

Surface acidity and basicity of γ -Al₂O₃ doped with K⁺ and La³⁺ and calcined at elevated temperatures

Hu Zou, Xin Ge, Jianyi Shen*

Laboratory of Mesoscopic Materials Science, Department of Chemistry, Nanjing University, Nanjing 210093, China

Received 15 January 2002; received in revised form 15 May 2002; accepted 16 May 2002

Abstract

High temperature reactions in industry require catalysts with high stability. Basic metal oxides, K₂O and La₂O₃, were added to γ -Al₂O₃ in order to obtain supports with low acidity and high surface areas at high temperatures. Microcalorimetry and FT-IR were employed to determine the surface acidity and basicity using ammonia and carbon dioxide as the probe molecules. It was found that the addition of basic metal oxides inhibited the transformation of γ -Al₂O₃ to the forms such as θ -Al₂O₃ and α -Al₂O₃ when calcined at 1000 °C. Instead, X-ray diffraction (XRD) results indicated the formation of aluminates for the supported samples. The 6% K₂O/ γ -Al₂O₃ sample retained high surface area of 188 m² g⁻¹ and strong basicity (170 kJ mol⁻¹ for CO₂ adsorption) when calcined at 600 °C. The sample retained the surface area of about 100 m² g⁻¹ when calcined at 1000 °C. In this case, the sample possessed low acidity and basicity and may be used as a neutral support with high thermal stability. The addition of La₂O₃ onto γ -Al₂O₃ might cause even more loss of surface area when calcined at high temperatures. The formation of a perovskite phase LaAlO₃ on the surface of the La₂O₃/ γ -Al₂O₃ samples calcined at 1000 °C led to the low acidity and basicity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Surface acidity; γ -Al₂O₃; FT-IR

1. Introduction

γ -Al₂O₃ is widely used as catalyst support because of its high surface area and acidity. However, surface acidity is sometimes undesirable and γ -Al₂O₃ may lose its surface area when heated at high temperatures. Aria and Machida [1] and Schaper et al. [2] pointed out that γ -Al₂O₃ would lose its surface area partly due to sintering when calcined at 1000 °C. When calcined above 1000 °C, sintering and phase transformation to α -Al₂O₃ are the two major factors for the decrease of surface area. Researchers tried to dope γ -Al₂O₃

with foreign elements while maintaining the surface area [3–15]. For example, Matsuda et al. [13] reported that an effect of adding La₂O₃ is obviously to retard the transformation of γ -Al₂O₃ to α -Al₂O₃ and the associated sintering. Oudet et al. [15] suggested that transition of alumina can be thermally stabilized by surface interactions with a perovskite-type oxide, LnAlO₃ (Ln = La, Pr, Nd), and this thermally stable compound on the surface of alumina has a neutralizing effect on the corundum nucleation areas, inhibiting the formation of the stable form of alumina. Machida et al. [7,14] also found that alkaline earth metal oxides such as BaO, SrO and CaO have the same stabilization effects. Later other oxides of elements such as P, Si [8,11], Pr and Nd [15] were used. It seemed that La₂O₃, BaO and SiO₂ had the positive effect on the

* Corresponding author. Tel.: +86-25-3592-909;

fax: +86-25-3317-761.

E-mail address: jyshen@nju.edu.cn (J. Shen).

stabilization of surface area of alumina at high temperatures.

The present study deal with the thermal stability of γ -Al₂O₃ support modified respectively by K⁺ and La³⁺. In particular, the surface acidity and basicity of the modified samples were studied in terms of nature, number and strength and were correlated with loading and calcination temperatures.

2. Experimental

The starting γ -alumina had the surface area of 203 m² g⁻¹. The various amounts of basic metals K⁺ and La³⁺, calculated according to the desired loadings were introduced onto the γ -alumina by the incipient wetness impregnation method using the corresponding aqueous nitrate solutions. After impregnation, the samples were dried at 373 K overnight followed by calcination for 6 h at 600, 800 and 1000 °C, respectively. Table 1 summarizes the samples used in this study.

The surface areas of the samples were measured by nitrogen adsorption at -196 °C using the BET method on an ASAP-2000 type instrument (Micrometrics Co., USA). Helium was used as the carrier gas.

The phases present of the catalysts were determined by X-ray diffraction (XRD) using the Rigaku D/Max-RA X-ray diffractometer equipped with a Cu target and graphite monochromator.

Microcalorimetric measurements for the adsorption of NH₃ and CO₂ were carried out using a Tian-Calvet heat-flux apparatus, which has been described elsewhere [16]. The microcalorimeter was connected to a gas-handling and volumetric adsorption system, equipped with a Baratron capacitance manometer (MKS, USA) for precision pressure measurement. The differential heat of adsorption versus adsorbate coverage was obtained by measuring the heats evolved when doses of a gas (2–5 μ mol) were admitted sequentially onto the catalyst until the surface was saturated by the adsorbate. Ammonia and carbon dioxide with a purity of 99.99% were used. Before microcalorimetric measurements, the samples were typically dried under vacuum at 350 °C for 1 h, calcined in 500 Torr O₂ at 400 °C for 2 h, and evacuated at 400 °C for 2 h. Microcalorimetric adsorption of ammonia and carbon dioxide were performed at 150 °C.

Infrared spectra were collected with an IFS66V Vacuum-type FT-IR Spectrophotometer (Bruker Co. Ltd., German). Each spectrum was recorded at 2 cm⁻¹ resolution with 32 co-added scans. Sample pellets were formed with a thickness of 20–30 mg cm⁻². The samples were loaded into a quartz cell equipped with CaF₂ windows. The treatment procedure of the samples for IR was the same as for microcalorimetric adsorption studies. Ammonia and carbon dioxide were dosed onto the sample at 150 °C for 0.5 h. The cell was then isolated, cooled to room temperature and evacuated. Infrared spectra were then collected.

Table 1
Surface areas and phases of γ -Al₂O₃ and γ -Al₂O₃ supported samples calcined at different temperatures

| Sample | Calcination temperature (°C) | Surface area (m ² g ⁻¹) | Phases by XRD |
|---|------------------------------|--|--|
| γ -Al ₂ O ₃ | 600 | 203 | γ -Al ₂ O ₃ |
| | 800 | 161 | γ -Al ₂ O ₃ |
| | 1000 | 82 | γ -Al ₂ O ₃ , θ -Al ₂ O ₃ , α -Al ₂ O ₃ |
| 6 wt.% K ₂ O/ γ -Al ₂ O ₃ (1280 μ mol Kg ⁻¹) | 600 | 188 | γ -Al ₂ O ₃ |
| | 800 | 161 | γ -Al ₂ O ₃ , K ₃ AlO ₃ |
| | 1000 | 107 | γ -Al ₂ O ₃ , K ₃ AlO ₃ |
| 10 wt.% La ₂ O ₃ / γ -Al ₂ O ₃ (700 μ mol Lag ⁻¹) | 600 | 178 | γ -Al ₂ O ₃ |
| | 800 | 135 | γ -Al ₂ O ₃ |
| | 1000 | 57 | γ -Al ₂ O ₃ , LaAlO ₃ |
| 25 wt.% La ₂ O ₃ / γ -Al ₂ O ₃ (2000 μ mol Lag ⁻¹) | 600 | 126 | γ -Al ₂ O ₃ |
| | 800 | 95 | γ -Al ₂ O ₃ |
| | 1000 | 36 | γ -Al ₂ O ₃ , LaAlO ₃ |

Each reported spectrum is the difference between the spectrum of the clean sample and the spectrum collected after dosing an adsorbate.

3. Results and discussion

3.1. γ - Al_2O_3 and K^+/γ - Al_2O_3

Table 1 shows the BET surface areas of all the samples with various loadings and calcination temperatures. Fig. 1 shows the diffraction patterns of the γ - Al_2O_3 and 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 calcined at various temperatures. It is seen that the γ - Al_2O_3 was transformed into θ - Al_2O_3 and α - Al_2O_3 phases when calcined at 1000 °C. No θ - Al_2O_3 or α - Al_2O_3 phase was detected for the $\text{K}_2\text{O}/\gamma$ - Al_2O_3 sample calcined at 1000 °C. The sample exhibited mainly the γ -phase with a new phase K_3AlO_3 . The new phase K_3AlO_3 was formed by the solid reaction between K_2O and γ - Al_2O_3 which inhibited the transformation of γ - Al_2O_3 into θ - Al_2O_3 and α - Al_2O_3 phases. The 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 sample remained high surface area (161 and 107 $\text{m}^2 \text{g}^{-1}$, respectively) when calcined at 600 and 1000 °C, respectively.

The acidity and basicity of the γ - Al_2O_3 and 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 calcined at various temperatures were characterized by the microcalorimetric adsorption method using ammonia and carbon dioxide, respectively, as the probe molecules. Figs. 2 and 3 show the results. The γ - Al_2O_3 calcined at 600 °C exhibited the initial heat of about 125 kJ mol^{-1} and the

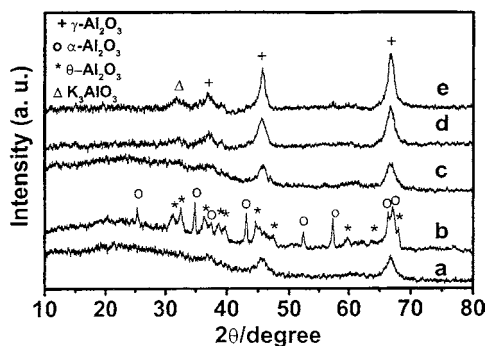


Fig. 1. X-ray diffraction patterns for γ - Al_2O_3 calcined at 600 °C (a) and 1000 °C (b) and for 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 calcined at 600 °C (c), 800 °C (d) and 1000 °C (e).

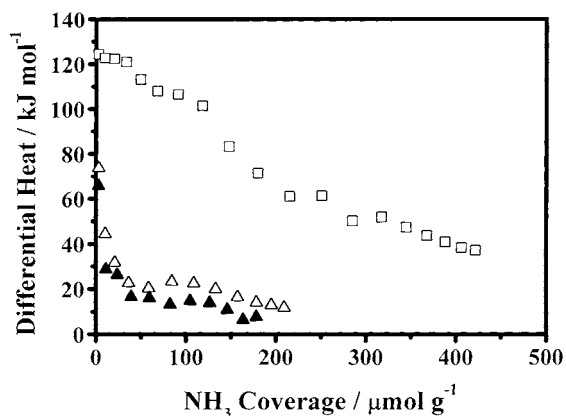


Fig. 2. Differential heat vs. adsorbate coverage for adsorption of NH_3 at 150 °C on γ - Al_2O_3 (\square), and on 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 calcined at 600 °C (Δ) and 1000 °C (\blacktriangle).

saturation coverage of about 420 $\mu\text{mol g}^{-1}$ for NH_3 adsorption. The addition of 6% K_2O almost killed all the acid sites with heats higher than 40 kJ mol^{-1} when the sample was calcined at temperatures higher than 600 °C. In fact, the acid sites with heat of 40 kJ mol^{-1} for ammonia adsorption are weak. On the other hand, the γ - Al_2O_3 exhibited the initial heat of about 132 kJ mol^{-1} and the saturation coverage of about 55 $\mu\text{mol g}^{-1}$ for CO_2 adsorption. The addition of K_2O greatly enhanced the basicity, especially for the sample calcined at 600 °C. In particular, the 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 sample calcined at 600 °C exhibited

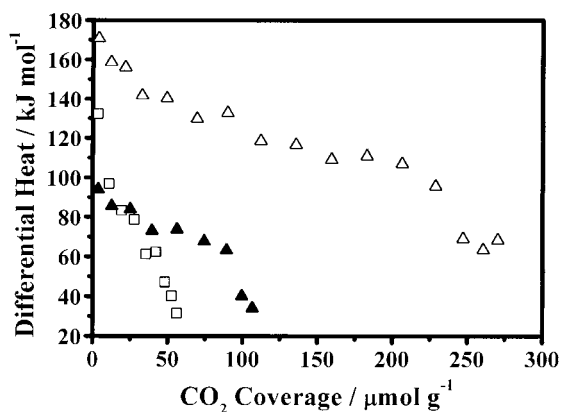


Fig. 3. Differential heat vs. adsorbate coverage for adsorption of CO_2 at 150 °C on γ - Al_2O_3 (\square), and on 6% $\text{K}_2\text{O}/\gamma$ - Al_2O_3 calcined at 600 °C (Δ) and 1000 °C (\blacktriangle).

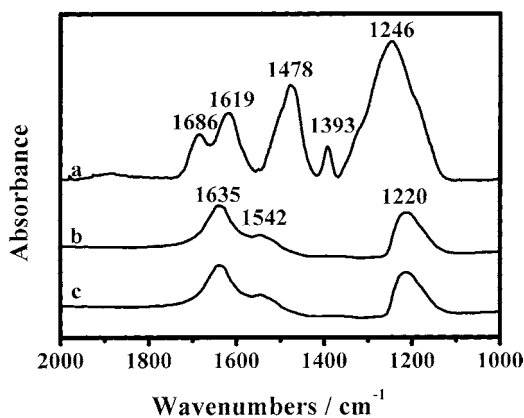


Fig. 4. FT-IR spectra collected after NH_3 adsorption at 150°C followed by evacuation at room temperature on $\gamma\text{-Al}_2\text{O}_3$ (a), and on 6% $\text{K}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ calcined at 600°C (b) and 1000°C (c), respectively.

the initial heat of 170 kJ mol^{-1} and saturation coverage of about $275\text{ }\mu\text{mol g}^{-1}$ for CO_2 adsorption. Even for the sample calcined at 1000°C , the initial heat and coverage for CO_2 adsorption were remained to be about 92 kJ mol^{-1} and $100\text{ }\mu\text{mol g}^{-1}$, respectively.

Fig. 4 shows the infrared (IR) spectra collected after exposure of the $\gamma\text{-Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ samples to ammonia at 150°C . Five bands around 686 , 1619 , 1478 , 393 and 1246 cm^{-1} were observed for the $\gamma\text{-Al}_2\text{O}_3$ sample calcined at 600°C . The bands around 1686 , 1478 and 1393 cm^{-1} are due to the deformation modes of NH_4^+ formed by the interaction of NH_3 with Brönsted acid sites on $\gamma\text{-Al}_2\text{O}_3$, while the bands around 1619 and 1246 cm^{-1} can be assigned to the asymmetric and symmetric deformation vibrations, respectively, of NH_3 molecules coordinated to aluminum cations, revealing Lewis acid sites on $\gamma\text{-Al}_2\text{O}_3$ [17,18]. With the addition of K_2O , the bands due to the Brönsted acid sites of $\gamma\text{-Al}_2\text{O}_3$ disappeared and the band at 1246 cm^{-1} shift to lower wavenumbers, indicating the decreased Lewis acidity upon the addition of K_2O . Calcination at different temperatures did not change the nature of surface acidity on the $\text{K}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ sample.

The IR spectra for CO_2 adsorbed on the $\gamma\text{-Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ samples were shown in Fig. 5. The bands around 1645 , 1442 and 1229 cm^{-1} can be assigned to the features normally seen for bicarbonate species (HCO_3^-) formed by adsorption of CO_2

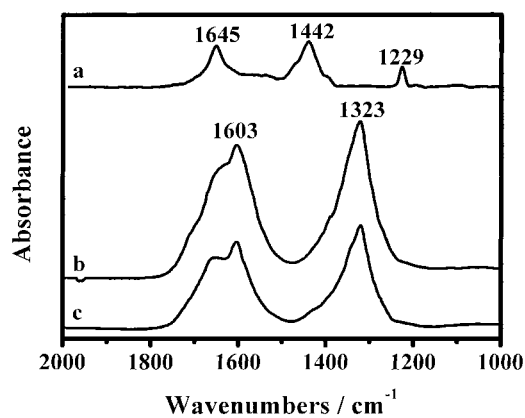


Fig. 5. FT-IR spectra collected after CO_2 adsorption at 150°C followed by evacuation at room temperature on $\gamma\text{-Al}_2\text{O}_3$ (a), and on 6% $\text{K}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ calcined at 600°C (b) and 1000°C (c), respectively.

on surface hydroxyl groups of $\gamma\text{-Al}_2\text{O}_3$. The band at 1229 cm^{-1} is due to the δ_{OH} mode and the other two are owing to the ν_{CO} modes [19]. The two bands at 1645 and 1229 cm^{-1} can also be attributed to the vibrations of bidentate carbonate species attached to Al_3^+ cations. The addition of K_2O onto $\gamma\text{-Al}_2\text{O}_3$ resulted in the two new bands around 1603 and 1323 cm^{-1} for the adsorption of CO_2 . These bands are due to the carbonate species formed upon the adsorption of CO_2 on K^+ . The band around 1645 cm^{-1} was remained for the carbonate species associated with Al^{3+} cations.

3.2. $\text{La}^{3+}/\gamma\text{-Al}_2\text{O}_3$

Fig. 6 shows the diffraction patterns for the $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ samples calcined at different temperatures. When the samples were calcined at 600°C and 800°C , only $\gamma\text{-Al}_2\text{O}_3$ phase was detected. The calcination at 1000°C lead to the formation of LaAlO_3 species, especially for the 25% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ sample, in which LaAlO_3 was the dominant phase. LaAlO_3 is a perovskite with a distorted cubic structure [20].

Fig. 7 shows the differential heat versus coverage for NH_3 adsorption on the $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ samples calcined at different temperatures. The 10% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ sample calcined at 600°C exhibited the initial heat of about 103 kJ mol^{-1} , 20 kJ mol^{-1}

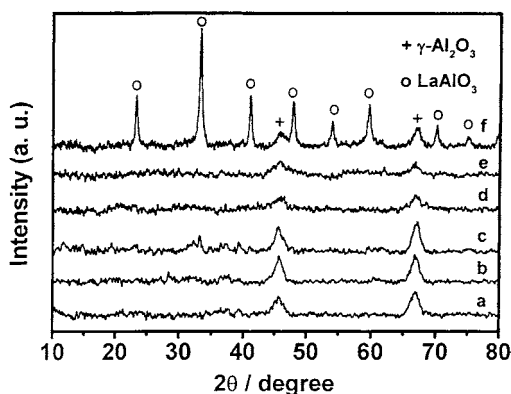


Fig. 6. X-ray diffraction patterns for 10% La₂O₃/γ-Al₂O₃ calcined at 600 °C (a), 800 °C (b) and 1000 °C (c) and for 25% La₂O₃/γ-Al₂O₃ calcined at 600 °C (d), 800 °C (e) and 1000 °C (f).

lower than that for γ-Al₂O₃. When calcined at 1000 °C, the samples exhibited similar surface acidity with the initial heat of about 70 kJ mol⁻¹ and saturation coverage of about 200 μmol g⁻¹, which might be due to the formation of LaAlO₃ phase on the surface. In Fig. 8 is shown the differential heat versus coverage for CO₂ adsorption on the La₂O₃/γ-Al₂O₃ samples. The 10% La₂O₃/γ-Al₂O₃ sample calcined at 600 °C exhibited a greatly increased basicity as compared to the support itself. However, the calcination at 1000 °C greatly decreased the basicity, probably because of the formation of the LaAlO₃ phase. In fact, the 25%

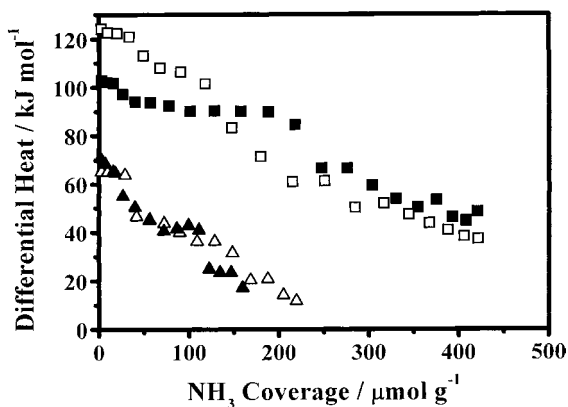


Fig. 7. Differential heat vs. adsorbate coverage for adsorption of NH₃ at 150 °C on γ-Al₂O₃ (□), on 10% La₂O₃/γ-Al₂O₃ calcined at 600 °C (■) and 1000 °C (△) and on 25% La₂O₃/γ-Al₂O₃ calcined at 1000 °C (▲).

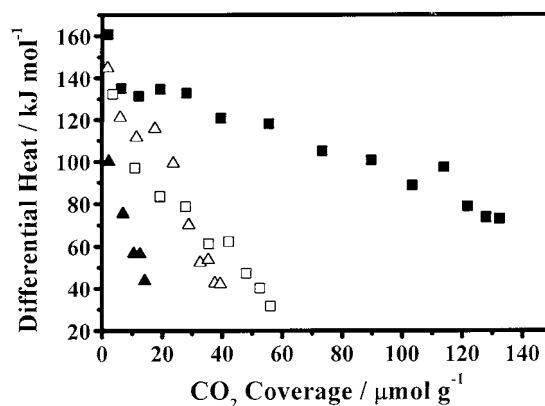


Fig. 8. Differential heat vs. adsorbate coverage for adsorption of CO₂ at 150 °C on γ-Al₂O₃ (□), on 10% La₂O₃/γ-Al₂O₃ calcined at 600 °C (■) and 1000 °C (△) and on 25% La₂O₃/γ-Al₂O₃ calcined at 1000 °C (▲).

La₂O₃/γ-Al₂O₃ sample calcined at 1000 °C exhibited even lower basicity. This sample has been shown to have mainly the LaAlO₃ phase on the surface.

4. Conclusions

γ-Al₂O₃ can be converted into θ-Al₂O₃ and α-Al₂O₃ upon the calcination at temperatures higher than 1000 °C, which may be responsible for the loss of surface area. The addition of K⁺ and La³⁺ inhibited the conversion of γ-Al₂O₃ because of the formation of aluminates. The 6% K₂O/γ-Al₂O₃ sample was found to be a strong solid base when calcined at 600 °C, since it retained the high surface area of about 180 m² g⁻¹ and exhibited the initial heat of 170 kJ mol⁻¹ and the saturation coverage of about 250 μmol g⁻¹ for CO₂ adsorption. On the other hand, the sample may be used as a neutral support when calcined at 1000 °C, since it retained the surface area of about 100 m² g⁻¹ and exhibited very low acidity and basicity.

The addition of La₂O₃ onto γ-Al₂O₃ did not seem to improve the loss of surface area of γ-Al₂O₃, although it did inhibit the transformation of γ-Al₂O₃ to other phases. The formation of the perovskite phase LaAlO₃ when calcined at 1000 °C for the La₂O₃/γ-Al₂O₃ samples led to the greatly decreased surface acidity and basicity.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (29973013) and the Department of Science and Technology of China (1999022408). Financial support from the “333” project of Jiangsu Province is also acknowledged.

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