the prehydrogenation of 5% Ru/C at room temperature was not such efficient as using the untreated catalyst after the first run at 60 °C.

As also seen in Fig. 3, there was a transient period ($v_0 = 0.11$ nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$) at the beginning of the reaction (0–30 min) which was followed by an accelerated phase (30–180 min, $v_0 = 0.55$ nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$). This near linear stage can refer to the slow reduction of the surface oxide layer to metallic Ru which takes place in parallel with the hydrogenation of MP. Thus, the effects of time and temperature of prehydrogenation on the conversion and initial rate were also investigated (Figs. 4, 5). Applying a longer catalyst pretreatment time (90 min) at 25 °C and 10 bar $H_2$, no significant decrease in the reaction time for complete conversion of MP (300 → 240 min) was observed during the first run, but no transient phase was detected (Fig. 4a). Furthermore, the sum of the reaction and prehydrogenation times (330 min) was the same after the 30 and 90 min pretreatment of catalyst at 25 °C, respectively (Fig. 5a). There was no difference between the reaction times for complete conversion of MP (70 min) during the first reuse of Ru/C (Fig. 5a), which was also confirmed by the practically same initial rate values ($v_0 = 5.03$ and $5.25$ nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$) (Fig. 5b). This indicates that the catalyst prehydrogenation at 25 °C resulted in no significant improvement in the activity of catalyst during its reuse.

As mentioned afore, the inhibitory effect of the presumed surface oxide layer could be eliminated at 60 °C, therefore prehydrogenation of the catalyst was also carried out under these conditions (60 °C, 10 bar $H_2$, 30 min), in the absence of substrate (MP). After this pretreatment, the fresh ruthenium on carbon showed a significantly higher activity ($v_0 = 6.64$ nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$) in the first run at 25 °C (Fig. 5b) and, among the reactions performed over the prehydrogenated catalysts, an appreciable shorter time (130 min) was enough to complete the hydrogenation of MP (Fig. 4b). Moreover, the reused catalyst provided an outstandingly high initial rate ($v_0 = 8.25$ nL $H_2$ $g_{Ru}^{-1}$ $min^{-1}$), also at 25 °C, which was accompanied by the shortest reaction time (25 min) observed in all hydrogenations (Fig. 5a, b). This indicates that the catalyst prehydrogenation at 60 °C resulted in significant improvement in the activity of catalyst during its reuse, presumably due to metallic ruthenium formed in situ in the course of this pretreatment.

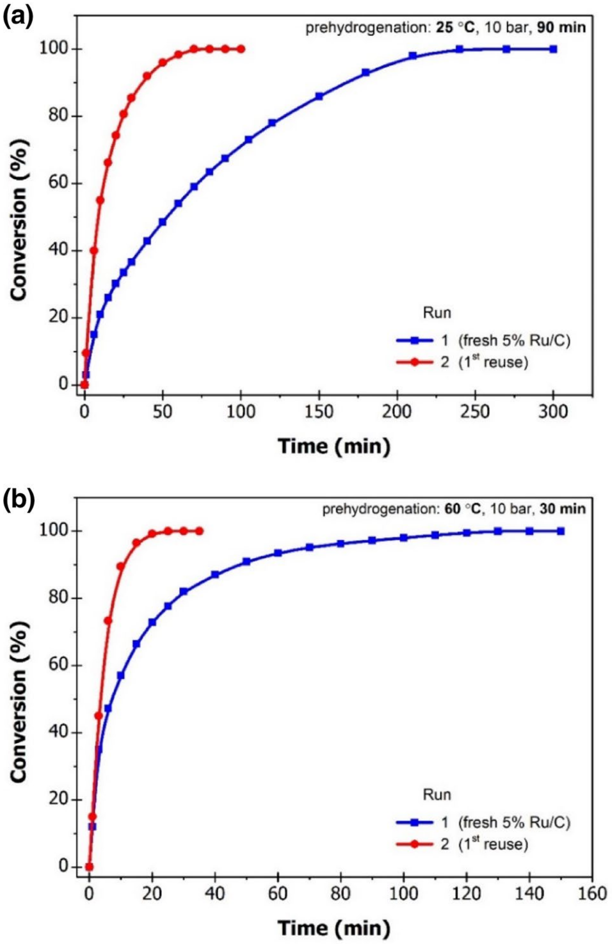


**Fig. 4** Conversion of 1-methylpyrrole (MP) vs. time over 5% Ru/C prehydrogenated at 25 °C and 90 min (**a**) or at 60 °C and 30 min (**b**). Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 0.4 g catalyst, 25 °C, 10 bar; pretreatment: 30 $cm^3$ methanol, 10 bar

According to these results, the prehydrogenation of ruthenium on carbon resulted in high catalytic activity, but

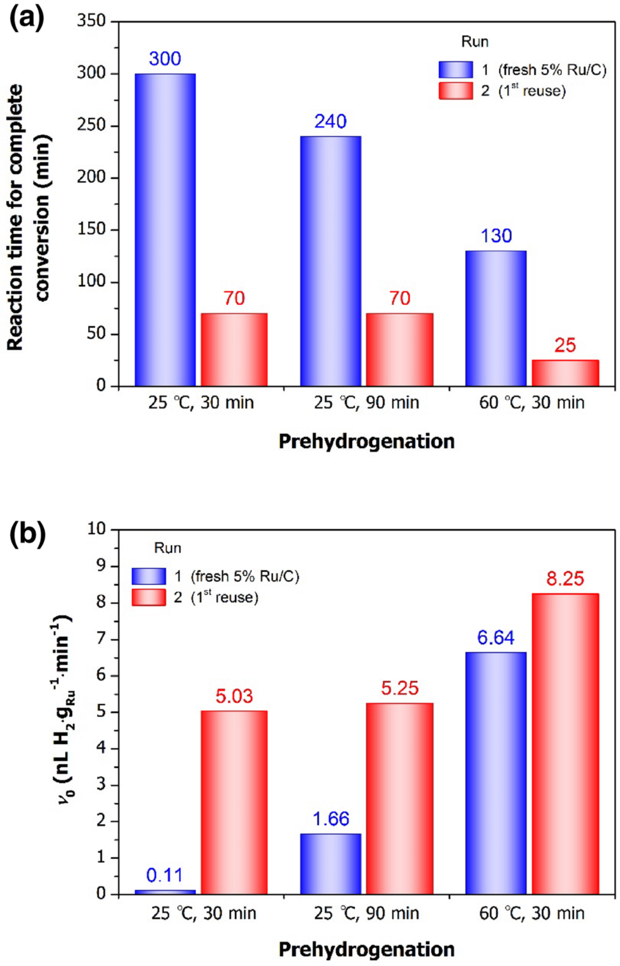


**Fig. 5** Effects of time and temperature of prehydrogenation on the reaction time for complete conversion (**a**) and the initial rate ($v_0$) (**b**) in the hydrogenation of MP over prehydrogenated 5% Ru/C. Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 0.4 g catalyst, 25 °C, 10 bar; pretreatment: 30 $cm^3$ methanol, 10 bar

it strongly depended on the temperature of this pretreatment. The best results were achieved after prehydrogenation of the catalyst at 60 °C and 30 min, but using these conditions is not practical on an industrial scale.

## 3.3 X-ray Investigations

To find an explanation to this unexpected catalytic behaviour of ruthenium, the fresh and used catalysts were examined by surface analytical methods (XRD and XPS).

### 3.3.1 XRD

Figure 6 shows the XRD patterns of the fresh and used (5×) 5% Ru/C catalysts, as well as that of the prehydrogenated one after also using (5×). In all cases, the most intensive peak can be observed at $2\Theta = 24.5°$ which refers to the activated carbon (PDF #41-1487). Although the reflections of metallic ruthenium (PDF #06-0663) at $2\Theta = 42.1°$ and 44.0° appear in the fresh catalyst, they are very wide and merged. Using the Scherrer Eq. (1), the Ru particle size (d) was calculated to be 4.1 nm. However, no characteristic peaks of $RuO_x$ (PDF #43-1027) are recognized at $2\Theta = 28.0°$, 35.0° and 54.1°, i.e. if there is ruthenium in oxide form in this catalyst, it should have a very fine texture.

There is no significant difference between the XRD scans of the used (5×) catalysts (prehydrogenated or without pretreatment) in wet form, because their variations from the fresh catalyst are due to the amorphous scattering of water. Furthermore, no significant dissimilarity can be observed in the Ru-containing phases.

These results suggest that the existence of the presumed fine $RuO_x$ layer cannot be proved by using this analytical method.

### 3.3.2 XPS

Figure 7a–e exhibit the XP spectra of anhydrous ruthenium(IV)-oxide (as a reference) and the 5% Ru/C catalyst in different forms: fresh, prehydrogenated at 25 °C and used (2×), prehydrogenated at 60 °C and used (2×), as well as prehydrogenated at 60 °C without substrate.

In the high-resolution XP spectrum of pure $RuO_2$ (Fig. 7a) the peak at a binding energy of 280.3 eV is assigned to the Ru $3d_{5/2}$ spin–orbit coupling which refers to the higher oxidation states of ruthenium ($RuO_2$) [39–42]. The appearance of the characteristic shake-up satellite features and the smaller full width at half maximum (FWHM) value of the $3d_{5/2}$ peak (1.37 eV, Table 3) indicate the presence of its anhydrous form [43].

As seen in Fig. 7b–d, the Ru 3*d* peaks are highly overlapped with the C 1*s* ones in the 5% Ru/C catalysts. The shoulders observed at around 281.6 eV binding energies indicate the oxidation state of 4+ for ruthenium in $RuO_2$ phase before and after the catalytic cycle. The other pairs of the spin–orbit splitting (SOS), the Ru $3d_{3/2}$ at 285.8 eV, and the satellites are also in overlap with the C 1*s* peak. However, the SOS of 4.17 eV with an area ratio of 0.67 were used for fittings. The Ru-content is ~4% (atomic conc.) in the Ru/C catalysts (Table 3), except in the sample prehydrogenated at 60 °C and used (2×). In this case the broadened shoulder at lower binding energies can indicate some differences in the chemical composition, e.g. the altered ratio of hydrated/anhydrous Ru-oxides. The XP spectrum of sample 5% Ru/C prehydrogenated at 60 °C without substrate (Fig. 7e) was recorded after its drying under reductive conditions (100 °C, $H_2$) in the atmospheric chamber of the XPS device, namely the sample was placed into the instrument in its wet form. The lower binding energy of Ru $3d_{5/2}$ peak at 280.5 eV can refer either to the oxide or to metallic state

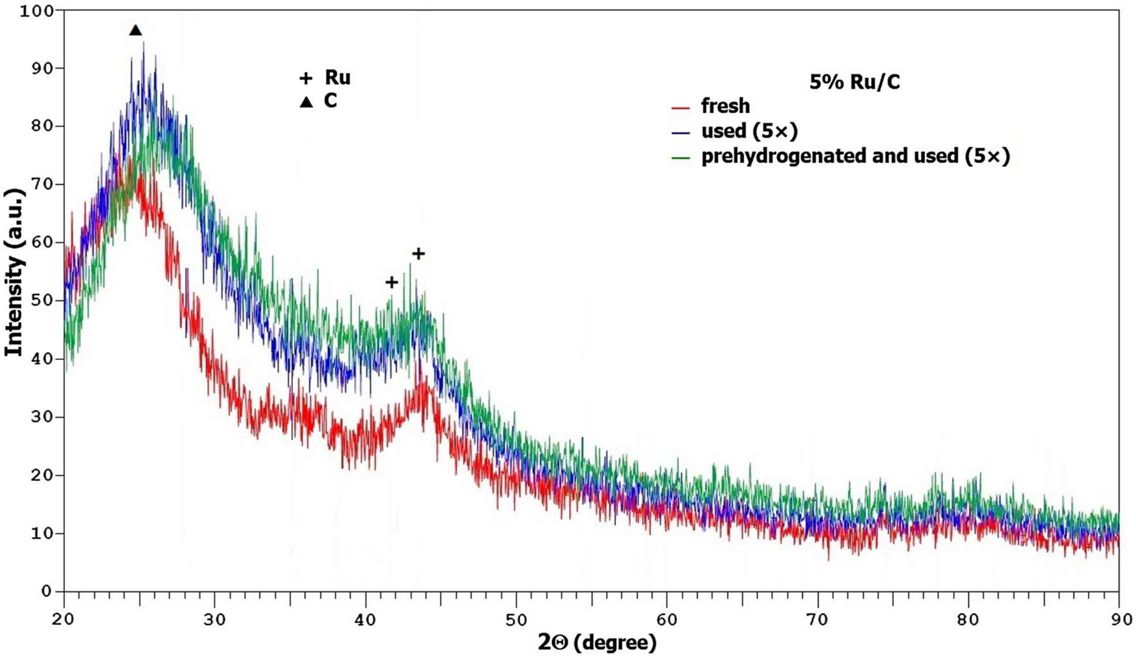


**Fig. 6** XRD patterns of 5% Ru/C catalyst in fresh and used (5×) forms

of ruthenium. Due to the position of Ru $3p_{3/2}$ at 461.6 eV, most probably, it is the mixture of these two states with the presence of anhydrous and hydrated form of $RuO_2$ (Figs. S1 and S2, Table S1).

Accordingly, these investigations can reveal the existence of a fine ruthenium(IV) oxide layer on the surface of ruthenium before and after catalysis and verify the favourable effect of catalyst prehydrogenation on the catalytic activity.

### 3.4 Influence of Amount of Catalyst

Conversion of MP over 5% Ru/C at lower catalyst/substrate ratios (0.1 and 0.05 g $g^{-1}$), depending on the number of reusing the catalyst, in methanol is shown in Fig. 8.

As seen, at 0.1 g $g^{-1}$ catalyst/substrate ratio, the saturation of pyrrole ring of MP was also complete until the second reuse of 5% Ru/C (runs 1–3, Fig. 8a), but this required longer reaction times (75, 100 or 160 min) than applying a 0.2 g $g^{-1}$ catalyst/substrate ratio (30–45 min, Fig. 2). High conversions were also obtained (99 and 98%) during the next hydrogenations of MP (runs 4–5), but they were not complete even after a much longer reaction time (240 or 360 min). At this stage, presumably, the extent of catalyst poisoning reached a threshold limit which caused the incomplete conversion of MP.

Further decreasing the amount of ruthenium on carbon to 0.05 g $g^{-1}$ catalyst/substrate ratio resulted in significant difference in the conversion of MP during the reuse of the catalyst (Fig. 8b). The reduction of MP was complete over the fresh 5% Ru/C at 25–60 °C (run 1), in turn, this required an appreciably longer reaction time (360 min). Although the hydrogenation of MP started already at 25 °C in the second run, the reaction stopped at 97% conversion. Drastic decreases were observed in the conversion values during the next reusing the catalyst (runs 3–4), namely they were only 60% and 5%, respectively, even after 420 min. Lastly, in the fifth run, the 5% ruthenium on carbon was completely deactivated, i.e. no product (MPD) was detected in the reaction mixture, at all.

To compare the effects of amount and reuse of 5% Ru/C catalyst on the course of the hydrogenation of MP, the initial rates ($v_0$) and the conversions at 60 min are also depicted in Fig. 9.

As seen in Fig. 9a, at 0.2 and 0.1 g $g^{-1}$ catalyst/substrate ratios, a similar decrease of $v_0$ values was observed by increasing the number of reusing the catalyst (5.53 → 4.43 nL $H_2$ $g_{Ru}{}^{-1}$ $min^{-1}$ and 5.09 → 3.32 nL $H_2$ $g_{Ru}{}^{-1}$ $min^{-1}$, respectively), while at the 0.05 g $g^{-1}$ one a significant activity diminution was experienced (5.01 → 0 nL $H_2$ $g_{Ru}{}^{-1}$ $min^{-1}$). Comparing the conversion at 60 min (Fig. 9b), more remarkable differences can be noticed. At 0.2 g $g^{-1}$ catalyst/substrate ratio complete conversion of MP was obtained during all runs, while in case of a lesser amount of catalyst (0.1 g $g^{-1}$ ratio) a significant conversion decrease could be observed after the fifth cycle (97 → 62%). Applying even less catalyst (0.05 g $g^{-1}$ catalyst/substrate ratio), the conversion drop was already occurred in the first run (66%), and this became much more appreciably during the

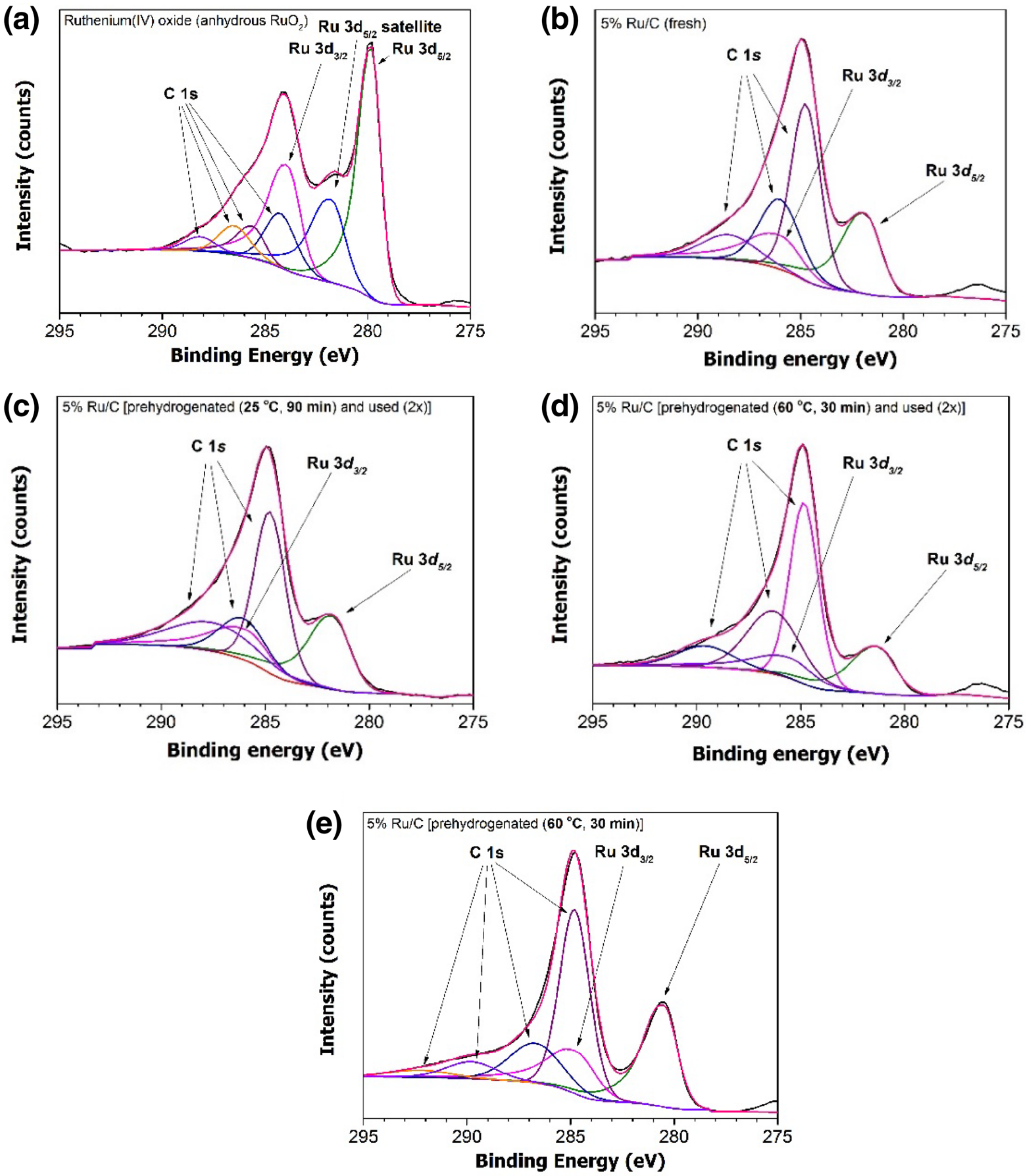


**Fig. 7** High-resolution and deconvolution XP spectra of anhydrous $RuO_2$ as a reference (**a**) and 5% Ru/C catalyst in different forms: fresh (**b**), prehydrogenated at 25 °C and used (2×) (**c**), prehydrogenated at 60 °C and used (2×) (**d**), as well as prehydrogenated at 60 °C without substrate (**e**)

last reuse of the catalyst (0%). These phenomena refer to the strong poisoning of ruthenium by nitrogen which becomes more significant at lower catalyst/substrate ratios (0.1 and 0.05 g $g^{-1}$) and room temperature, after several reusing the 5% Ru/C.

According to these results, it is favourable to apply a relatively high catalyst/substrate ratio (0.2 g $g^{-1}$) to achieve complete conversion of MP even after more catalytic runs and without regeneration of the catalyst. Despite the higher amount of ruthenium on carbon, it could be applied economically on an industrial scale considering the low price of Ru (65 USD/tr. oz.).

### 3.5 Acidic Treatment of Catalyst

Since the product (1-methylpyrrolidine) has a strong basic character due to its tertiary nitrogen, an acidic treatment can be an alternative method for avoiding deactivation of

**Table 3** Ru $3d_{5/2}$ binding energies, FWHM and Ru/C surface atomic concentrations of the fresh and spent catalysts with the fitted line shape of AS (30; 0.6)

| Samples | Position of the peaks Ru $3d_{5/2}$ and Ru $3p_{3/2}$ (eV) | | FWHM (eV) | Atomic concentrations in Ru/C catalysts (%) |
|---|---|---|---|---|
| $RuO_2$ (anhydrous) | 280.3 | 462.6 | 1.37 | – |
| 5% Ru/C (fresh) | 281.9 | 463.5 | 2.77 | 4.16 |
| 5% Ru/C [prehydrogenated at 25 °C and used (2×)] | 281.7 | 463.8 | 2.93 | 4.01 |
| 5% Ru/C [prehydrogenated at 60 °C and used (2×)] | 281.3 | 463.6 | 3.11 | 2.67 |
| 5% Ru/C (prehydrogenated at 60 °C) | 280.5 | 461.6 | 2.37 | 4.12 |

*FWHM* full width at half maximum

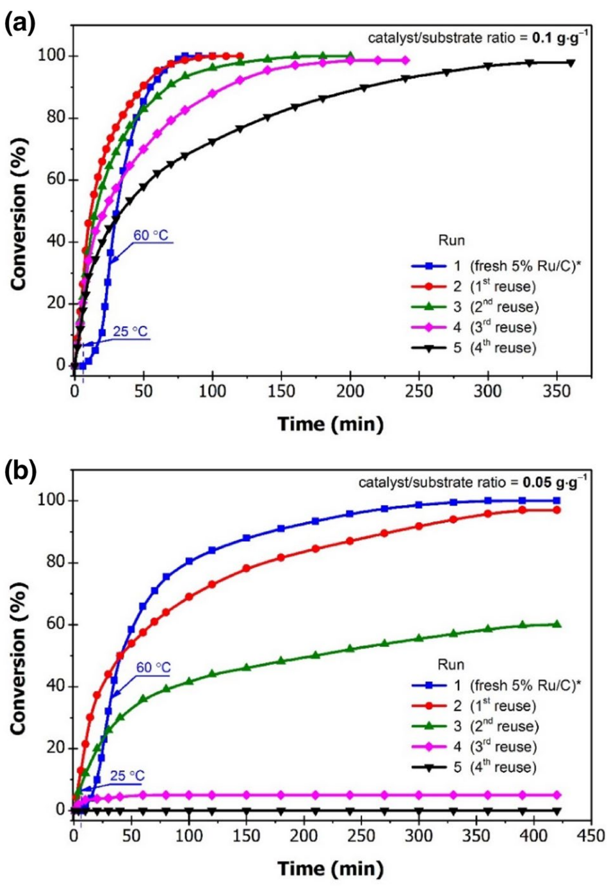


**Fig. 8** Conversion of 1-methylpyrrole (MP) vs. time over 5% Ru/C, at different catalyst/substrate ratios: 0.1 g $g^{-1}$ (**a**) and 0.05 g $g^{-1}$ (**b**). Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 25 °C, *25–60 °C 10 bar

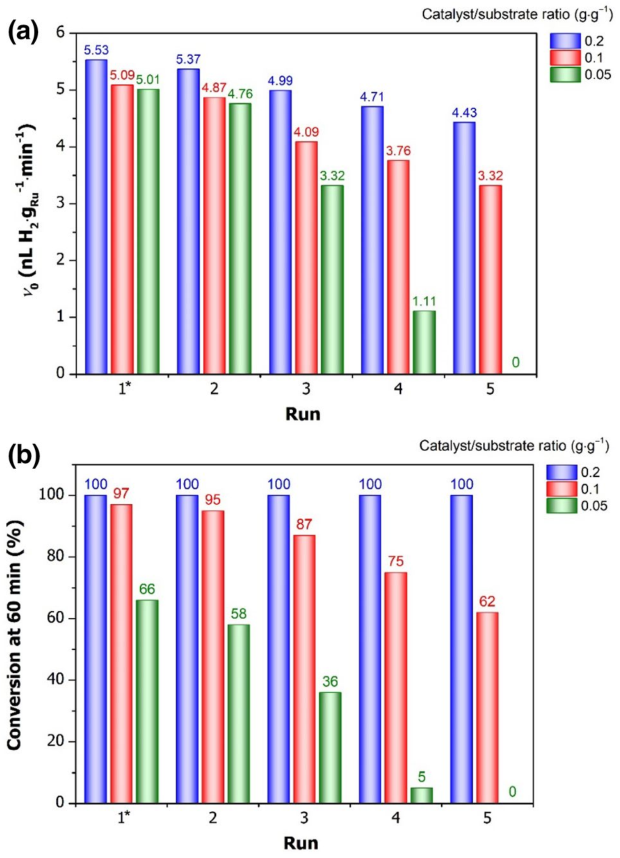


**Fig. 9** Effects of amount and reuse of the catalyst on the initial rate ($v_0$) (**a**) and the conversion at 60 min (**b**) in the hydrogenation of 1-methylpyrrole (MP) over 5% Ru/C. Conditions: 2.0 g substrate, 50 $cm^3$ methanol, 25 °C, *25–60 °C 10 bar

the catalyst. As it is discussed in Sect. 3.4, a very drastic decrease was observed in both the activity and the conversion values (Fig. 9) during the reuse of 5% Ru/C at 0.05 g $g^{-1}$ catalyst/substrate ratio, therefore an acetic acidic handling of the spent catalyst was also investigated.

Conversion of MP over 5% ruthenium on carbon treated with 5% acetic acidic after each run, at 0.05 g $g^{-1}$ catalyst/substrate ratio, depending on the number of reusing the catalyst, in methanol is shown in Fig. 10.

As seen, the acidic treatment of the spent 5% Ru/C catalyst resulted in higher conversions of MP in every recycling experiment (runs 2–5) than without it (Fig. 8b). The reduction of MP was also complete during the first reusing the catalyst (run 2), already at 25 °C, contrary to the result obtained sans its acidic handling (97%). Similar decreases were observed in the conversions in the third and fourth runs

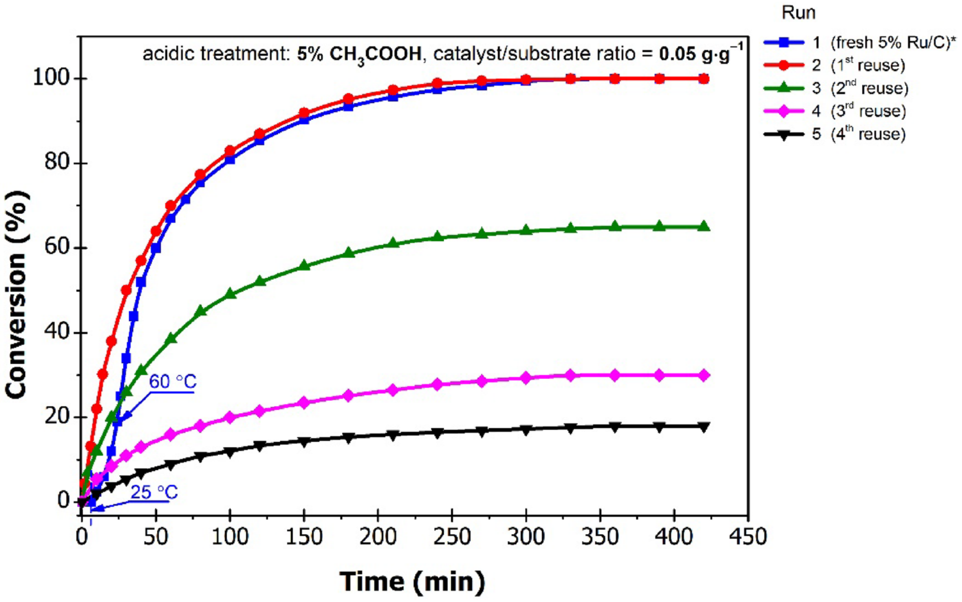


**Fig. 10** Conversion of 1-methylpyrrole (MP) vs. time over 5% Ru/C using acidic treatment after each run. Conditions: 2.0 g substrate, 0.1 g catalyst, 50 cm$^3$ methanol, 25 °C, *25–60 °C, 10 bar; acidic treatment: 2 × 5 cm$^3$ 5% acetic acid, then 2 × 10 cm$^3$ distilled water

as did in those reactions where 5% ruthenium on carbon was applied without acidic treatment, but better results (65 and 30%, respectively) were achieved. Finally, in the fifth run, a significantly higher conversion value was obtained over the acidic treated catalyst (18%) than using the untreated one (0%).

Figure 11a, b exhibit the initial rates ($v_0$) and the conversions at 60 min to compare the effects of acidic handling and reuse of 5% Ru/C catalyst on the course of the hydrogenation of MP.

As seen in Fig. 11a, a decrease of $v_0$ values was observed by increasing the number of reusing the acidic treated catalyst (5.06 → 0.44 nL $H_2$ $g_{Ru}{}^{-1}$ min$^{-1}$), but they were higher than those were experienced in the presence of the untreated one (5.01 → 0 nL $H_2$ $g_{Ru}{}^{-1}$ min$^{-1}$). Similarly, the conversions were also diminished (70 → 9%) during the reuse of 5% Ru/C treated with acetic acid (runs 2–5), but these values were significantly higher than those achieved with the untreated catalyst (58 → 0%) (Fig. 11b).

Although better results were obtained applying an acidic treated 5% Ru/C catalyst, the strong poisoning of ruthenium by nitrogen cannot be avoided at 0.05 g g$^{-1}$ catalyst/substrate ratio and room temperature after its several reusing.

## 4 Conclusions

Poisoning phenomena caused by nitrogen and the reuse of a heterogeneous, carbon supported ruthenium catalyst were investigated in the liquid-phase hydrogenation of 1-methylpyrrole (MP), as a model compound, in non-acidic medium. Reusing the spent, unregenerated 5% Ru/C catalyst, the activity of catalyst and the conversion of MP were strongly dependent on the amount of catalyst and the number of recycling, respectively.

It was found, surprisingly, that ruthenium on carbon showed high activity already at room temperature during its first reuse, contrary to the fresh catalyst which worked at only 60 °C. The prehydrogenation experiments showed that high catalytic activity could be obtained after these pretreatments, but this required a higher temperature (60 °C). Whereas, using these conditions is inexpedient on an industrial scale. This unexpected catalytic behaviour of 5% Ru/C was clarified by XPS measurements which revealed the existence of a fine $RuO_2$ layer on the surface of the catalytic metal in the fresh catalyst and verified the favourable effect of catalyst prehydrogenation on the catalytic activity.

To obtain the complete conversion of MP over 5% Ru/C even after more catalytic runs and without regeneration of the catalyst, a relatively high catalyst/substrate ratio (0.2 g g$^{-1}$) was applied, because in the presence of lesser amounts of catalyst (0.1 or 0.05 g g$^{-1}$ ratios) significant conversion and activity decreases were observed. This was due to the strong poisoning of ruthenium caused by basic nitrogen of the product (MPD). Although an acidic treatment of the used catalyst resulted in better conversions at 0.05 g g$^{-1}$ catalyst/substrate ratio and 25 °C, the poisoning caused by nitrogen cannot be avoided. However, reusing the spent and unregenerated ruthenium on carbon, above a limit catalyst/substrate ratio, can be an alternative method for Ru-catalysed, heterogeneous catalytic hydrogenation processes applied in fine chemical industry.

Further investigations to clear poisoning mechanism of these nitrogen containing heterocycles, over other catalytic metals (rhodium, palladium), are in progress.

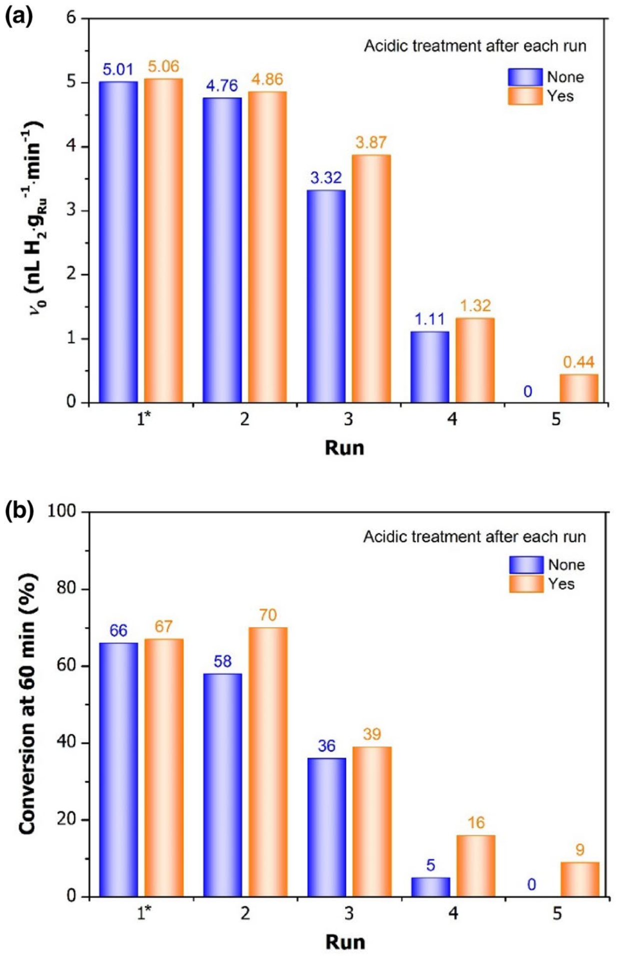


**Fig. 11** Effects of acidic treatment after each run and reuse of the catalyst on the initial rate ($v_0$) (**a**) and the conversion at 60 min (**b**) in the hydrogenation of 1-methylpyrrole (MP) over 5% Ru/C. Conditions: 2.0 g substrate, 0.1 g catalyst, 50 $cm^3$ methanol, 25 °C, *25–60 °C 10 bar; acidic treatment: 2×5 $cm^3$ 5% acetic acid, then 2×10 $cm^3$ distilled water

**Acknowledgements** The authors thank Dr. Antal Sárkány for determining the catalyst dispersion, as well as Dr. László Vida for GC–MS measurements.

## Compliance with Ethical Standards

**Conflict of interest** The authors declare no competing financial interest.

## References

1. Bartholomew CH (2001) Appl Catal A Gen 212:17–60
2. Hegedus LL, McCabe RW (1984) Catalyst poisoning. Marcel Dekker, New York
3. Moulijn JA, van Diepen AE, Kapteijn F F (2008) In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) Handbook of heterogeneous catalysis. Wiley, Weinheim, pp 1829–1845
4. Argyle MD, Bartholomew CH (2015) Catalysts 5:145–269
5. Hamilton TS, Adams R (1928) J Am Chem Soc 50:2260–2263
6. Maxted EB, Walker AG (1948) J Chem Soc 1093–1097
7. Maxted EB (1951) Adv Catal 3:129–178
8. Devereux JM, Payne KR, Peeling ERA (1957) J Chem Soc 2845–2851
9. Maxted EB, Briggs MS (1957) J Chem Soc 3844–3847
10. Freifelder M (1971) Practical catalytic hydrogenation. John Wiley, New York
11. Petró J (1976) In: Szabó ZG, Kalló D (eds) Contact catalysis, vol 2.Elsevier, Amsterdam, pp 65–75
12. Hegedűs L (2007) Magy Kém Folyóirat 113:139–144
13. Hegedűs L, Máthé T, Tungler A (1996) Appl Catal A Gen 143:309–316
14. Hegedűs L, Máthé T, Tungler A (1996) Appl Catal A Gen 147:407–414
15. Hegedűs L, Máthé T, Tungler A (1997) Appl Catal A Gen 153:133–139
16. Hegedűs L, Máthé T, Tungler A (1997) Appl Catal A Gen 152:143–151
17. Leete E (1989) Heterocycles 28:481–487
18. Fournier AM, Brown RA, Farnaby W, Miyatake-Ondozabal H, Clayden J (2010) Org Lett 12:2222–2225
19. Lee SY, Jung JW, Kim T-H, Kim H-D (2015) Arch Pharm Res 38:2131–2136
20. Hegedűs L, Máthé T (2002) Appl Catal A Gen 226:319–322
21. De Pablo RS, Benedict HN (1973) US Patent 3,766,089
22. Stillman NW, Osgood ER (1975) US Patent 3,864,361
23. Zhang M, Pei Q, Chen W, Liu L, He T, Chen P (2017) RSC Adv 7:4306–4311
24. Hagelüken C (2006) Chim Oggi/Chem Today 24:14–17
25. Hagelüken C (2008) In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) Handbook of heterogeneous catalysis. Wiley, Weinheim, pp 1846–1863
26. Axon SA, Casci JL (2008) In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) Handbook of heterogeneous catalysis. Wiley, Weinheim, pp 1863–1871
27. Trimm DL (2001) Appl Catal A Gen 212:153–160
28. Grumett P (2003) Platinum Metals Rev 47:163–166
29. Marafi M, Stanislaus A (2003) J Hazard Mater B101:123–132
30. Jackson SD (2006) Chem Eng J 120:119–125
31. Dufresne P (2007) Appl Catal A Gen 322:67–75
32. Al-Sheeha H, Marafi M, Raghavan V, Rana MS (2013) Ind Eng Chem Res 52:12794 – 12801
33. EudraLex – Vol. 4, Good manufacturing practice (GMP) guidelines, http://ec.europa.eu/health/documents/eudralex/vol-4/index_en.htm
34. NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (2017) In: Linstrom PJ, Mallard WG (eds) National Institute of Standards and Technology, Gaithersburg MD, 20899, https://doi.org/10.18434/T4D303
35. Sárkány A, Zsoldos Z, Furlong F, Hightower JW, Guczi L (1993) J Catal 141:566–582
36. Sárkány A, Stefler G, Hightower JW (1995) Appl Catal A Gen 127:77–92
37. Bruce LA, Hoang M, Hughes AE (1998) J Catal 178:84–93
38. Knapp M, Crihan D, Seitsonen AP, Lundgren E, Resta A, Andersen JN, Over H (2007) J Phys Chem C 111:5363–5373
39. Walker J, King RB, Tannenbaum R R (2007) J Solid State Chem 180:2290–2297
40. Over H (2012) Chem Rev 112:3356 – 3426
41. Wang L, Abudukelimu N, Ma Y, Qing S, Gao Z, Eli W (2014) Reac Kinet Mech Cat 112:117–129
42. Szabados E, Srankó DF, Somodi F, Maróti B, Kemény S, Tungler A (2016) J Ind Eng Chem 34:405–414
43. Morgan DJ (2015) Surf Interface Anal 47:1072–1079

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