Alumina Supported Silver Lanthana Catalyst for N$_2$O Decomposition

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Abstract

A series of La$_2$O$_3$–modified Al$_2$O$_3$ supported Ag catalysts were synthesized with varying content of La$_2$O$_3$ (1-5 wt %) and Ag (1-5 wt %). Their catalytic activity was evaluated for N$_2$O decomposition in a fixed bed reactor. The catalysts were characterized by several techniques like BET surface area, X-ray diffraction (XRD), Scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). XRD patterns revealed the crystalline nature of the catalysts and the presence of Ag^0 state in reduced samples. Surface morphology studied using SEM gave information regarding the agglomeration of active component in the case of high La$_2$O$_3$ loaded catalysts. TPR profiles revealed valuable reduction properties of the catalysts. The combination of Ag and La$_2$O$_3$ showed higher catalytic performance along with long term stability during N$_2$O decomposition. 5% Ag/1%La$_2$O$_3$-γ-Al$_2$O$_3$ catalyst yielded 100 % N$_2$O conversion at 600 °C.

Key words: N$_2$O decomposition, Silver, Lanthana, Alumina.

Introduction

N$_2$O is a greenhouse gas with significant global warming potential (GWP) when compared with carbon dioxide (CO$_2$) and methane (CH$_4$). N$_2$O has a lifetime of 114 - 130 years under atmospheric conditions and its GWP is 310 times and 15 times more than that of carbon dioxide and methane, respectively[1]. N$_2$O is formed by both natural and human related activities. The natural source of N$_2$O is from a wide variety of biological reactions in soil and water, whereas the human related sources of N$_2$O are due to agricultural soil management, combustion of fossil fuels, adipic and nitric acid plants. The agricultural soil management occupies the first place in N$_2$O emissions followed by mobile combustion, nitric acid plant, manure management and stationary combustion. Catalytic decomposition and selective catalytic reduction (SCR) of N$_2$O are the promising technologies for N$_2$O remediation. Many research groups are working with the aim of N$_2$O abatement. Extensive work has been done on the decomposition of nitrous oxide to nitrogen and oxygen using transition metal exchanged silicon rich zeolites, metal oxides and noble metals[2-7]. Selective catalytic reduction of N$_2$O with hydrocarbons as reducing agents has been studied using numerous catalysts. Ag/Al$_2$O$_3$ catalysts were extensively studied for the removal of

NO$_x$ by propane/propene/ethane[8-16], methane[17] and CO[18]. The major drawback of the Ag/Al$_2$O$_3$ system is the high temperature required to activate hydrocarbons like methane, ethane and propane, which are most stable and least reactive. However Ag/Al$_2$O$_3$ system exhibited interesting results with long chain hydrocarbons at slightly lower temperatures when compared to lighter hydrocarbons.[19-20] Kannisto et al. have studied the influence of preparation method and reductant on the activity of Ag/Al$_2$O$_3$.[21] Studies on direct decomposition of N$_2$O over Ag/γ-Al$_2$O$_3$ catalysts are scarce. The aim of the present work is to study the effect of La$_2$O$_3$ addition to alumina, taken as a support for Ag catalyst during the N$_2$O decomposition reaction.

Experimental

Catalyst Preparation

Two series of catalysts (i.e Ag/γ-Al2O3 and Ag/La2O3-γ-Al2O3) were prepared. The first series involves preparation of alumina supported Ag catalysts and the second series involves the preparation of La2O3- modified alumina supported Ag catalysts.

Preparation of Ag/Al$_2$O$_3$

Silver nitrate (> 99.5%, Sigma Aldrich) was dissolved in distilled water. Required amount of this solution was slowly added to γ-Al2O3 (Harshaw Al-111-E)   under vigorous stirring. Excess water was evaporated at 80 °C on a hot plate. The solid mass was oven dried at 110 °C for 6 h and calcined in air flow at 500 °C for 4 h. Three different loadings of Ag (1, 3 and 5 wt %) supported on alumina catalysts were prepared.

Preparation of Ag/La$_2$O$_3$-Al$_2$O$_3$

(1-5 wt%) La2O3-Al2O3 catalysts were prepared using wet impregnation method following the similar procedure as earlier (wt % of La2O3, was varied as 1, 3 and 5%). The catalysts were dried at 110 °C for 6 h and calcined at 500 °C for 4h. 5 wt % Ag was impregnated over (1-5 wt%) La2O3-Al2O3 catalysts and calcined in air flow at 500 °C for 4 h.

Catalyst Characterization

The catalysts thus prepared were characterized by a number of techniques. The surface areas (BET-SA) of the catalysts were determined on NOVA® 4200 (Quantachrome Instruments, USA) by nitrogen physisorption at -196 ℃, taking 0.169 nm2 as the cross sectional area for di-nitrogen. Prior to the measurements, the known amount of catalyst was evacuated for 2 h at 200 °C to remove physically adsorbed water. XRD patterns of the catalysts were obtained with a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ= 1.5406 Å) with a scan speed of 2° min−1 and a scan range of 2–80° at 30 kV and 15 mA. SEM micrographs of the catalysts were obtained in a Hitachi S-520 electron microscope at an accelerated voltage of 10 kV. Samples were

mounted on aluminum stubs using double adhesive tape and were gold coated in a Hitachi HUS-5GB vacuum evaporator. The oxidation states of silver and the atomic ratio of silver to aluminum in the surface region of the Ag–alumina catalysts were examined on a Kratos analytical X-ray photoelectron spectrometer, with Mg Kα mono chromated excited radiation (1253.6 eV). The residual pressure in the analysis chamber was around 10^{-9} mbar. The binding energy (BE) measurements were corrected for charging effects with reference to the C1s peak of the adventitious carbon (284.6 eV).. The Al 2p signal of Al_2O_3 was used as internal reference to correct the XPS spectra. The atomic ratio of Ag/Al was based on the core level spectra of Ag 3d and Al 2p.

Experimental Setup and Procedure

The evaluation of catalysts was carried out in a fixed-bed down flow reactor (made of SS, length 300 mm and internal diameter of 10 mm) at atmospheric pressure. Catalyst (particles of 18/25 mesh size were used) sample diluted with equal weight of quartz beads, was placed in the reactor between two quartz wool plugs. The catalyst was reduced in H2 atmosphere (30 ml/min) at 450 ºC for 2 h just before use. 5000 ppm N2O balanced He gas was fed into the reactor using mass flow controllers (Alborge). Two thermocouples were connected to the reactor; one to measure the catalyst bed temperature and the other for reactor skin temperature. The bed temperature was maintained with the help of a PID temperature controller. The products were analyzed by an on-line GC (Nucon 5765) equipped with TCD detector and two packed columns: Molecular sieve and Poroplot Q. The blank run revealed no conversion with quartz wool in the temperature range (400 - 600 ºC).

Results and Discussion

Bet Surface Area:

BET surface areas of catalysts with different Ag and La2O3 loadings are given in Table 1. The surface area of the pure support Al2O3 was also measured as 290.5 m2/g. The catalysts showed a wide range of surface areas depending upon the content of active component in the samples. The specific surface areas of the Al2O3 supported catalysts were lower than the pure support. The surface area of pure Al2O3 however, decreased considerably after addition of active component (Ag and La2O3). Ag loading had a clear impact on the surface areas of the samples. The surface areas were observed to decrease from 281.3 m2/g to 261.2 m2/g with increase in Ag loading from 1 wt% to 5 wt% whereas they varied in the region of 198 m2/g to 161.6 m2/g with increase La2O3 from 1 wt% to 5 wt%. A sharp decrease in surface area (from 261.2 to 198 m2/g) was observed with the addition of La2O3 to Al2O3.This was mainly due to the blockage of alumina pores with La2O3.

TABLE 1: BET Surface Area of samples

S.No	Catalyst	Surface area (m^2/g)
1	γ-Al_2O_3	290.5
2	La_2O_3	36.6
3	1 Ag/γ-Al_2O_3	281.3
4	3 Ag/γ-Al_2O_3	272.1
5	5 Ag/γ-Al_2O_3	261.2
6	5 Ag -1 La_2O_3/γ-Al_2O_3	198.0
7	5 Ag -3 La_2O_3/γ-Al_2O_3	180.4
8	5 Ag -5 La_2O_3/γ-Al_2O_3	161.6

X-Ray Diffraction:

The XRD patterns of the catalyst samples (reduced samples) are shown in Fig.1. The samples exhibited crystalline nature with dominating γ-Al2O3 phase. The diffraction lines due to metallic silver ($2\theta \approx 38.12°$, $44.4°$, $64.6°$, $77.5°$) were observed in XRD patterns. The intensity of XRD reflections corresponding to Al2O3 phase decreased with increase in La2O3 loading. XRD did not showed any evidence of AgAlO2 (silver aluminate) formation in the catalysts. This could be due to lower loading of Ag and high dispersion.[22] The non-appearance of lanthana phases in XRD suggested that lanthana was highly dispersed within the Al2O3.[23]
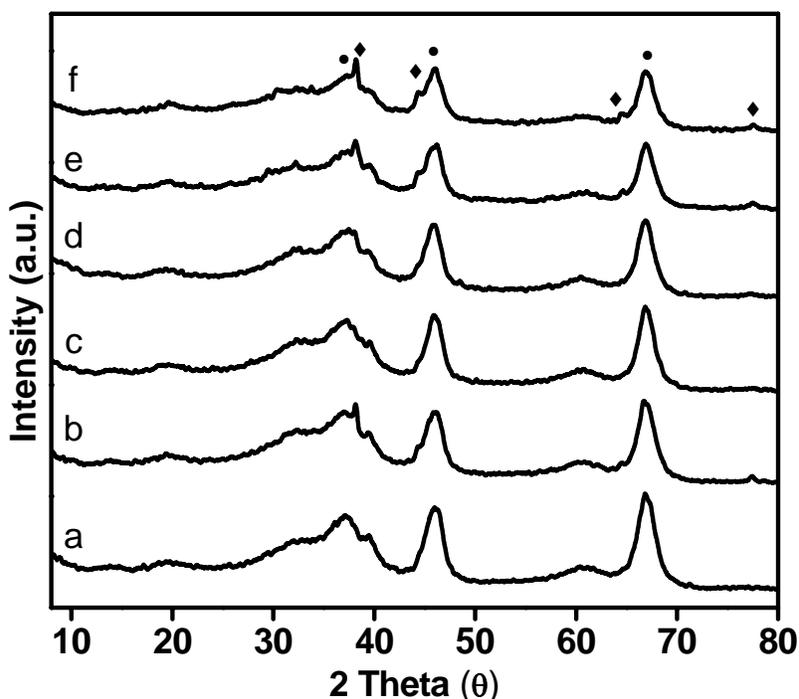
Figure 1 XRD patterns of (a) 1 Ag/Al$_2$O$_3$, (b) 3 Ag/Al$_2$O$_3$. (c) 5 Ag/Al$_2$O$_3$, (d) 5 Ag/1 La$_2$O$_3$–Al$_2$O$_3$, (e) 5 Ag/3 La$_2$O$_3$–Al$_2$O$_3$, (f) 5 Ag/5 La$_2$O$_3$–Al$_2$O$_3$, ($\blacklozenge$) Ag^0, ($\bullet$) Al$_2$O$_3$

Scanning Electron Spectroscope (SEM):

The SEM pictures of 5% Ag/Al2O3, 5% Ag/1% La2O3-Al2O3 and (b) 5% Ag/5% La2O3-Al2O3 catalysts are presented in Fig. 2 (a), 2 (b) and Fig. 2 (c) respectively. The white crystals clearly indicated that the silver was present in the metallic form. No particles of silver oxide were observed in the SEM images. From the Fig. 2 (a) it is clear that silver was present in a more agglomerated form in 5% Ag/Al2O3 catalyst. However, in the case of lanthana containing catalysts silver was observed to be in dispersed sate. Further increase in lanthana loading resulted in increase of average particle size.
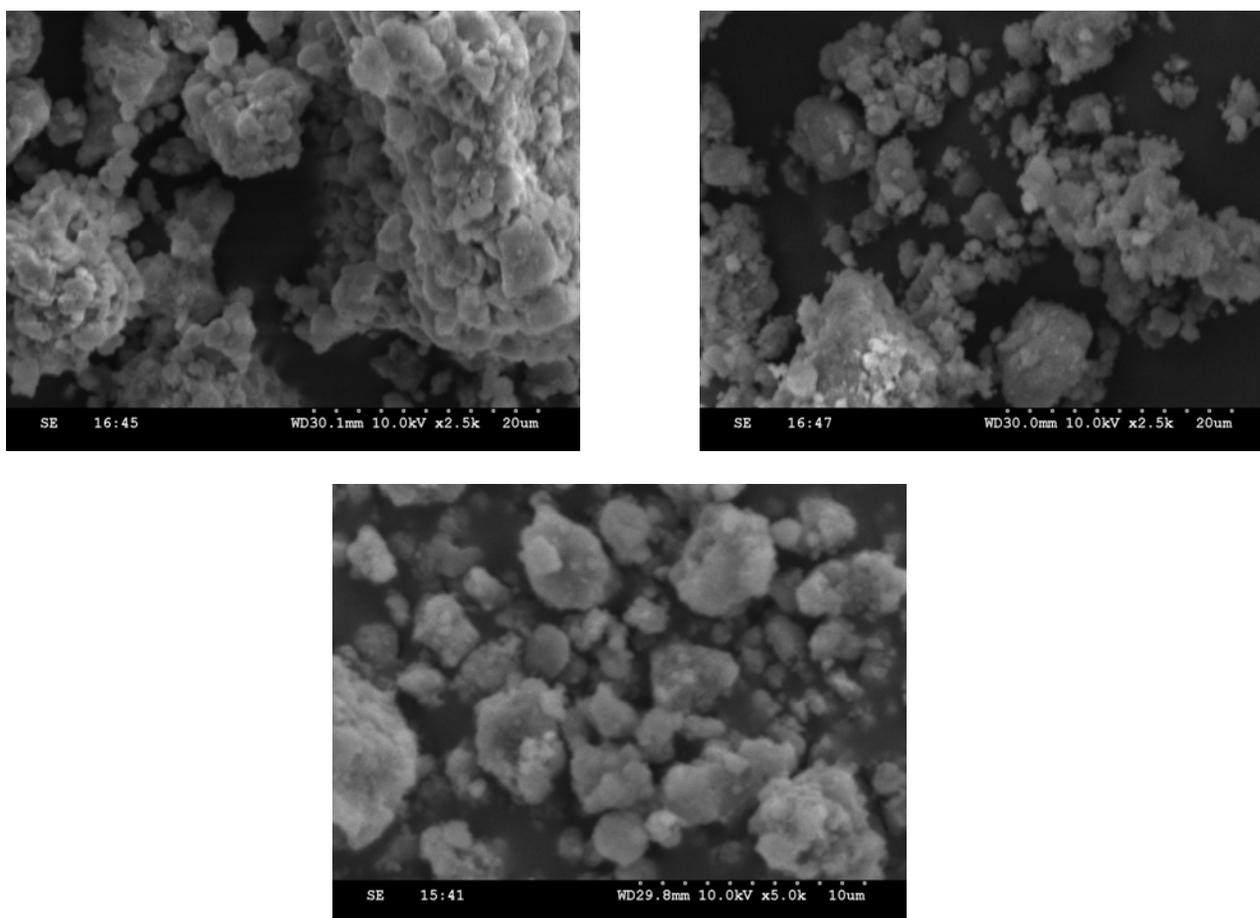
FIGURE 2: SEM images of (a) 5% Ag/Al$_2$O$_3$ (b) 5% Ag/1% La$_2$O$_3$–Al$_2$O$_3$ and (c) 5% Ag/5% La$_2$O$_3$–Al$_2$O$_3$.

X-ray photoelectron spectroscopy (XPS):

XPS analysis provides information on the oxidation state of silver and concentration of surface elements. XPS spectra of reduced Ag/La2O3-Al2O3 catalysts are given in Fig.3. The Ag 3d5/2 binding energy of sample Ag/Al2O3 at 368.5eV were compared with binding energies of

368.3 and 367.5 eV for metallic silver and Ag2O, respectively8, 24-25. Thermally, bulk Ag2O decomposes to Ag metal at higher temperatures.25 A comparison of binding energies of sample Ag/Al2O3 with the literature data favored metallic silver formation. The binding energy value at 368.5 eV clearly stated the presence of silver in metallic state. The results obtained from XPS were in good agreement with those of XRD. The La $3d_{5/2}$ binding energy (not shown in Fig) was observed at 837.2 eV. This binding energy was substantially higher than the values measured for La_2O_3 (833.2 eV) and $LaAlO_3$ (833.8 eV) standards by Haack et al.[26]. However, it was close to the binding energy observed for ionic La^{3+}.[27] A La $3d_{5/2}$ binding energy of 836.1 eV was observed by Ledford et al.[28] for dispersed lanthanum on alumina at a calcination temperature of 600 °C and La $3d_{5/2}$ binding energy was observed as 836 eV by Cardona et al.[29], likewise significantly higher than that observed for La_2O_3, or $LaAlO_3$. No clarification for this discrepancy in binding energies was given. At the same calcination temperature, Alvero et al.[30] observed a dispersed phase lanthanum with a binding energy of 835.5 eV. They attributed this higher binding energy species to the presence on the surface of deficiently coordinated La^{3+} ions. In the present case with 1 wt% La_2O_3 there might be an intense interaction between silver and the deficiently coordinated lanthana species, which resulted in achieving high catalytic activity. However, further increase in La_2O_3 caused agglomeration of particles and increase in average particle size, which was evident from the SEM images.
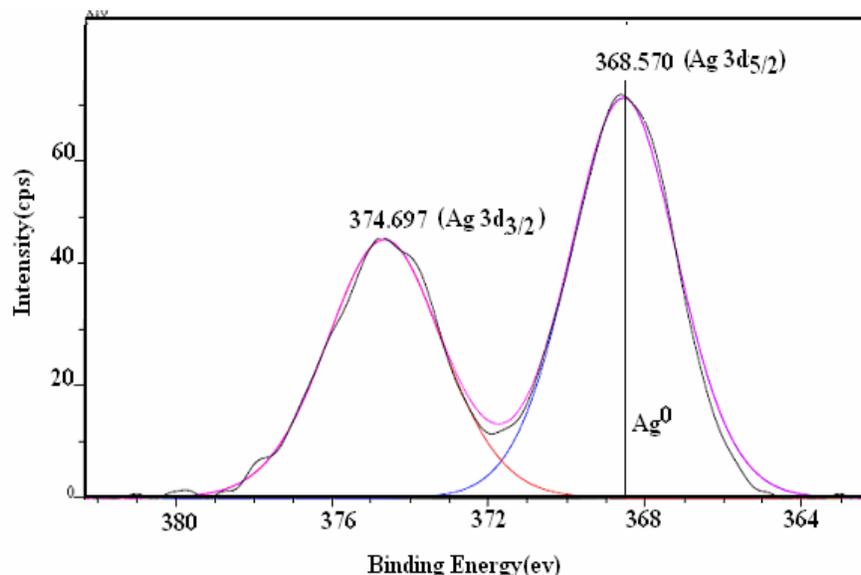
Figure 3 XPS analysis of 5% Ag/1% La₂O₃–Al₂O₃ catalyst

Catalytic Activity:

N$_2$O decomposition studies were carried out on alumina supported Ag and La$_2$O$_3$ containing catalysts. The reaction temperature was varied from 400 to 600 °C. No considerable activity was observed below 400 ºC. At a reaction temperature of 600 ºC, the bulk Al$_2$O$_3$ solid gave only 8% conversion of N$_2$O. The activity of Ag/Al$_2$O$_3$ catalysts for N$_2$O decomposition was also studied (results presented in Fig.4) and it was found that catalytic activity increased up to 5 % Ag loading and thereafter there was no significant increase in the catalytic activity. Activity data of catalysts with Ag loading more than 5 wt% are not presented for brevity. Kannisto et al. also suggested 5 % Ag as the optimum loading for NO$_x$ reduction.[21] N$_2$O conversion of around 43 % was obtained over 5 % Ag/Al$_2$O$_3$ catalyst at a temperature of 600 °C. As expected the catalytic activity followed increasing trend with reaction temperature. Among all the catalysts tested, bulk Al$_2$O$_3$ showed the poorest performance. As 5% Ag/Al$_2$O$_3$ was optimum in Ag/Al$_2$O$_3$ catalysts, it was considered for further studies to ascertain the loading effect of La$_2$O$_3$.
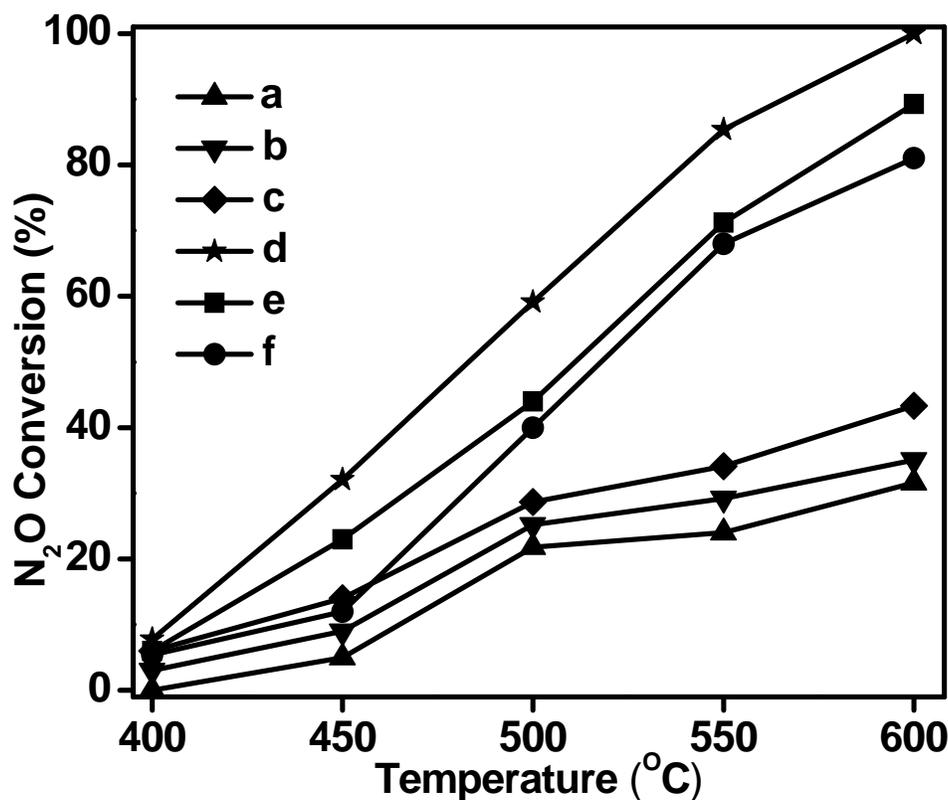
Figure 4 N$_2$O decomposition activity over Ag/Al$_2$O$_3$ and Ag–La$_2$O$_3$/Al$_2$O$_3$ catalysts, (a) 1 Ag/Al$_2$O$_3$, (b) 3 Ag/Al$_2$O$_3$, (c) 5 Ag/Al$_2$O$_3$, (d) 5 Ag/1 La$_2$O$_3$–Al$_2$O$_3$, (e) 5 Ag/3 La$_2$O$_3$–Al$_2$O$_3$, (f) 5 Ag/5 La$_2$O$_3$–Al$_2$O$_3$.

La_2O_3 addition enhanced the catalytic activity of 5 % Ag/Al_2O_3 catalysts. 5% Ag/1% La_2O_3–Al_2O_3 catalyst exhibited maximum activity (X = ca. 100%) and thereafter followed a decreasing trend with the increase in La_2O_3 loading. The catalytic activity decreased from over 100% (on 1 wt% La_2O_3) to around 80% (on 5 wt% La_2O_3). This fact suggested that an increase in La_2O_3 loading beyond 1 wt% was not effective in improving the performance. This might be due to the filling of alumina pores with lanthana. The raise in the intensity of the Ag peak in XRD with increase in the La_2O_3 loading also supported that the pores of alumina were filled by lanthana at high loadings and the silver was retained on the surface, without much interaction with support. The decrease in surface area with lanthana loading also came in strong support to this phenomenon. The well interaction of the surface of deficiently coordinated La^{3+} ions and silver might be the reason for highest activity of 5% Ag/1% La_2O_3–Al_2O_3 catalyst. The average particle size was also found to increase with the increase in the La_2O_3 loading, which was revealed from the SEM images. Possessing long term stability is industrially a very important beneficial aspect of a catalyst. Time on stream studies were carried on 5% Ag/1% La_2O_3-Al_2O_3 using optimum conditions. The catalyst did not show any significant decrease in activity up to 30 h (as tested in the laboratory).

Conclusions

XRD and XPS confirmed the presence of Ag^0 phase in the catalysts. BET surface area was found to depend on the content of Ag and La_2O_3 in the total catalyst. La_2O_3 loading on Ag-Al_2O_3 had a strong influence on the catalytic performance. La_2O_3 containing Ag-Al_2O_3 catalysts exhibited superior performance compared to Ag-Al_2O_3. Among the catalysts tested, 5% Ag/1% La_2O_3–Al_2O_3 displayed the best performance in terms of activity (X-N_2O=100%) and long term stability.

Acknowledgment

References

1. F. Kapteijn, J. Rodriguez-Mirasol, J.A. Moulijn, Appl. Catal., B, 1996, 9, 25-64.

2. K. Jíša, J. Nováková, M. Schwarze, A. Vondrová, S. Sklenák, Z. Sobalik, J. Catal., 2009, 262, 27-34.

3. M. Rivallan, G. Ricchiardi, S. Bordiga, A. Zecchina, J. Catal., 2009, 264, 104-116.

4. S. Sklenak, P.C. Andrikopoulos, B. Boekfa, B. Jansang, J. Nováková, L. Benco, T. Bucko, J.

Hafner, J. Dĕdeček, Z. Sobalík, J. Catal., 2010, 272, 262-274.

5. P.J. Smeets, M.H. Groothaert, R.M. van Teeffelen, H. Leeman, E.J.M. Hensen, R.A. Schoonheydt, J. Catal., 2007, 245, 358-368.

6. K. Sun, H. Xia, E. Hensen, R. van Santen, C. Li, J. Catal., 2006, 238, 186-195.

7. H. Xia, K. Sun, Z. Liu, Z. Feng, P. Ying, C. Li, J. Catal., 2010, 270, 103-109.

8. K.A. Bethke, H.H. Kung, J. Catal., 1997, 172, 93-102.

9. R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal., B, 2002, 39, 283-303.

10. F. Dury, M.A. Centeno, E.M. Gaigneaux, P. Ruiz, Appl. Catal., A, 2003, 247, 231-246.

11. A. Martínez-Arias, M. Fernández-García, A. Iglesias-Juez, J.A. Anderson, J.C. Conesa, J. Soria, Appl. Catal., B, 2000, 28, 29-41.

12. K. Masuda, K. Tsujimura, K. Shinoda, T. Kato, Appl. Catal., B, 1996, 8, 33-40.

13. F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal., 1999, 187, 493- 505.

14. M. Tatsuo, Appl. Catal., B, 1993, 2, 199-205.

15. T.N. Angelidis, N. Kruse, Appl. Catal., B, 2001, 34, 201-212.

16. T.N. Angelidis, S. Christoforou, A. Bongiovanni, N. Kruse, Appl. Catal., B, 2002, 39, 197- 204.

17. A. Keshavaraja, X. She, M. Flytzani-Stephanopoulos, Appl. Catal., B, 2000, 27, L1-L9.

18. T.N. Angelidis, V. Tzitzios, Appl. Catal., B, 2003, 41, 357-370.

19. K.-i. Shimizu, A. Satsuma, T. Hattori, Appl. Catal., B, 2000, 25, 239-247.

20. K.-i. Shimizu, J. Shibata, H. Yoshida, A. Satsuma, T. Hattori, Appl. Catal., B, 2001, 30, 151- 162.

21. H. Kannisto, H.H. Ingelsten, M. Skoglundh, J. Mol. Catal. A: Chem., 2009, 302, 86-96.

22. X. She, M. Flytzani-Stephanopoulos, J. Catal., 2006, 237, 79-93.

23. A. Barrera, S. Fuentes, M. Viniegra, M. Avalos-Borja, N. Bogdanchikova, J. Campa-Molina, Mater. Res. Bull., 2007, 42, 640-648.

24. E. Seker, J. Cavataio, E. Gulari, P. Lorpongpaiboon, S. Osuwan, Appl. Catal., A, 1999, 183, 121-134.

25. G.B. Hoflund, Z.F. Hazos, G.N. Salaita, Phys. Rev. B, 2000, 62, 11126-11133.

26. L.P. Haack, J.E. deVries, K. Otto, M.S. Chattha, Appl. Catal., A, 1992, 82, 199-214.

27. C.K. Jørgensen, H. Berthou, Chem. Phys. Lett., 1972, 13, 186-189.

28. J.S. Ledford, M. Houalla, A. Proctor, D.M. Hercules, L. Petrakis, J. Phys. Chem., 1989, 93, 6770-6777.

29. M. Cardona, L. Ley, Photoemission in Solids I: General Principles (Springer-Verlag, Berlin) with additional corrections, 1978.

30. R. Alvero, A. Bernal, I. Carrizosa, J.A. Odriozola, Inorg. Chim. Acta, 1987, 140, 45-47.