Catalytic decomposition of sulfuric acid over Fe$_2$O$_3$ and Pt/Al$_2$O$_3$: A comparative study

Chemistry Division

This paper received the Best Paper Award (II prize), at the International Symposium on Materials Chemistry (ISMC-2010), held at Mumbai, during December 7-11, 2010

Abstract

The catalytic activities of Fe$_2$O$_3$ and Pt/Al$_2$O$_3$ were compared for sulfuric acid decomposition reaction. In the temperature-dependent catalytic activity runs, it was found that at lower temperatures in the range of 725 – 750 °C, the SO$_2$ yield for the supported noble metal catalyst, was found to be higher than that of Fe$_2$O$_3$ while at higher temperatures in the range of 800 – 825 °C, the catalytic activities of the two catalysts were comparable. Both the spent catalysts and the fresh catalysts were characterized by XRD and FTIR, to evaluate any structural or surface modifications of the catalysts, due to their use in sulfuric acid decomposition at high temperatures. The investigation reveals that, Fe$_2$O$_3$ can be a good substitute for noble metal catalysts for sulfuric acid decomposition reaction, at temperatures of 750 °C and above.

Introduction

Large scale generation of hydrogen from water via thermochemical cycles or high temperature steam electrolysis employing nuclear/solar heat, appears to be promising options to meet the increasing global energy demands, without emitting green house gases. Owing to its higher efficiency (~47%) and other advantages, S-I (Sulfur–Iodine) cycle is widely considered as a preferred choice, among various thermochemical cycles, proposed for hydrogen generation via water-splitting$^1$. Decomposition of sulfuric acid is the most energy-demanding step of S-I thermochemical cycle and the efficiency of the cycle largely depends on the kinetics of this step. The sulfuric acid decomposition is comprised of the following two reactions in series:

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_3 \quad (~450 \degree \text{C}) \quad ... \quad (1.1) \]
\[ \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad (~800-900 \degree \text{C}) \quad ... \quad (1.2) \]

Sulfuric acid can be decomposed to its anhydride SO$_3$ (Eqn.1.1) without a catalyst, while the decomposition of SO$_3$ (Eqn.1.2) has been known to be a catalytic reaction. Research on newer catalysts is vital from the view point of understanding the fundamental surface phenomenon and finally the development of active and stable catalysts, under high temperature and acid environments.

Various catalysts reported to be active for decomposition of sulfuric acid include noble metals, metal oxides and mixed metal oxides$^2$. Both the activity and the stability of the catalyst are very important, as the reaction environment is extremely hostile like high temperatures, presence of aggressive chemicals, including sulfur oxides, high temperature steam and oxygen. While noble metal catalysts are highly active for SO$_3$ decomposition reaction, loss of active metal has been reported during their long term use$^3$. Earlier results from our laboratory have shown

...
effectiveness (chemical and thermal stability and high catalytic activity) of iron-oxide based catalysts, for decomposition of sulfuric acid. In the present study, we compare the catalytic activities of iron oxide with a commercial Pt (1 wt.%) /Al₂O₃ catalysts, for decomposition of sulfuric acid in the temperature range of 700 °C to 825 °C.

Experimental

The Fe₂O₃ catalyst was prepared by precipitation method, using ferric nitrate as iron source and ammonia as the precipitating agent. The resulting precipitate was washed, dried in an air oven at 120°C and calcined in air at 750°C for 4 h. Calcined product was characterized using XRD, FTIR and N₂-BET surface area techniques. Sulfuric acid decomposition experiments were carried out in an indigenously developed flow, through quartz catalytic reactor as shown in Fig. 1. In a typical experiment, the powder catalyst sample (200 mg, 75 - 100 μ size) was loaded into the reactor at room temperature and a flow of nitrogen carrier (HP) at a rate of 40 ml min⁻¹ was initiated. The furnace temperature was increased to 700 °C, over a time interval of 1 h. Concentrated sulfuric acid was then pumped into the system (~ 25 g acid g⁻¹ h⁻¹) by syringe pump and it was carried by the carrier gas to the pre-heater, where the acid vaporized and then finally decomposed to SO₂, O₂ and H₂O over the catalyst bed. The unreacted SO₃ recombined with H₂O in the condenser downstream and was collected as a liquid solution. The gaseous SO₂ and O₂ products along with the carrier were passed through a NaOH solution, where SO₂ was trapped and the other gases (O₂ and N₂) were vented. For analysis of product SO₂, the decrease in concentration of the NaOH solution was measured by titration, with standardized sulfuric acid solution. Similarly, the unreacted sulfuric acid collected downstream of the reactor was determined by chemical titration, with standardized NaOH solution. The percentage conversion of sulfuric acid to sulfur dioxide was calculated based on the product yield of SO₂. The catalytic activities were measured in the temperature range 700 - 825 °C, at an interval of 25°C after equilibrating for ~ 1 h at each temperature.

Results and Discussion

The temperature-dependent catalytic activity of the Fe₂O₃ and Pt (1 wt.%) /Al₂O₃ catalysts are shown in Fig. 2. Catalytic activity of both the samples increases with temperature, Fe₂O₃ showing maximum conversion of ~ 79% at 825 °C. At lower temperatures in the range of 725 – 750 °C, the SO₂ yield for the supported noble metal catalyst was found to be higher than that of Fe₂O₃, while at higher temperatures in the range of 800 – 825 °C, the catalytic activities of the two catalysts were comparable. It is pertinent to mention here, that blank experiments in the absence of catalysts verified that homogeneous vapor phase reaction did not occur under these conditions. Thus, Fe₂O₃ can be a good substitute for noble metal catalysts for sulfuric acid decomposition at temperatures of 750 °C and above. Since the operation temperatures of the high temperature nuclear reactors would be high (>800 °C), Fe₂O₃ can be considered as a suitable catalyst for sulfuric acid decomposition. After two such temperature-dependent catalytic activity runs, the spent catalysts were collected and characterized by XRD and FTIR and compared
with the fresh catalysts to evaluate any structural or surface modifications of the catalysts, due to their use in sulfuric acid decomposition at high temperatures.

The N2-BET surface area of the fresh Fe2O3 and Pt/Al2O3 samples were 17 m2g-1 and 290 m2g-1, respectively. The XRD patterns of the fresh and used catalyst samples are shown in Fig. 3. The XRD pattern of the fresh Fe2O3 sample, matches with the α-Fe2O3 or hematite phase (JC-PDS card No. 33-0664 hematite). From the XRD pattern of the spent Fe2O3 catalyst collected after the reaction, it is evident that there is no change in phase and neither is there any formation of other phases. Thus, the oxide catalyst retains its structural integrity during the course of the sulfuric acid decomposition reaction. On the other hand, the XRD of the fresh Pt/Al2O3 catalyst exhibited AlO(OH), α-Al2O3 and Pt phases (marked in the fig) while the spent catalyst was less crystalline and showed only α-Al2O3 phase as seen in Fig. 3c and 3d.

A comparison of the FTIR spectra of the fresh and spent catalyst samples is shown in Fig. 4. The prominent infrared absorption bands (cm-1) for fresh Fe2O3 are observed at 479 and 560 cm-1 while a weak IR band appeared at 440 cm-1. In contrast, in the used catalyst sample, the two dominant bands and the weak band coexist at the same peak position. In addition to the characteristic peaks due to Fe2O3, there are four prominent peaks in the range of 1000–1200 cm-1 which is an indication of C2v symmetry and bidentate sulphate coordination, because a clear distinction between monodentate and bidentate coordination can be made, based on the number of observed bands (monodentate, C3v, with three bands, and bidentate, C2v, with four bands). The peaks arise due to SO bond stretching in metal sulfates with the lowest wave number observed. The peaks are marked in Fig. 4a and 4b.
number peak assigned to $\tilde{\omega}_5$, stretching mode while the higher three peaks are due to $\tilde{\omega}_3$ mode. Thus, the FTIR spectra of the spent catalyst samples, confirm the presence of bidentate sulfates species. These metal sulfates are probably the transient intermediates of sulfuric acid decomposition to sulfur dioxide, over these metal oxide catalysts. In the case of Pt/Al$_2$O$_3$, the spent catalysts does not show any evidence of sulfates.

From the comparison between the thermal analyses of metal sulfates and the activity of the corresponding metal oxides reported earlier in our work$^{4,5}$, we suggest, that the metal sulfate decomposition should be considered as the rate determining step for SO$_3$ decomposition. The presence of sulfate species on the used samples is in agreement with the above hypothesis. On the other hand, it is reported$^6$, that sulfur trioxide decomposition proceeds over Pt/Al$_2$O$_3$ through a different mechanism - adsorption and dissociation of SO$_3$ at the surface active sites, which are the active noble metal centre via the intermediate formation of adduct [SO$_2$.O] on the metal centre.

**Conclusion**

The catalytic properties of Fe$_2$O$_3$ and Pt/Al$_2$O$_3$ are compared for sulfuric acid decomposition reaction. At lower temperatures in the range of 725 – 750 °C, the SO$_2$ yield for the supported noble metal catalyst was found to be higher while at higher, temperatures in the range of 800 – 825 °C the catalytic activities of the two catalysts were comparable. The Fe$_2$O$_3$ catalyst retained its phase in the course of the reaction, while AlO(OH) phase present in the fresh Pt/Al$_2$O$_3$ catalyst disappeared after use in the decomposition. FTIR spectra suggest the formation of metal sulfates on the spent Fe$_2$O$_3$ samples, while spent Pt/Al$_2$O$_3$ catalysts do not show any evidence of sulfates. This along with the thermal decomposition data of the metal sulfates, suggested the formation and dissociation of metal sulfates as the probable mechanism over iron oxide catalysts, while a different mechanism is reported for SO$_3$ decomposition over Pt/Al$_2$O$_3$ catalyst. The investigation reveals that, Fe$_2$O$_3$ can be a good substitute for noble metal catalysts, for sulfuric acid decomposition reaction at temperatures of 750 °C and above.

**References**