

WUSTITE AS A NEW PRECURSOR OF INDUSTRIAL AMMONIA SYNTHESIS CATALYSTS

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Abstract

Contradictory results about the best oxidic precursor of Fe ammonia synthesis catalyst prompted the present comparative investigation on wustite- and magnetite-based catalysts. Many physical (density, porous texture, crystalline phases, reduction rate, metal surface, abrasion loss) and catalytic (kinetic constants, thermoresistancy) properties have been determined on both catalysts. The wustite-based catalyst proved to be much more active, especially at lower temperatures, approaching the performances of Ru/C catalyst, except at high conversion. Possible reasons for such a behavior of the wustite-based catalyst are discussed, suggesting that a reconsideration of the present consolidated knowledge on Fe ammonia synthesis catalyst might be convenient.

Keywords: Ammonia synthesis; Wustite catalyst; Magnetite catalyst.

1. Introduction

The traditional ammonia synthesis catalyst, developed in the first years of 20th Century by BASF researchers in Germany [1], is prepared from magnetite, promoted with small amounts of unreducible oxides, typically of Al, K and Ca. Magnetite is then reduced to metallic iron by synthesis gas in the reactor itself. The industrial catalyst presently used is not basically different from that developed about 100 years ago. It is widely accepted that magnetite is indispensable as precursor, because it allows an easy cationic substitution of Al⁺⁺⁺ for Fe⁺⁺⁺, thus giving homogeneous distribution of Al in the solid [2]. This gives, after reduction of magnetite to metallic iron, Fe particles either partly covered by well-dispersed Al oxide isles [3] or including paracrystalline Fe aluminate species [4-6], both of which prevent Fe from sintering, thus increasing the catalyst life. It is also thought that the Fe surface produced from magnetite by reduction with synthesis gas contains the largest amount of sites having the geometrical configuration most convenient for the dissociative chemisorption of dinitrogen, thus giving high catalytic activity. In fact, it has been experimentally found that, when the Fe⁺⁺/Fe⁺⁺⁺ ratio of the catalyst is different from 0.5 (stoichiometric magnetite), either higher or lower, the activity decreases, thus giving support to the above-mentioned opinions [3]. On the whole, this catalyst was considered well consolidated and no special improvement was still expected, so that a completely different Ru/C catalyst was recently developed for low-pressure ammonia synthesis [7-9].

In 1996 some Chinese researchers reported [10] and patented [11] a new high-activity ammonia synthesis catalyst based on wustite as precursor in place of magnetite, the oxidic promoters being substantially the same. It was shown that the reaction rate of the new catalyst is 30-90% higher than that of the traditional one and that such an activity difference increases when

temperature decreases, thus rendering this catalyst well suited to low-pressure synthesis. Moreover, as wustite can be reduced to Fe more easily than magnetite, the new catalyst allows to shorten appreciably the duration of plant start-up. Resistance to sintering and mechanical strength are reported to be the same of the traditional catalyst, while resistance to CO impurities is higher. It was also reported [10] that the new catalyst is being used successfully in Chinese ammonia plants since 1991. The ammonia productivity was claimed to be increased by 20%, but further advantages are to be expected when the new catalyst is used in big modern plants.

Very recently some Polish researchers reported [12] that wustite-based ammonia synthesis catalysts are slightly less active than those based on magnetite and much less resistant to thermal deactivation. The high industrial impact of the ammonia synthesis catalyst and also the underlying scientific implications led us to face the problem of such contradictory data. To this purpose the Chinese wustite-based A301 catalyst and a widely used magnetite-based industrial catalyst have been extensively characterized for both physical and catalytic properties, aiming at reaching definite conclusions about the relative performance of the two catalyst types. It is clear that, should wustite be a more effective precursor than magnetite, a substantial revision of the present knowledge of ammonia synthesis catalysts should be worth.

2. Experimental

2.1 Catalysts

Two commercial catalysts, based on wustite and on magnetite, respectively, were chosen for this investigation. The wustite-based catalyst (A301) is manufactured by Shangyou Catalyst Co. Ltd., while the magnetite-based one is a widely used European product. Catalyst A301 is reported to contain the same promoters as the traditional ones [13], so that the main difference between the two catalysts is in the precursor.

2.2 Physical characterizations

The bulk density was measured according to the standard ASTM test method D4164-99 [14], without any sample pretreatment.

XRD measurements were carried out with a Philips powder X-ray diffract meter, equipped with a graphite focusing monochromator on the diffracted beam and a proportional detector. Ni-filtered $\text{CuK}\alpha$ radiation and a step by step (0.05° in 2 theta) technique were employed.

TPR experiments were performed with a home-made equipment. The following experimental conditions have been selected:

Temperature range	25-1200°C
Heating rate	10°C/min
Reducing gas	5% H_2/Ar
Gas flow rate	40 cm^3/min
Sample mass	50 mg
Water absorption trap	Mg perchlorate

The same equipment was used for the measurement of the BET surface area by the continuous flow method.

The percentage of free Fe surface in the catalysts has been determined as previously described [15]. In practice it is given by the ratio $2V_{\text{CO}}/V_{\text{N}}$, where V_{CO} is the volume of CO chemisorbed at -78°C , measured by pulse flow technique, and V_{N} is the nitrogen monolayer volume, both of them expressed per catalyst gram. The factor 2 comes from calibration on pure Fe powder. In practice an average Fe/CO chemisorption stoichiometry of about 1.5 has been adopted.

Pore volume and pore size distribution were measured by mercury porosimetry, using a Micromeritics AutoPore IV instrument.

The abrasion loss was measured according to the ASTM standard test method D4058-96 [16], without any sample pretreatment, using a ROTAB-AS instrument by Ma.Tec. Materials Technologies.

2.3 Catalytic tests

The activity tests were performed at 100 bar in the temperature range 400-460°C, using the equipment and procedure previously described [8]. The catalyst particle size was 0.15-0.25 mm. Before the test the catalysts have been activated in synthesis gas at 30 bar and GHSV = 20 000 h⁻¹. Temperature was increased by 50°C/h from 25°C to 350°C, then by 10°C up to 500°C. Full catalyst reduction was checked by TPR. The feed gas was purified through a trap filled with pre-reduced catalyst particles. The trap was periodically activated in the above-mentioned conditions. Catalyst thermoresistancy was determined by repeating the test at 430°C after catalyst treatment at 600°C for 16 hours in synthesis gas.

3. Results

3.1 Bulk density

The following values have been obtained for the bulk densities of the two catalysts (particle size 1.5-3 mm):

A301 wustite catalyst	3.25 g/cm ³
Magnetite catalyst	2.85 g/cm ³

As the whole available volume of industrial reactors is usually filled with the catalyst, the activity per volume (for instance, moles of ammonia produced per hour per cubic meter of catalyst) must be considered for industrial purposes. Therefore, an activity increase of 14% for catalyst A301 is simply due to the higher bulk density. Moreover, as wustite contains 7.4% more Fe than magnetite, a total activity increase of about 21% must be assigned to catalyst A301, should the activity per unit weight of the two catalysts be the same. The higher bulk density of catalyst A301 with respect to the magnetite-based one comes mainly from the more compact ionic arrangement in the wustite structure. The above-mentioned 21% activity increase was therefore easily foreseeable.

3.2 Surface area and porosity

The values of BET surface area and of free Fe surface percentage of the reduced catalysts are reported in Table 1. The higher surface area of the wustite-based catalyst shows that sintering of Fe particles during reduction is less effective than for the magnetite-based catalyst. The following possible reasons can be envisaged:

- 1) Higher amount of water (about 20% more) evolved during reduction of magnetite. Water is known to increase strongly the rate of Fe sintering [17].
- 2) Higher reduction temperature of the magnetite-based catalyst (see TPR data).

Conversely, the free Fe surface percentage is much higher for the magnetite-based catalyst. This means that in the porous structure of the wustite-based catalyst a large fraction of the Fe area is covered by the oxide promoters. This is in agreement with the data of surface chemical composition reported by the Chinese authors, who found that the surface content of Al and K of the wustite-based catalysts is higher than that of the magnetite-based ones.[18]. The different behavior of Al ions during the reduction of Al₂O₃-promoted wustite and magnetite catalysts is perfectly in line with the representation of the reduced magnetite catalyst as alumina or Fe aluminate isles embedded in the α -Fe structure [4-6]. Conversely, during wustite reduction alumina will distribute over the Fe surface.

A detailed study of the porous structure of the two catalysts after reduction and passivation was performed by mercury porosimetry. The integral Hg intrusion curves of the two catalysts are reported in Fig.1. The values of the related properties are given in Table 2. The larger pore size of the magnetite-based catalyst will bring to better efficiency when it is used in large-size particles (more than 3 mm). For the most common particle size range (1.5-3 mm) the efficiency increase is expected to be negligible. It is noteworthy that the surface area values are only slightly higher than those obtained by nitrogen adsorption, what allows to exclude the presence of an appreciable amount of micropores in both catalysts.

3.3 X-ray diffraction

The XRD pattern of the A301 catalyst is reported in Fig.2. It can be seen that only the diffraction lines of wustite are present. The maximum amounts of metallic Fe and magnetite, if any, can be estimated as 0.5%. As for the oxidic promoters, they must be either very well dispersed or dissolved in the wustite structure.

The XRD pattern of the magnetite-based catalyst (not reported) shows the diffraction lines of magnetite with a small amount (1-2%) of wustite.

It is well known that wustite is never stoichiometric, being usually represented as Fe_{1-x}O . In other words, the Fe/O ratio is lower than 1, due to the presence of some ferric ions in the wustite lattice. A linear relationship exists between wustite cell dimension and x (see Fig. 3, from data reported in Ref. 19). As the wustite present in catalyst A301 shows a cell dimension of 0.4310 nm (exactly the same value reported by Liu et al [10]), from such a linear relationship one obtains $x = 0.039$. If the wustite non-stoichiometry is expressed in terms of $\text{Fe}^{++}/\text{Fe}^{+++}$ ratio, the following relationship holds [10]: $\text{Fe}^{++}/\text{Fe}^{+++} = (1-3x)/2x$, from which for catalyst A301 one obtains $\text{Fe}^{++}/\text{Fe}^{+++} = 11$. However, the latter ratio could be lower, if some cationic substitution occurs in the wustite lattice, giving an increase of cell dimension. Such a substitution could occur with Ca^{++} , that has a larger size with respect to Fe^{++} (0.212 nm against 0.166 nm). Liu et al [10] report an average value of 6.5 for $\text{Fe}^{++}/\text{Fe}^{+++}$ of catalyst A301, corresponding to $x = 0.0625$ and to $d = 0.4294$ nm. The wustite lattice enlargement, from the value calculated on the basis of chemical analysis (0.4294 nm) to the XRD experimental value of 0.4310 nm, is very reasonably due to the cationic substitution given by Ca^{++} . Moreover, it is a matter of fact that wustite is not stable below 570°C [19], so that during cooling of the wustite melt (the manufacturing procedure of catalyst A301 [11] does not differ from that of the magnetite-based catalyst [20]) disproportionation to Fe and magnetite should occur, as clearly evidenced for pure wustite [19]. Conversely, in catalyst A301 wustite is stabilized down to room temperature, as shown by the XRD pattern. The only reasonable hypothesis for such a phenomenon appears to be Ca^{++} substitution for Fe^{++} to an extent sufficient to stabilize the

wustite. Such a cationic substitution has been already suggested by both the Chinese [18] and the Polish [21] researchers.

3.4 TPR

The two catalysts were subjected to a TPR test in order to check the claim of Chinese researchers about the better reducibility of catalyst A301, with respect to the magnetite-based one [10]. The two TPR patterns are shown in Fig.4. It can be seen that the reduction peak of catalyst A301 is shifted towards lower temperatures, thus confirming the advantage of this catalyst as to shorter reduction period in the industrial reactor. This result is in agreement with the better reducibility of wustite with respect to magnetite [22].

3.5 Mechanical properties

While the crushing strength of ammonia synthesis catalysts is not usually measured, as it is always high enough for the current needs, the abrasion resistance must be as high as possible, in order to avoid dust formation during reactor loading. So, the abrasion loss was measured for both catalysts, using the ASTM standard method D4058-96 [16]. The following wt % values of fines formed during the standard abrasion treatment were found:

Catalyst A301	0.7%
Magnetite catalyst	1.0%

So, catalyst A301 shows a higher abrasion resistance, in agreement with the data reported by the Chinese researchers [10].

3.6 Kinetic data

The experimental data of conversion as a function of space velocity have been elaborated according to the Temkin-Pyzhev equation [23]. The Arrhenius plots for the two catalysts are shown

in Fig.5. It is immediately evident that catalyst A301 is much more active than the magnetite-based one.

Furthermore, the following values have been obtained for the kinetic constant k_{20} and for the apparent activation energy E_2 (1 cal = 4.187 J):

Catalyst A301	$k_{20} = 0.874 \times 10^{16}$	$E_2 = 44.9$ kcal/mol
Magnetite-based catalyst	$k_{20} = 3.319 \times 10^{16}$	$E_2 = 47.5$ kcal/mol

From these data it can be calculated that, in the temperature range 400-460°C, typical of a modern low-pressure ammonia synthesis unit, the reaction rate of catalyst A301 is, on the average, 70% higher than that of the magnetite-based catalyst. This activity gap decreases when temperature increases, but the equality of the reaction rates is obtained only at the very high temperature of 700°C. The level of such an activity gap substantially agrees with that reported by the Chinese authors (30-90%) [10].

As for the resistance to deactivation, after the standard sintering treatment (16 hours at 600°C in synthesis gas) the following percentages of the original reaction rate at 430°C have been retained by the two catalysts:

Catalyst A301	78%
Magnetite-based catalyst	80%

Therefore the two catalysts do not differ appreciably as to resistance to deactivation.

4. Discussion

The first announcement of wustite as a better precursor than magnetite for ammonia synthesis catalysts was given in 1996 in an international journal by the Catalyst Group of the Zhejiang University of Technology in Hangzhou [10]. It is clear that such a discovery has a strong impact on the consolidated scientific knowledge of ammonia catalysts and moreover opens the way to interesting industrial application. It was therefore surprising that after six years no papers had appeared from other groups on this subject, except for a very recent one from the University of

Szczecin, Poland [12]. In such circumstances we deemed necessary to start an investigation on the comparison of wustite- and magnetite-based ammonia catalysts with the main purpose of confirming, or not, the data reported by the Chinese authors. This need was even more evident as the Chinese researchers chose, as reference catalyst, a magnetite-based catalyst of local production (A110-2), whose performance is unknown to most specialists. Hence, we have chosen as reference an industrial catalyst frequently used worldwide.

From the present results it can be stated that the Chinese data have been fully confirmed and, in some aspects, even improved. We have shown that about one third of the increase of reaction rate, with respect to the magnetite-based catalyst, must be ascribed to the higher bulk density and Fe content of the wustite-based catalyst. On the other hand, the extent of Fe surface per catalyst unit weight is much higher for the magnetite-based catalyst (see Table 1). Simple calculations show that the reaction rate per unit Fe surface of the wustite-based catalyst is twice that of the magnetite-based one. This higher specific activity (converted moles/hour/m² Fe), sometimes incorrectly called turnover frequency, appears to be due to electronic effects. In fact, the kinetic data show that both the activation energy and the preexponential factor are lower for the wustite-based catalyst. Therefore, the active sites of the Fe surface coming from wustite are much more effective in performing the dissociation of dinitrogen, the well-known rate-determining step of the ammonia synthesis reaction. In fact, recent TPD data from the same Chinese group [24] pointed to the same conclusion. Unfortunately, no extensive structural or surface investigations have been performed up to date on the wustite-based catalyst, so that, for the time being, only some speculation can be done on this subject. For instance, it can be remarked that a clear difference between wustite and magnetite precursors is found in the higher ability of the former to dissolve Ca⁺⁺ ions [21]. After reduction, very dispersed CaO should be present on the surface of the wustite-based catalyst and could contribute, due to its basic nature, to activate dinitrogen dissociation on the geometrically suitable Fe sites. Our experimental data, and also the Chinese ones, are in full agreement with this tentative explanation, which however should be checked by further experiments. On this respect, it

should be stressed that Fe^{++} substitution with Ca^{++} is favoured by the presence of Fe^{+++} ions in the wustite lattice. In fact, Liu et al [10] found a flat maximum of catalytic activity for a $\text{Fe}^{++}/\text{Fe}^{+++}$ ratio of about 7. This maximum could be due to the opposite effects of increasing magnetite content and increasing Fe^{++} - Ca^{++} substitution when the $\text{Fe}^{++}/\text{Fe}^{+++}$ ratio decreases.

From the industrial point of view, a very important property of the ammonia catalyst is thermoresistancy, namely resistance to sintering of the Fe nanoparticles, being this the main reason for the progressive catalyst deactivation. The data reported by Liu et al [10] are not significant, because 500°C is a too low temperature for giving any appreciable sintering effect within 20 hours on-stream. Our thermoresistancy test (sintering treatment at 600°C for 16 hours) allowed an effective comparison of wustite- and magnetite-based catalysts, showing that they behave in the same way as to deactivation and therefore to catalyst life. So, it can be inferred that the higher activity of the wustite-based catalyst will be maintained during the whole plant operation. While in the magnetite-based catalyst the resistance to sintering is mainly due to the presence of very well dispersed Al oxide and/or Fe aluminate, Al^{+++} ions are likely to be much less dispersed in wustite, so that an additional similar effect of CaO in wustite seems to be reasonable. As previously discussed, a further key role of Ca^{++} ions is to give stability to the wustite phase at low temperature. Then, on the whole, the addition of CaO seems to have been the decisive factor for the discovery of the new catalyst.

According to Liu et al [10, 13, 24], when wustite and magnetite phases are present together in the catalyst, a low activity results. This experimental fact is attributed to an unclear non-uniform distribution of the promoters within the two phases. An alternative simpler explanation is that water, coming from later reduction of magnetite, decreases the surface area of Fe formed from wustite, which is reduced at lower temperature.

As to the kinetic data, the values of apparent activation energy reported by the Chinese authors [24] are different from ours, but they used a different α value in the Temkin equation (0.50 instead of our 0.75) Nevertheless, it is noteworthy that the ratio between the activation energies of

wustite- and magnetite-based catalysts is exactly the same (0.945). The Chinese authors recently suggested [18] that the reaction rate, referred to the catalyst volume, of the wustite-based catalyst is similar to that of the best Ru/C catalyst reported by Kowalczyk et al [25], who made the measurements at 8 vol % ammonia in the exit gas. In Fig.6 we compare the activity of catalyst A301 and of our best Ru/C catalyst [8]. It can be seen that they are practically equal, except for very high conversion, where the lower sensitivity of Ru to ammonia plays a decisive role. However, it should be stressed that, to give the highest activity, the Ru/C catalyst requires a H₂/N₂ feeding ratio of 1.0-1.5 [8]. Moreover, support degradation by Ru-catalyzed methanation under ammonia synthesis conditions, sometimes accompanied by additional adverse effects due to water traces, can occur, if the carbon support is not properly designed [8]. So, catalyst A301 appears to be competitive with Ru/C, and the related choice should be made on the basis of the specific plant characteristics and working conditions. A possible optimal solution, resulting from ammonia plant simulation [26], consists of loading catalyst A301 in the first two or three beds and the Ru/C catalyst in the final one, while keeping the stoichiometric feeding composition used with Fe catalysts.

Finally, Lenzion-Bielun et al. recently investigated activity and thermoresistance of laboratory prepared ammonia catalysts as a function of the Fe⁺⁺/Fe⁺⁺⁺ ratio [12]. Their conclusion was that wustite-based catalysts have lower activity and much lower thermoresistancy than magnetite ones, thus strongly contradicting the Chinese results. However, careful inspection of the Polish data shows that the catalysts they have tested for activity and thermoresistancy consist of a mix of wustite and magnetite phases. The Chinese authors clearly state that high activity can be obtained only when the wustite phase is present alone in the catalyst, while, when wustite and magnetite are present together, the catalysts show always a low activity. So, the Polish experimental data substantially agree with the Chinese ones, while the conclusion that wustite-based catalysts have low activity is clearly incorrect. Our investigation clearly demonstrates that catalyst A301, consisting of pure wustite phase, is much more active than the best magnetite-based

catalysts. As for the thermoresistancy data of Lenzion-Bielun et al., it should be remarked that 650°C is a very high sintering temperature for ammonia catalysts. The criteria to be adopted for the quantitative choice of the factor accelerating catalyst deactivation were discussed in some detail in a previous paper [27]. In particular, when the sintering temperature is too high, phenomena may occur having nothing to do with those occurring, with much lower rate, during catalyst life in the industrial reactor. As a consequence, the risk of obtaining an unreliable evaluation of catalyst thermoresistancy is not negligible.

5. Conclusions

The higher activity of ammonia synthesis catalysts from wustite, with respect to those obtained from magnetite, has been definitively established. The presence of wustite as the only crystalline phase in the catalyst precursor is indispensable for high activity. The activity gap between the two catalysts increases at lower temperatures. The higher activity, referred to bed volume, of the wustite-based catalyst is due in part to its higher density, but mostly to the higher efficiency of Fe surface sites in the activation of dinitrogen. It is suggested that highly dispersed Ca oxide plays a decisive role in this mechanism, besides stabilizing the wustite structure down to room temperature. From an industrial point of view, the wustite-based catalyst has also the advantage of being more easily reducible, while thermoresistancy and mechanical strength are fully satisfactory. In modern radial multibed ammonia reactors the optimal catalyst assembly appears to consist of loading the wustite-based catalyst in the first beds and the Ru/C catalyst in the last one. It is possible that an extensive and deeper investigation of the new catalyst will bring to some revision of the present consolidated knowledge on ammonia synthesis.

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TABLE 1**CHEMICAL COMPOSITION OF WUSTITE- AND MAGNETITE-BASED CATALYSTS**

(before reduction)

	Wustite	Magnetite
Fe oxide	93%	93%
Al ₂ O ₃	2.7%	3.1%
K ₂ O	0.8%	0.7%
CaO	2.8%	2.4%
Others ^a	0.7%	0.8%

^a Impurities in raw material (natural magnetite)

TABLE 2

PHYSICAL PROPERTIES OF WUSTITE- AND MAGNETITE-BASED CATALYSTS

(after reduction)

	Wustite	Magnetite
BET total surface area	16.6 m ² /g	12.6 m ² /g
CO uptake at -78°C	0.21 cm ³ /g	0.36 cm ³ /g
Free Fe surface (CO chemisorption)	11%	25%
Pore volume ^a	0.071 cm ³ /g	0.087 cm ³ /g
Surface area ^a	14.3 m ² /g	9.6 m ² /g
Average pore diameter ^a	20 nm	36 nm
Most frequent pore diameter ^a	13 nm	24 nm

^a Hg porosimetry

Figure captions

Fig. 1 Hg intrusion curves of wustite- and magnetite-based catalysts after reduction and passivation.

Fig. 2 XRD spectrum of wustite-based catalyst. The positions of the main magnetite reflections are also reported (dashed lines).

Fig. 3 Relationship between wustite cell dimension and x in Fe_{1-x}O .

Fig. 4 TPR patterns of wustite- and magnetite-based catalysts.

Fig. 5 Arrhenius plots for wustite- and magnetite-based catalysts (100 bar, $\text{H}_2/\text{N}_2 = 3$).

Fig. 6 Conversion curves of wustite-, magnetite- and Ru/C-based catalysts (100 bar, 430°C , H_2/N_2 is 3 for the two Fe catalysts, but 1.5 for Ru/C).