

EFFECT OF Ru LOADING AND OF Ru PRECURSOR IN Ru/C CATALYSTS FOR AMMONIA SYNTHESIS

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ABSTRACT

One of the key points in the study of Ru/C catalysts for ammonia synthesis is the structure sensitivity of the reaction, which usually determines the proper metal loading, so governing the cost of the final catalyst. In the present work the effect of Ru loading on catalytic activity and thermal stability (*i.e.* catalyst resistance against support methanation and metal sintering) was investigated. The optimal Ru loading was found to be around 3-3.5 wt%, a value considerably lower with respect to that commonly found in literature. Furthermore, top activity was obtained with 10-15% Ru dispersion, higher dispersion values leading to a less performing catalysts. Finally, the effect of some different water-soluble Ru precursors on catalyst behaviour was also investigated.

Keywords: Ru loading; Ammonia synthesis; Ru/C catalyst.

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1 – INTRODUCTION

Ru-based catalysts proved since long time to be very active for ammonia synthesis [1,2]. Due to the high cost, the metal has to be supported on a high surface area material and thermally treated active carbons showed satisfactory from both points of view of activity and stability [3-6]. Differently from other supported noble metal catalysts, a high Ru loading seems to ensure a better activity. Indeed, in some patent literature [4] metal loading as high as 20 wt% has been reported. However, in the usual practice [7], the optimal Ru loading seems to be 6-11 wt%, referred to the support, the advantages of an increase of metal content being overcome by the cost of the catalyst.

To our knowledge, in spite of the considerable body of investigations on Ru catalyst so far reported, a systematic study on metal loading effect on activity and stability of carbon-supported Ru catalyst is substantially still lacking, though in a recent paper [8] the activity of a set of catalysts with metal content between 2 and 8 wt% has been studied, the metal precursor being RuCl_3 , supported onto different active carbons. Indeed, a similar investigation [9] on KOH-promoted $\text{Ru}/\text{Al}_2\text{O}_3$, showed the highest reaction rate with 8 wt% Ru loading and interesting results on catalysts with low (0.1-2 wt%) and high (10 wt%) metal content were also reported [10-15], the low loading being predominantly adopted for structural or kinetic studies. In addition, ca. 5 wt% Ru loading was adopted for a kinetic study of ammonia synthesis on Ru/MgO and $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts [16]. Furthermore, intermediate (ca. 5 wt%) [17,18] and high (8-10 wt%) [3-7,19-23] Ru loading is commonly found in more applicative studies, aiming at better understanding the catalytic behaviour under conditions similar to the industrial ones. Needless to say that, from the latter point of view, the goal is to keep metal loading as low as possible. Unfortunately, however, the simultaneous variation of support (Al_2O_3 , MgO , lanthanide oxides, active carbon) and of promoters (alkali metals and lanthanides), together with Ru loading, does not allow a direct comparison between all those catalysts.

As for the nature of Ru precursor, in the mentioned studies Ru is usually loaded from different Ru compounds. The most commonly used are $\text{Ru}_3(\text{CO})_{12}$ [9,24] and RuCl_3 (in acetone or THF solution) [8,19]. In practical application carbonyls are less preferred, due to their high volatility and toxicity, though an improvement has been proposed by employing $\text{K}_2\text{Ru}(\text{CO})_{12}$ [18,25] *i.e.* by adding the metal and the promoter at once. However, this procedure prevents a free modulation of catalyst composition, the K/Ru atomic ratio being fixed. An interesting comparison between these precursors [26] showed a poor Ru particle size homogeneity for the chloride-prepared sample, while in the carbonyl-prepared one Ru was present prevalently as Ru_6 clusters. Generally speaking, chlorides of the Pt-group metals show often good precursors, due to their solubility and high reducibility. Unfortunately, however, some residual Cl^- ions can remain tightly bound to metal surface or to the support, so affecting the catalytic behaviour. Moreover, after promoters addition, macrocrystalline alkali chlorides can form, so reducing the amount of active promoter [2]. A comparison [9] of two sets of catalysts prepared from RuCl_3 or from $\text{Ru}(\text{CO})_{12}$, respectively, showed that the carbonyl precursor seems to guarantee a better performance than the chloride, the latter leading to a lower metal dispersion. By contrast, according to another investigation [11,12], the lower reaction rate should be ascribed to the electron-attractive effect of the chlorides, acting as poison for the catalyst. A third option as Ru precursor is K_2RuO_4 [3,18,27], deposited from aqueous solution. Such a reagent is easier to handle with respect to carbonyls and does not add any poison. Finally, $\text{Ru}(\text{NO})(\text{NO}_3)_3$ was recently mentioned as a further option for Ru impregnation [28].

The aim of the present work was then to minimise Ru loading in Ru/C ammonia synthesis catalyst, taking into account the effect of loading on catalytic activity, resistance to metal sintering and stability towards support methanation. The goal was to define an active and stable Ru/C catalyst, economically competitive with the cheap Fe-based commercial catalyst. A second aim was to better investigate the effect of Ru precursor by

comparing three samples of similar composition, but prepared from different precursors (K_2RuO_4 , $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Ru}(\text{NO})(\text{NO}_3)_3$). Furthermore, the effect of Ru loading on metal dispersion and its relationship with catalytic activity was also investigated.

2 - EXPERIMENTAL

2.1 – Catalyst preparation

Potassium ruthenate as precursor

A graphitised carbon (BET surface area $>250 \text{ m}^2/\text{g}$, total pore volume $0.4 \text{ cm}^3/\text{g}$, $0.07 \text{ cm}^3/\text{g}$ of which due to micropore contribution) and as supplied Aldrich and Acros 'pro-analysi' reagents were used. Details about this preparation route can be found elsewhere [5]. Briefly, Ru was added by impregnation with aqueous K_2RuO_4 . The catalyst was then reduced in flowing hydrogen at 320°C for 5 h and carefully washed to remove excess potassium. Then promoters were added by impregnation from aqueous solutions of hydroxides (K and Cs) or nitrates (Ba), in the optimal amount determined in a previous work [18]: Ba/Ru = 0.6 (mol/mol), Cs/Ru = 1 (mol/mol), K/Ru = 3.5 (mol/mol). The composition of these catalysts is reported in Table 1.

Ru chloride as precursor

An aqueous solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich, $\geq 99.98\%$) was used for support impregnation. The catalyst was then reduced in flowing hydrogen at 320°C for 5 h. Before promoters addition the sample was splitted into two portions. One of them was repeatedly washed with distilled water, till complete absence of chlorides in the washing solution, as measured by the usual AgNO_3 test. The second portion was promoted (*vide supra*) directly just after Ru reduction.

Ru nitrosylnitrate as precursor

The support was impregnated with Ru(NO)(NO₃)₃ (Alpha, 31.3 wt% in aqueous solution) and reduced as previously described. Before promoters addition the sample was splitted into two portions, one of which was carefully washed in order to remove nitrates, while the other was directly promoted with the same promoter/Ru molar ratio (*vide supra*).

2.2 - Catalyst characterisation

XRD analysis was carried out by means of a Philips mod. PW 1820 instrument, by employing the Ni-filtered Cu K α radiation ($\lambda=1.5148 \text{ \AA}$). Ru dispersion and metal surface area were determined for the unpromoted samples as described elsewhere [29]. Briefly, the analysis was carried out on a TPD/TPR-TCD apparatus, equipped with independent feeding lines for He (SAPIO, purity ≥ 99.9999 vol. %), Ar (SAPIO, ≥ 99.9995), H₂ (SIAD, ≥ 99.9995), O₂ (SIAD, ≥ 99.999) and a six-way valve with sampling loop for O₂ pulsed chemisorption. Ca. 0.15 g of catalyst, in 0.15-0.25 mm particle size, were loaded in a "U" shaped Pyrex reactor. Temperature was controlled by an Eurotherm, mod. 818 TRC, through a thermocouple tightly bound to the reactor and the outlet gas was analysed by a thermoconductivity detector (DANI, mod. HWD 85/4), kept at 150°C.

The sample was reduced by feeding 40 cm³/min of a 5 vol. % H₂ in Ar gas mixture and heating (10°C/min) from r.t. up to 400°C, then kept for 1 h. After flushing in He at 450°C for 1 h, pulsed chemisorption was carried out at 0°C [29].

Metal dispersion (D) and metal surface area (A_M , m²/g_{Ru}) were calculated by taking into account the contribution of the support, by subtracting the oxygen consumption of blank samples. These were prepared by impregnating the support with a volume of a 0.5

M solution of KOH corresponding to that of the K_2RuO_4 solution employed for the impregnation of the catalyst [29].

2.3 - Apparatus and procedure for activity tests

Activity tests were performed by means of a bench scale, fixed bed, downflow Incoloy 800 reactor. A detailed description of the apparatus and procedure was given elsewhere [5]. Briefly, the catalyst, in 0.15-0.25 mm particle size, was loaded after dilution (1/22 vol/vol) with quartz particles of the same size, in order to minimise the hot-spot along the catalyst bed. The catalyst was activated *in situ* by flowing a $H_2 + N_2$ mixture ($H_2/N_2 = 1.5/1$ vol/vol), at GHSV = 20,000 h^{-1} , 30 bar, while increasing temperature by 1°C/min up to 450°C, maintained for 5 h and then decreased down to 430°C. The reactant gas mixture was carefully purified from oxygenates by passing through a trap packed with a proper amount of frequently regenerated, reduced Fe-based commercial ammonia synthesis catalyst. Activity tests have been carried out under standard reaction conditions, *i.e.* 100 bar and 430°C, by varying the gas mixture space velocity from GHSV=30,000 to 200,000 h^{-1} . The effluent gas was bubbled in a known amount of diluted H_2SO_4 , followed by titration of the residual acid with NaOH. Catalytic activity was expressed as vol % of NH_3 in the effluent gas at GHSV=30,000 h^{-1} (Table 1) or 60,000 h^{-1} (Table 2).

2.4 – Deactivation tests

Metal sintering and resistance to methanation were tested [5,18] at 100 bar, by increasing temperature by 1°C/min up to 550°C, maintained for 10 h and then lowered back to 430°C. After checking the residual activity through a further test at 100 bar and GHSV=30,000 h^{-1} (test S1, Table 1), temperature was increased by 2°C/min up to 700°C, while monitoring methane formation by on-line gas-chromatography. At last, temperature

was dropped rapidly down to 430°C and a final activity test was carried out at GHSV=30,000 h⁻¹, to check for any further change of activity due to methanation+sintering (test S2, Table 1).

3 - RESULTS AND DISCUSSION

3.1 Effect of Ru loading

Catalytic activity

A first set of five catalysts was prepared for this purpose, characterised by Ru loading ranging between 1.5 and 9 wt% (samples A-E, Table 1). Their activity is reported in Table 1. A significant increase in ammonia productivity can be noticed ongoing from sample A (ca. 2 wt% Ru) to sample B (ca. 4 wt% Ru), while for higher loading activity seems to attain a plateau. Similar conclusions were also reported by Liang et al. [8] on activated carbon supported catalysts, prepared from RuCl₃. This result is of high practical significance, since it shows that the present catalyst can become cost-competitive with respect to the traditional Fe-based one.

The increase in activity when passing from 2 to 4 wt% Ru suggested a deeper investigation in this concentration range. This was carried out by means of a second series of samples (catalysts M-U, Table 2) prepared from a different Ru precursor (*vide infra*). Their activity showed a roughly linear increase when increasing Ru loading up to 3.2 wt%. Beyond this value productivity levelled off, as previously reported, confirming that the optimal Ru loading lies around 3.0–4.0 wt% (Table 2), at least for the present set of catalysts prepared as previously described. By contrast, metal loading lower than 3.0 wt% seems insufficient to guarantee a high performance.

Through different approaches, such as density functional theory calculations, single

crystal studies or ^{15}N isotopic exchange kinetics, it was concluded that: *i)* only a small portion of the Ru surface is covered by reaction intermediates [30,31]; *ii)* the activation of the N_2 molecule is predominantly due to the presence of so-called B_5 sites, located on the steps of the surface [32,33]; *iii)* the population of dissociated nitrogen atoms onto the surface terraces is due to diffusion from the B_5 N_2 -splitting sites [34]; *iv)* Ru clusters with diameter smaller than 1 nm expose only a few B_5 sites [35]. The present results, obtained through a more applicative approach, are perfectly in line with such findings. Indeed, on one hand low Ru loading very likely leads to too small metal particle size, *i.e.* to an insufficient amount of B_5 active sites. On the other hand, an increase of Ru loading beyond a certain value reveals useless, because it does not lead to an increase of these sites, but simply to an increase of the overall particle size.

According to these results, we would expect a clear relationship between catalytic activity and metal dispersion, including a breakthrough point, beyond which no substantial further activity increase should be noticed.

The XRD patterns of most of the present samples don't allow even a rough measurement of particle size through the Scherrer equation, due to the low metal loading. However, by correlating Ru dispersion, measured by O_2 chemisorption [29], with activity data (Table 2, samples M-U), one can see, as expected, that Ru dispersion decreases with increasing metal loading. Furthermore, a plot relative to both our series of data (Fig.1), shows that activity increases when decreasing metal dispersion, the highest conversion being attained at *ca.* 10-15% dispersion. A comparison with the results reported by others [8] can only be indicative, due to the different catalytic systems studied and to the methods used for determining the Ru dispersion. However, also in that case a breakthrough point at about 20% Ru dispersion, based on H_2 chemisorption, was noticed, below which no significant change in activity was observed. These results confirm the structure sensitive character of the ammonia synthesis reaction over Ru/C and the tight

relationship between metal dispersion and activity.

Catalyst stability

Catalyst resistance to methanation was checked for temperature up to 700°C. The behaviour of samples A and E (*i.e.* lowest and highest Ru loading) are reported in Fig.2. The effect of carbon pretreatment on its resistance to methanation was discussed in our previous investigation [5] and recently confirmed by others [36]. Moreover, promoters addition in proper amount can further improve support stability [18]. However, Ru itself catalyses methane formation under the usual ammonia synthesis reaction conditions. Hence, the change of metal concentration can have an effect on catalyst stability. However, every one of our samples behaved similarly, showing very low methane concentration in the outlet gas, very near to the detection limit of the apparatus, even at the highest temperature (Fig. 2). Notice the highly expanded y axis, and the virtual absence of any trace of CH₄ at least up to 500°C, a temperature by far higher than the usual NH₃ synthesis temperature in industrial application. A comparison with the methane formation reported in our previous papers [5,18] can be easily done by multiplying such data by a calibration factor 0.024 to obtain the present Fig.2 CH₄ vol % data. This confirms the high stability of the catalyst with respect to methanation, which showed mainly related to the nature of the support, *i.e.* its graphitisation degree [5,18] and almost independent of Ru loading.

The results of the metal sintering tests of samples A-E are reported in Table 1, as residual activity after deactivation at 550°C and 700°C (S1 and S2, respectively). After deactivation at 550°C a higher resistance to metal sintering was found for low metal loading, with an almost linear decrease of activity with increasing Ru content. This is in line with a metal sintering mechanism based on surface aggregation, the aggregation rate increasing with metal content. The activity test after deactivation at 700°C (*i.e.* after the

methanation test) shows that the main effect of this high temperature treatment is a deeper metal sintering, due to the high support stability. As expected, a further activity decrease was observed. However, the residual ammonia productivity was still rather high for samples A and B, characterised by the lowest metal loading (1.9 and 3.8 %, respectively). By contrast, the samples with higher Ru content underwent a dramatic deactivation, becoming almost completely or totally inactive. Although from a practical application point of view these operating conditions are not realistic, this further confirms the higher stability connected with low metal loading. From these results it can be concluded that it is possible to obtain a high activity, together with a perfectly satisfactory thermal stability, with Ru loading as low as 3.5-4 wt%.

By comparing the performance with that of a Fe-based commercial catalyst [37], it was observed that with the present Ru/C samples it is possible to obtain a noticeable increase of activity. A direct comparison between the performance of two of the most significant samples is reported in Table 3, where M% is the metal wt% in the catalyst, ρ_B is the bulk density of the sample, m_c is the mass of catalyst used for the activity test and m_M is the corresponding mass of metal. The comparison of catalytic activity under identical reaction conditions, except for H₂/N₂ vol. ratio (equal to 3 for Fe-based and 1.5 for the Ru-based samples), allows to conclude that, on a catalyst bed volumetric basis ammonia productivity can be doubled when substituting the Ru-based catalysts for the traditional magnetite-derived ones. Furthermore, by comparing a “first generation” [5] high-Ru sample with the present low-Ru catalyst (Table 3) it can be concluded that almost the same volumetric conversion can be obtained decreasing to ca. one third the amount of precious metal needed. Finally, the comparison of ammonia productivity on a catalyst weight basis is much more favourable, being the bulk density of the C-supported catalysts much lower than that of the massive Fe-based system. Finally, by referring to a metal weight basis, a value of NH₃ productivity ca. 150 times higher can be obtained with the present low-Ru

catalyst, with respect to the commercial Fe-based sample.

3.2 Effect of metal precursor

K_2RuO_4 was selected as Ru precursor in our previous investigation [5,18,29]. This choice was due to the possibility to operate with aqueous solutions, to avoid harmful reagents such as carbonyl derivatives and to the absence of potential poisons such as chlorides. However, to our knowledge, so far no direct comparison between different Ru precursors has been reported in detail. Then, by keeping water as solvent, an important characteristic from the application point of view, we compared the activity of catalyst samples prepared by impregnation with solutions of three different Ru precursors: K_2RuO_4 , $RuCl_3 \cdot 3 H_2O$ and $Ru(NO)(NO_3)_3$.

The activity of these samples was tested at $GHSV=60,000 h^{-1}$. Sample F (Table 2) was prepared from $RuCl_3 \cdot 3 H_2O$, without promoters addition. As expected, after adding the promoters the activity increased considerably, from 0.7 up to 8.5 vol% NH_3 in the outlet gas (sample G). However, an activity comparable to that of our previously prepared sample B (11.5 vol% of NH_3 in the outlet gas at $GHSV=60,000 h^{-1}$) was reached only after carefully washing the reduced catalyst before promoters addition. This confirms the poisoning effect of chlorides, due to their electron attractive character [2]. Their removing increased conversion from 8.5 to 12 vol% NH_3 (sample H).

The elimination of the anion through washing proved to be beneficial also for samples prepared from $Ru(NO)(NO_3)_3$, though to a lower extent (samples I and L, Table 2). In fact, catalyst washing brought about an activity enhancement from 6.2 to 7.0 NH_3 vol% only. The possibility to remove nitrates by thermal decomposition during Ru reduction was also checked by means of a TPR experiment. The reduction of the unpromoted sample I was monitored through mass spectrometry and showed that NO_x can be completely removed at $T \leq 320^\circ C$, allowing to eliminate the washing step (needed for both

the ruthenate and the chloride precursor) from the preparation procedure. Finally, by comparing samples B, H and Q (Tables 1, 2), with similar composition, but prepared from different precursors, one may notice a further improvement of activity due to the use of nitrosylnitrate as precursor.

4 – CONCLUSIONS

The present results allow to conclude that: *i)* It is possible to obtain a highly active catalyst with Ru loading of the order of 3.5 wt%, with a significant dropping of the catalyst cost. *ii)* A further increase of metal loading does not improve activity significantly. *iii)* A low Ru loading improves also catalyst stability, mainly as for metal resistance to sintering. *iv)* The correlation between Ru dispersion and activity confirms the structure sensitivity of the ammonia synthesis reaction. *v)* A relatively low metal dispersion (*ca.* 10-15%) is sufficient to maximise catalytic activity, *vi)* Both the chloride and the nitrosylnitrate precursors can lead to activity comparable or even higher than with the ruthenate, provided the electronegative anion is properly removed.

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Table 1: Ru loading (referred to the final catalyst weight) and catalytic activity, under standard testing conditions (S) and after the deactivation tests at 550°C (S1) and at 700°C (S2). Samples prepared from K₂RuO₄.

SAMPLE	Ru wt%	S^a	S1^a	S2^a
A	1.9	12.4	8.4	6.9
B	3.8	13.8	8.7	7.4
C	5.2	13.3	n.d. ^b	n.d. ^b
D	6.0	13.1	7.2	0.48
E	8.9	13.0	7.6	0

^a NH₃ vol% in outlet gas at 100 bar, 430°C, H₂/N₂=1.5 (vol/vol), GHSV=30,000 h⁻¹

^b n.d. = not determined

Table 2: Ru loading (referred to the final catalyst weight), catalytic activity and metal dispersion of the samples prepared from different precursors.

SAMPLE	Ru wt%	Ru precursor	NH ₃ vol% ^a	Ru dispersion
F	3.8	RuCl ₃ 3 H ₂ O ^b	0.7	n.d. ^d
G	3.2	RuCl ₃ 3 H ₂ O	8.5	n.d.
H	3.2	RuCl ₃ 3 H ₂ O ^c	12.0	n.d.
I	2.8	Ru(NO)(NO ₃) ₃	6.2	n.d.
L	2.8	Ru(NO)(NO ₃) ₃ ^c	7.0	n.d.
M	1.6	Ru(NO)(NO ₃) ₃	6.4	0.46
N	1.9	Ru(NO)(NO ₃) ₃	7.3	n.d.
O	2.2	Ru(NO)(NO ₃) ₃	9.3	0.37
P	2.8	Ru(NO)(NO ₃) ₃	9.9	0.17
Q	3.2	Ru(NO)(NO ₃) ₃	12.4	0.11
R	3.3	Ru(NO)(NO ₃) ₃	12.4	0.11
S	4.0	Ru(NO)(NO ₃) ₃	12.6	0.20
T	5.1	Ru(NO)(NO ₃) ₃	11.8	0.16
U	8.1	Ru(NO)(NO ₃) ₃	10.8	0.14

^a measured in effluent gas at 100 bar, 430°C, H₂/N₂=1.5 (vol/vol), GHSV=60,000 h⁻¹

^b without promoters

^c washed after reduction

^d n.d. = not determined

Table 3: Comparison of the activity of a commercial Fe-based catalyst [37] and of the present Ru/C catalysts, on the basis of metal content. M% = metal wt% in the sample; m_C = mass of catalyst (g); m_M = mass of metal (g); ρ_B = bulk density (g/cm³).

Sample	M%	NH ₃ vol%*	ρ_B	m_C	m_M
Fe-based	≈96	7.3	2.8	0.36	0.36
High Ru loading	11.0	13.0	0.8	0.11	0.012
Low Ru loading	3.2	12.4	0.8	0.11	0.0035

* NH₃ vol% in the outlet gas at P=100 bar, T=430°C and GHSV=60,000 h⁻¹.

FIGURE CAPTIONS

Fig.1: Catalytic activity (◆) and Ru dispersion (○) of samples M-U (Table 2) at 100 bar, 430°C, $H_2/N_2=1.5$ (GHSV=60,000 h^{-1}).

Fig.2: CH_4 concentration in exit gas during the methanation test of samples A (◆) and E (×) (Table 1).

Fig.1

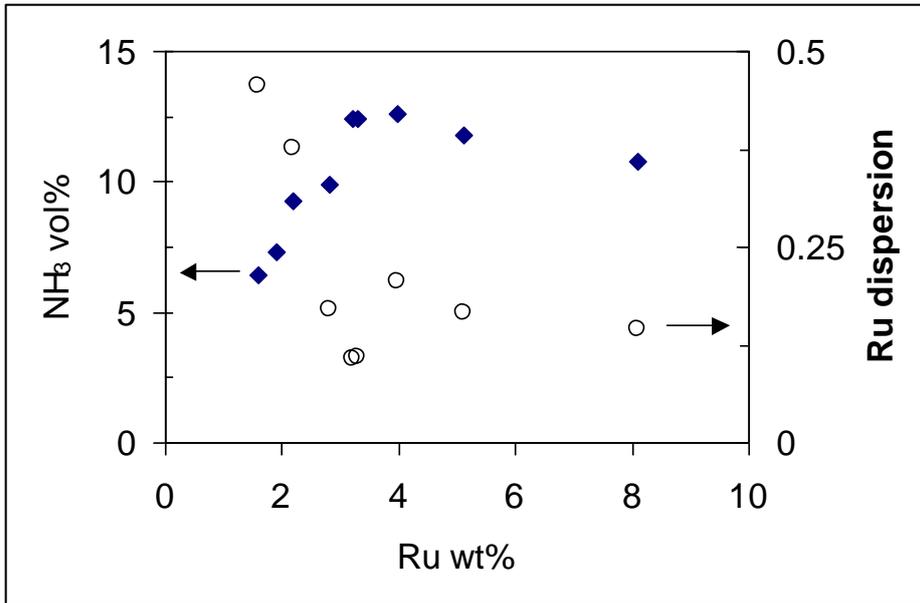


Fig.2

