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A New Way for Silver Alumina Catalyst Preparation

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Abstract A new preparation of silver supported alumina catalysts, with highly dispersed and stable silver particles, is reported. The preparation, performed from a mixture of silver oxide and alumina, consists simply of heating this mixture under an oxidizing gas containing a water vapour concentration higher than 5.0 mol% in a temperature range between 903–948 K.

Keywords Catalyst preparation · Silver · Alumina · Solid-state reaction · Selective catalytic reduction

1 Introduction

Silver alumina based catalysts are usually employed in the epoxidation of ethylene to form ethylene oxide, one the most important heterogeneous catalytic oxidation processes [1]. They also exhibit remarkable catalytic performances in the following reactions: NOx reduction [2, 3], soot combustion and oxidation of ammonia [4], methane, carbon monoxide and organic volatile compounds [5–8]. The silver has to be deposited on the support in the form of small particles since the particle size is, mostly, a predominant factor in the effectiveness of the catalyst. Silver deposition can be achieved by numerous techniques among them the impregnation and the precipitation are frequently used. These techniques involve several individual steps as washing, separation, drying, and thermal processing to obtain the final catalyst, and imply gaseous or liquid rejections, which require special treatments. On the industrial scale, this means that large quantities of wastewater must be disposed and treatment of exhaust gases must be performed. Preparation through solid-state reaction (SSR) allows to reduce, to a minimum, the number of steps of catalyst preparation and does not require the handling and disposal of large volumes of metal salt solutions [9]. In the 80's and 90's, this approach has been successfully used for preparing vanadium and molybdenum oxide monolayers on alumina and titania [10–12]. It was furthermore found that the water vapour addition during the calcination of MoO_3/Al_2O_3 catalysts, prepared by Solid–Solid Wetting (SSW), enhances catalytic activity by modifying the nature of polymolybdate species, dispersed onto the surface of the support.

Herein, we report the successful preparation of highly dispersed silver oxide particles on alumina, using only silver oxides as silver source, without the use of solvent and without any rejection of pollutant fumes. The effectiveness of the preparation was controlled through the activity of the catalysts in the selective catalytic reduction of NO by hydrocarbon (HC-SCR of NOx), where the Ag/Alumina system with an optimal silver content around 2 wt% is most promising [13–20]. To have very efficient catalysts for HC-SCR of NOx, both a high dispersion of silver oxide particles with a narrow particle size distribution and strong interaction of these particles with the alumina support are required. Thus, this reaction is excellent for the characterisation of Ag/Al_2O_3 catalysts, obtained by this new preparation method.

2 Experimental Section

2.1 Preparation

The standard preparation of 2.5% Ag/Al_2O_3, schematized in Fig. 1, was the following: 0.0285 g of Ag_2O was added

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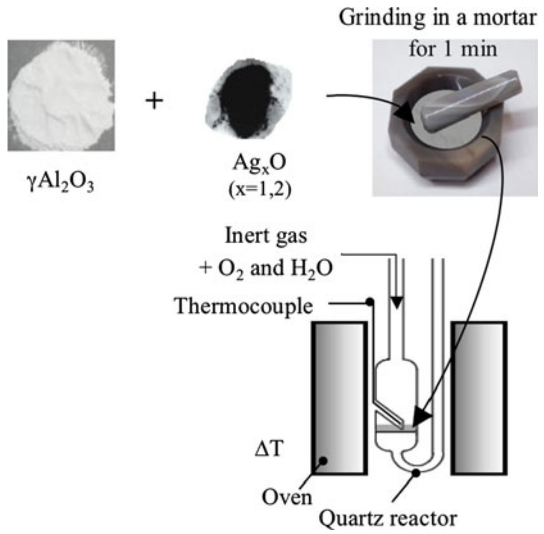


Fig. 1 Schematic method of this new Ag/Al_2O_3 preparation

to 1.0305 g of gamma alumina (STREM Reference No. 13-2525) in a mortar. This mixture is manually ground for one minute for spreading Ag_2O on alumina surface. Then, this mixture is placed in a dynamic fixed-bed reactor made of quartz. The mixture is heated to 1023 K, with a ramp of 6 K/min, under $18\%O_2/He$ flowrate of 3 L/h, containing 10% of water vapour, for 16 h.

2.2 Characterization

BET surfaces were determined from adsorption–desorption isotherms measured at 77 K in an automatic Micromeritics Asap 2000 Analyser. Before the measurement, the samples were outgassed at 473 K during 7 h.

TEM images were collected on a JEOL 1200 EX II (80–100 kV) microscope.

Powder X-ray diffraction data were obtained on a Brüker AXS D8 diffractometer by using Cu Ka radiation and a Ni filter.

2.3 Catalytic Tests

The SCR of NO by n-decane was performed in a flow reactor operating at atmospheric pressure. An aliquot (0.040 g) of the powdered catalyst was placed in a reactor and pretreated in situ at 823 K for 1 h in air. After cooling to 473 K, the reaction was performed using a gas mixture containing 0.04 vol% NO (purity $> 99.995\%$), 0.02 vol% n-decane (purity $> 99.5\%$), 2.5 vol% H_2O (purity $> 99.5\%$) and 8 vol% O_2 (purity $> 99.995\%$), the balance with helium. The total flow rate was 100 cm^3/min (space velocity: 150,000/h) and the temperature was varied from 473 to 823 K (ramp: 5 K/min). The composition of the effluents was monitored continuously by sampling on line to a quadrupole mass spectrometer (Pfeiffer Vacuum) equipped with Faraday and SEM detectors (0–200 amu) and following the masses 28, 30, 44, 46, and 57. The possible N_2O and CO formations were checked by analysing the outlet gas with a two module micro gas chromatograph (CP-4900 Micro-GC Varian), each module being equipped with a thermal conductivity detector (TCD). The first module with a 5 Å molecular sieve column, allows the analysis of $O_2/N_2/CO/CH_4$ and a back flush system to send the heavy products and CO_2 towards the second module. The latter has a PORAPLOT Q column in order to separate CO_2 and N_2O. With the CP-4900 μGC, a sample analysis of the gas phase, which injection is performed through a system capillary/micro-pump, can be realised every 20 K.

3 Results and Discussion

Mixing of alumina with silver oxide was carried out by grinding but also other processes were used. This simple grinding has already led to a spreading of silver oxide on alumina. TEM images revealed a broad silver particle size distribution with a very large number of particles up to 80 nm in diameter (Fig. 2a). The X-ray diffraction pattern of this mixing is shown in Fig. 3. It is observed (Fig. 3b) both peaks corresponding to gamma-alumina (see Fig. 3a) and to silver oxide Ag_2O (black circle). The intense peak at $2\theta = 32.7°$ (Ag_2O d(111)) indicates the presence of large particles of this silver oxide. The resulting catalyst, calcined at 823 K during 1 h, exhibits better NOx conversions in the SCR of NO by *n*-decane than alumina alone, only for temperatures above 683 K (see Fig. 4). The calcination of this catalyst at more high temperatures (1023 K, 16 h) did not improve the activity. As expected, in keeping with TEM results, these two catalysts are not efficient in the HC-SCR of NOx. However, on both materials, the oxidation of *n*-decane takes place efficiently since it starts at quite low temperature and increases gradually with the reaction temperature to reach total conversion at 823 K. This oxidation is selective towards CO_2 above 533 K.

Very efficient catalysts, with highly dispersed silver particles (Fig. 2b), are designed when the mixing of silver oxide and alumina is set under an oxidizing gas, containing a sufficient concentration of vapour water, at an appropriate temperature. Based on TEM images, the obtained materials present silver particles very homogeneous in terms of particle size, with an average diameter smaller than 5 nm. The XRD patterns of these samples (see Fig. 3c for an example) did not contain any peaks that can be attributed to silver species like for the silver alumina sample prepared by impregnation (see Fig. 3d). Moreover, XPS measurements were also performed. Unfortunately, we observed a

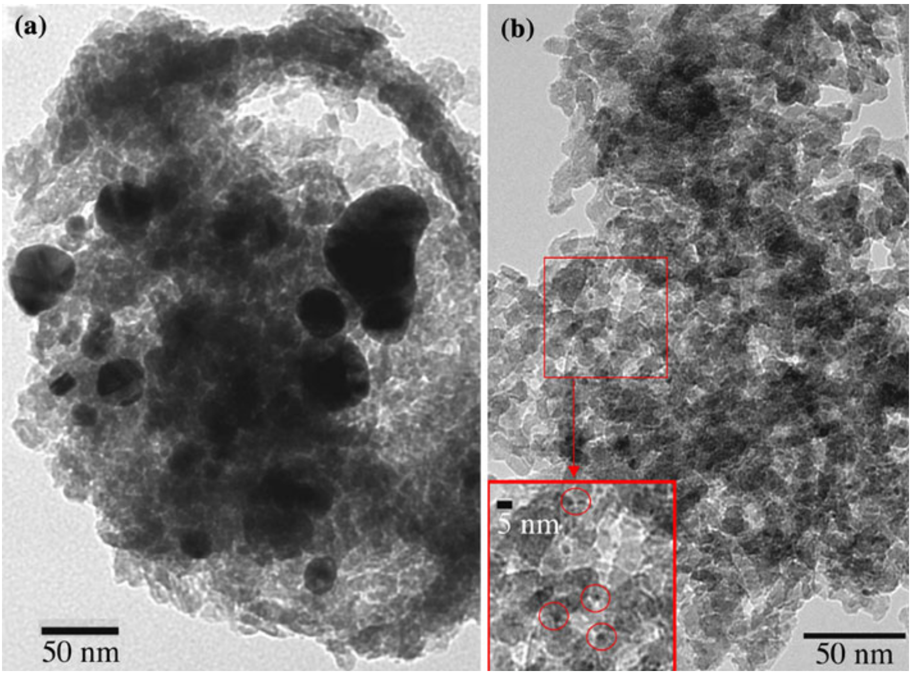


Fig. 2 TEM image of **a** a mixture by grinding of Ag_2O (0.0285 g) and Al_2O_3 (1.0305 g) and **b** the previous mixture after hydrothermal treatment at 938 K with 10% H_2O in the calcination gas; in the inset, a zoom with some silver particles hooped with *red*

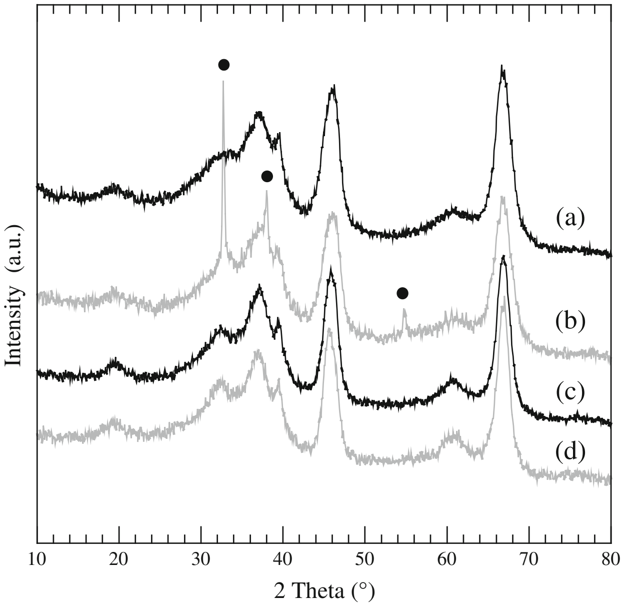


Fig. 3 XRD pattern of: **a** γ-Al_2O_3 **b** an uncalcined mixture by grinding of Ag_2O (0.0285 g) and Al_2O_3 (1.0305 g) **c** 2.0 Ag/Al_2O_3 prepared using this new preparation and **d** 2.0 Ag/Al_2O_3 prepared by impregnation in aqueous phase using silver nitrate. *Filled circle* Ag_2Oprepared by impregnation in aqueous phase using silver nitrate

reduction of silver species during the analysis. From this, we can assume that the silver is mainly in oxide form in solids at room temperature as it was reported previously [21, 22] but without excluding the presence of metallic silver particles.

The two parameters, water vapour concentration and final temperature of the thermal treatment, are crucial. Other parameters like oxygen concentration, calcination time, nature of the silver oxide, and temperature at which water vapour is introduced were studied and can have an impact on the activity but to a smaller extent.

The effect of water vapour concentration in the calcination gas is clearly shown in Fig. 5. When the thermal treatment is performed at 1,023 K, a minimum of 5.0 mol% of water vapour is required to obtain catalysts with an appreciable activity in a wide temperature range. Above this concentration, there is a slight activity enhancement at 7.5 mol% of water vapour, whereas a very slight activity decrease is observed at 10.0 mol% of water vapour, which can be ascribed to a decrease of the surface area of the solid (Fig. 6). Indeed, the hydrothermal treatment induces a decrease of the catalyst surface. The diminution increases with increasing vapour pressure of water from 2.5 to 7 mol%. At this value, the surface stabilizes at around 135 m^2/g for a treatment temperature of 1023 K.

As far as the final hydrotreatment temperature value is concerned, at least 823 K is needed to prepare a catalyst with good SCR activity. The value of the ideal hydrotreatment temperature should be in the range 903–948 K (Fig. 7). For example at 938 K, the 2.5% Ag/Al_2O_3 resulting catalyst exhibited a remarkable activity over a large temperature range. TEM images of this catalyst (see Fig. 2b for one example) revealed highly dispersed silver particles. Moreover, at this hydrotreating temperature, even with a water vapour concentration of 10%, only minimal loss in catalyst surface area is observed, presenting a surface area of 160 m^2/g. This low decrease of surface area can be one explanation for the results obtained in the SCR,

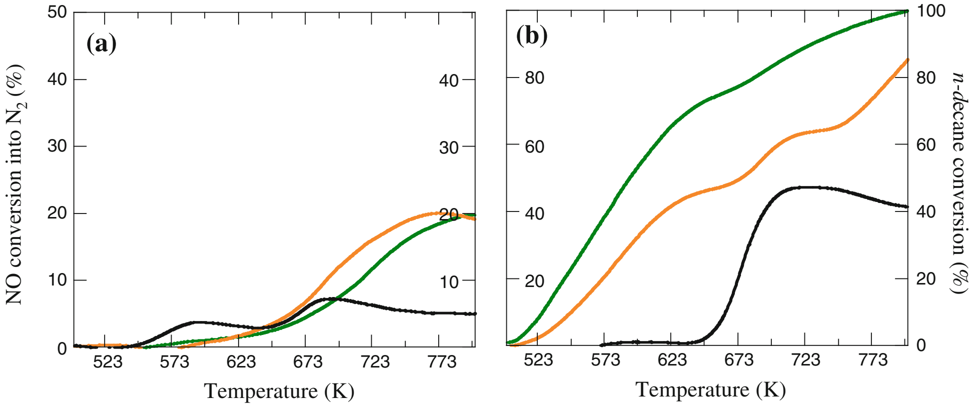


Fig. 4 Reaction temperature dependence of: **a** NO conversion and **b** *n*-decane conversion over Al_2O_3 (*black*) and over a mixture by grinding of Ag_2O (0.0285 g) and Al_2O_3 (1.0305 g) calcined at 823 K for 1 h (*orange*) and calcined at 1023 K for 16 h (*green*). SCR Test conditions: Total flowrate = 6 L/h, catalyst amount = 40 mg, [*n*-decane] = 0.02%, [NO] = 0.04%, $[H_2O]$ = 2.50%, $[O_2]$ = 8.00% and balance with He

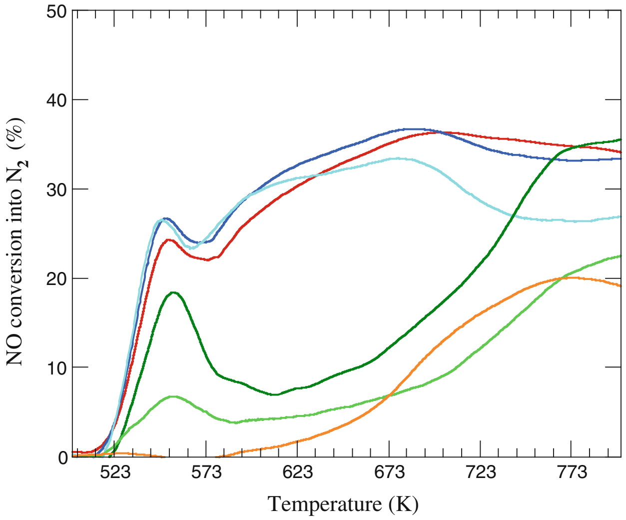


Fig. 5 Reaction temperature dependence of NO conversion over a mixture by grinding of Ag_2O (0.0285 g) and Al_2O_3 (1.0305 g) hydrotreated for 16 h at 1023 K with a water vapour concentration of: 1.5% (*light-green*), 2.5% (*dark green*), 5.0% (*light-blue*), 7.5% (*dark blue*) and 10.0% (*red*). SCR test conditions: see Fig. 4

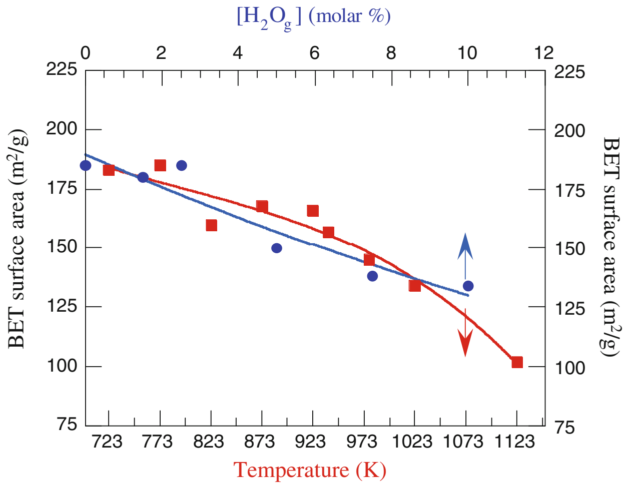


Fig. 6 Evolution of BET surface area of the solids (a mixture by grinding of Ag_2O (0.0285 g) and Al_2O_3 (1.0305 g)) versus the value of the temperature of the hydrotreatement at 10.0 mol% water vapour (*red*) and, versus the water concentration in the calcination gas at 1023 K (*blue*). Hydrothermal treatment conditions: sample amount = 1.0 g, temperature ramp = 6 K/min, total gas flowrate = 3 L/h, time = 16 h

since the SCR efficiency begins to decrease for superior hydrotreating temperature values. To the design of catalyst, there is thus an optimal treating temperature, associated with a minimal vapour water concentration.

Finally, a catalyst with 2%wt silver content, was prepared with the two following optimised conditions ($[H_2O] = 10\%$ and $T_{final} = 938$ K) and its NO SCR conversion was compared to that of a conventional impregnated $2\%Ag/Al_2O_3$ at different reaction temperatures. The catalyst prepared by this new method showed significantly higher activity (Table 1) than the conventional one, with NO conversions above 40% between 573 and 823 K. Nevertheless the low temperature efficiency of these catalysts, prepared by this new method, is delayed compared to catalysts prepared by sol–gel process [17, 23].

This new and simple preparation method, implying only oxide precursors, allows to obtain silver/alumina catalysts with highly dispersed silver particles, which strongly interact with the support. As previously mentioned in the text, the mixture of precursor oxides does not necessarily require grinding. Nevertheless, if the mixing is performed by grinding, big silver oxide particles on the alumina surface are obtained due to the wetting properties of silver oxide (see Scheme 1). It is known that by the SSW, it is possible to spread an oxide on another oxide surface [24].

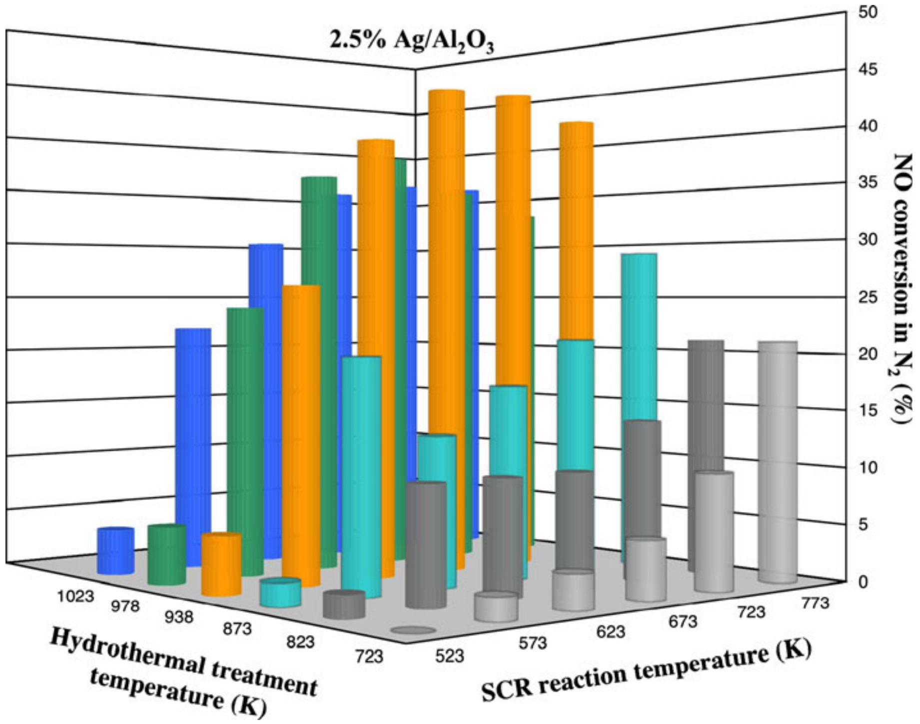


Fig. 7 NO conversion as function of SCR reaction temperature for 2.5%Ag/Al_2O_3 catalysts obtained from different hydrothermal treatment temperature values of the mixture by grinding of Ag_2O (0.0285 g) and Al_2O_3 (1.0305 g). Hydrothermal treatment conditions: sample amount = 1.0 g, temperature ramp = 6 K/min, 18% O_2/10% H_2O/He, gas flowrate = 3 L/h, time = 16 h. SCR test conditions: see Fig. 4

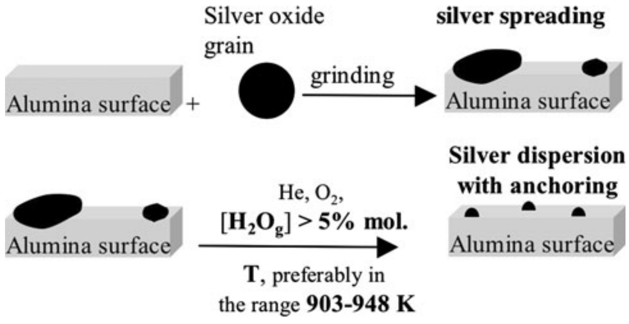
Table 1 Catalytic performance comparison of Ag/Al_2O_3 catalyst prepared according to this new preparation with an Ag/Al_2O_3 prepared by conventional impregnation

Catalysts	NO conversion in N2 (%) at temperature (K)[c]						
	523	573	623	673	723	773	823
2.0 Ag/Al_2O_3[a]	6	44	55	60	65	64	60
2.0 Ag/Al_2O_3[b]	5	20	38	52	50	46	40

[a] catalyst prepared using this new preparation

[b] catalyst prepared by impregnation in aqueous phase using silver nitrate

[c] SCR test conditions: see Fig. 4



Scheme 1 Proposed schematic way of this new Ag/Al_2O_3 preparation from a mixture of silver oxide and Al_2O_3

Conventional calcination (in the absence of water vapour) of an alumina–silver oxide mixture, even at high temperatures (which does not improve silver dispersion), leads to a catalyst able to oxidise *n*-decane efficiently into CO_2 at low temperatures. In accordance with previous works on the spreading of MoO_3, WO_3 and V_2O_5 on alumina, titania and silica supports [10, 11], the spreading of silver on alumina surface (see Scheme 1) occurs because the physical properties of silver and alumina are favourable. Firstly, it is known that silver oxides are inherently unstable. The stoichiometric oxides AgO and Ag_2O decompose into Ag_2O and AgO at 373 and 503 K, respectively. Secondly, Tamman temperature of silver [25] (617 K; T_{Tamman} (K) $\approx$ 0.5 TF (K); TF representing the melting point) and Hüttig temperature of silver (370 K; $T_{Hüttig}$ (K) $\approx$ 0.3 × TF (K)) suggest that both bulk and surface silver atoms tend to move at relatively low temperatures and thus migration of silver onto the alumina surface and its dispersion should occur easily. On the contrary, alumina has a very high T_{Tamman} (1,163 K), which inhibits migration of silver oxide in the core of alumina.

But, relative to the spreading on alumina of other oxides reported in the literature (for example, molybdenum oxide), which does not require the presence of water for the preparation of a monolayer (molybdate species well dispersed) [10, 11, 24, 26], it is absolutely imperative, in our case, to have the appropriate concentration of water vapor in the calcination gas to obtain highly dispersed silver species on alumina. Thus, the hydrothermal process, with a value of treating temperature around 925 K and a vapour pressure greater than 5%, has a dispersing effect added of an embedding effect of silver particles on the alumina support (see Scheme 1). Its role can be attributed to a combination of two phenomena: (i) water vapour at high temperature acts as a strong chelator of aluminum atoms by forming surface cations $Al(H_2O)_6^{3+}$ [27] and (ii) silver species react with water forming silver hydroxyl species that become mobile due to attainment of the Tamman temperature [28]. The hole defects, created on the surface of alumina, can stabilize and anchor the silver hydroxyl species and explain thus the formation of very small and stable silver particles interacting with the alumina surface.

4 Conclusion

A new preparation of silver supported alumina catalysts, with highly dispersed and stable silver particles, is reported. The preparation, performed from a mixture of silver oxide and alumina, consists simply of heating this mixture under an oxidizing gas containing a water vapour concentration higher than 5.0 mol% in a temperature range between 903–948 K. This extremely simple preparation technique can be extended to other kind of materials, depending on physical properties of their involved oxides, for example for preparing gold supported alumina based materials. Besides, this procedure was successfully applied for large-scale preparation of 2% Ag/Al_2O_3 catalysts for HC-SCR of NOx; in this case the hydrothermal treatment was performed in a static oven under optimised conditions of temperature and water vapour concentration.

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References

1. Berty JM (1983) In: Leach BE (ed) Applied industrial catalysis. Academic press Inc, London, p 207
2. Park PW, Boyer CL (2005) Appl Catal B 59:27
3. Brosius R, Arve K, Groothaert MH, Martens JA (2005) J Catal 231:344
4. Gang L, Anderson BG, van Grondelle J, van Santen RA, van Gennip WJH, Niemantsverdriet JW, Kooyman PJ, Knoester A, Brongersma HH (2002) J Catal 206:60
5. Imamura S, Yamada H, Utani K (2000) Appl Catal A 192:221
6. Qu Z, Cheng M, Huang W, Bao X (2005) J Catal 229:446
7. Luo M, Yuan X, Zheng X (1998) Appl Catal A 175:121
8. Einaga H, Ogata A (2010) Environ Sci Technol 44:2612
9. Karge HG, Beyer HK (1991) Zeolite and Catalysis. In: Jacobs PA, Jaeger NI, Kubelková L, Wichterlová B (eds) Studies in Surface Science and Catalysis 69:43
10. Knözinger H, Taglauer E (1993) Catalysis (R Soc Chem Camb)10:1
11. Leyrer L, Margraf R, Taglauer E, Knözinger H (1998) Surf Sci 201:603
12. Liu D, Zhang L, Yang B, Li J (1993) Appl Catal 105:185
13. Hoost TE, Kudla RJ, Collins KM, Chattha MS (1997) Appl Catal B 13:59
14. Meunier FC, Breen JP, Zuzaniuk V, Olsson M, Ross JRH (1999) J Catal 187:493
15. Shimizu K, Shibata J, Yoshida H, Satsuma A, Hattori T (2001) Appl Catal B 30:151
16. Lindfors LE, Eranen K, Klingstedt F, Murzin DY (2004) Top Catal 28:185
17. Kannisto H, Ingelsten HH, Skoglundh M (2009) J Mol Catal A Chem 302:86
18. Granger P, Parvulescu VI (2011) Chem Rev 111:3155
19. He H, Zhang XL, Wu Q, Zhang CB, Yu YB (2008) Catal Surv Jpn 12:38
20. Shimizu K-I, Satsuma A (2006) Phys Chem Chem Phys 8:267
21. Seker E, Cavataio J, Gulari E, Lorpongpaiboon P, Osuwan S (1999) Appl Catal A 183:121
22. Bogdanchikova N, Meunier FC, Avalos-Borja M, Breen JP, Pestryakov A (2002) Appl Catal B 36:287
23. Petitto C, Mutin HP, Delahay G (2011) Chem Commun (Camb) 47:10728
24. Xie Y-C, Tang Y-Q (1990) Adv Catal 37:1
25. Moulijn JA, van Diepen AE, Kapteijn F (2001) Appl Catal A 212:3
26. Koranyi TI, Paal Z, Leyrer J, Knözinger H (1990) Appl Catal 64:L5
27. Hagaman EW, Jiao J, Chen B, Ma Z, Yin H, Dai S (2010) Solid State Nucl Magn Reson 37:82
28. Millar GJ, Nelson ML, Uwins PJR (1998) J Chem Soc, Faraday Trans 94:2015