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Investigation of N-TiO_2 Nanocatalyst Performance in Direct Oxidation of Hydrogen Sulfide to Sulfur

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INTRODUCTION

Nowadays, a main problem is air pollution and environmental standard regulations have been hardened so we need to until treat sulfur-containing gas before transpiration into the atmosphere [1]. The Claus process has been engaged to remove H_2S from sulfur-containing gas such as natural gases or refinery Plants. The Claus process includes two steps: thermally (Equation 1) and catalytic (Equation 2) [2].

$$H_2S + \frac{3}{2}O_2 \xrightarrow{Thermally} SO_2 + H_2O \quad (1)$$

$$SO_2 + 2H_2S \xrightarrow{Catalytic} 2H_2O + \frac{3}{n}S_n \quad (2)$$

Selective catalytic oxidation of H_2S has achieved great interest in recent decades, which H_2S can catalytically oxidize to elemental sulfur in one step. Metal-based [3] and carbon-based [4] and hybrid [5] catalysts are used for removing H_2S for direct oxidation process. Also, doping with metallic (Nb, Ag, Pt, W, Mn, Fe, V, Mn, Co, Ni etc.) and non-metallic (C, N, P, F etc.) has been demonstrated as an effective route in various application such as lithium batteries, gas sensors, photocatalysis and electrochronic devices and adsorption [6]. In previous work, TiO_2 nanoparticles and TiO_2-CNT hybrid nanocatalyst, were synthesized, and its activity in direct oxidation of H_2S to S is investigated [7]. As respects, nitrogen modifies the acido-basic properties or changes the electronic surface state of the support and interaction with the deposited active phase and thus provides a new catalyst with better efficiency [8]. In this work, N doped TiO_2 was used as a catalyst for direct oxidation H_2S to S for the first time in 200 °C and O_2/H_2S of 0.5. The influence of the nitrogen concentration in N doped TiO_2 nanocatalyst on the desulfurization activity and sulfur selectivity has been investigated, and the results will be compared with undoped TiO_2.

EXPERIMENTAL PROCEDURE

CATALYST PREPARATION

TiO_2 nanocatalyst: TiO_2 nanoparticles were synthesized according to previous research [7]; moreover, Titanium (IV) isopropoxide precursor was mixed with isopropanol labeled as solution I. Some nitric acid and distilled water were mixed to reach pH=1 and labeled as solution II. Solution II was stirred vigorously and simultaneously added dropwise to the solution I. The resulting colloidal solution was stirred continuously for 2 hours to form a sol. Solution was aged for 24 hours in ethylene glycol bath at 80 °C and exposed to air for 24 hours at ambient temperature to produce a gel. Samples were dried at 110 °C for at least 12 hours in an oven and were calcined under nitrogen gas atmosphere in a furnace at 400 °C for 2 hours.

N doped TiO2: In order to synthesiz N-TiO_2 with 15% nitrogen, at first a certain amount of urea was mixed as nitrogen source with distilled water and dissolved with the aid of the stirrer. Then a certain amount of TiO_2 nanoparticles synthesized is added into distilled water, and urea and is stirred for one hour. The suspensions is sonicated for 30 minutes. The resulting mixture is dried at 80 °C for 24 hours. Then, is calcined in a furnace at 400 °C in atmospheres of nitrogen for 2 hours.

CATALYTIC ACTIVITY TEST

Catalytic activity test is done in a setup of catalytic. The mixture of N_2 and H_2S gas and O_2 gas are used as feed. In addition, 5 g mixture catalyst (1g catalyst and 4g quartz glass with 30-60 mesh) in the reactor was placed, which was fasten by quartz wool from both sides, and it was placed into the tubular reactor. The H_2S and SO_2 concentrations were monitored used gas chromatograph (Agilent 7890b) model to measure their concentrations from the outlet of reactor. H_2S conversion, sulfur selectivity and sulfur yield is obtained by equation 3 to 5, respectively.

$$H_2S\ Conversion = \frac{H_2S_{in} - H_2S_{out}}{H_2S_{in}} \tag{3}$$

$$Sulfur\ selectivity = \frac{H_2S_{in} - H_2S_{out} - So_{2out}}{H_2S_{in} - H_2S_{out}} \tag{4}$$

Sulfur yield= H_2S Conversion× Sulfur Selectivity (5)

RESULTS AND DISCUSSION

BET surface area measurements are given for TiO_2 and N doped TiO_2 in Table 1 and Figure 1. The surface areas of TiO_2 nanoparticles, N-TiO_2 were 162, 178m^2/g respectively. It is anticipated that the interstitial space of TiO_2 increased because of nitrogen groups inserted into TiO_2 network and inhibited from agglomeration of TiO_2, and surface area N-TiO_2 increased than to TiO_2. Therefore, the addition of nitrogen has led that the N-TiO_2 catalyst has higher surface area than undoped TiO_2.

Figure 2 shows the EDX analysis for 15% N-doped TiO_2. Furthermore, content of metal ions and nitrogen doped in the TiO_2 matrices is calculated by this analysis. 15 wt.% of nitrogen doped TiO_2 shows the presence of O, Ti, C and N according to atomic weight stoichiometric, and no unexpected impurities have been observed in catalyst. It indicates that the nitrogen has been inserted into TiO_2 matrices.

Table 1: Surface area, pore volume and pore diameter measurements for catalysts.

Catalyst	$a_{s, BET}$ (m^2/g)	Pore volume (cm^3/gr)	d(nm)
TiO_2[7]	162	0.14	3
N- TiO_2	178	0.17	3.4

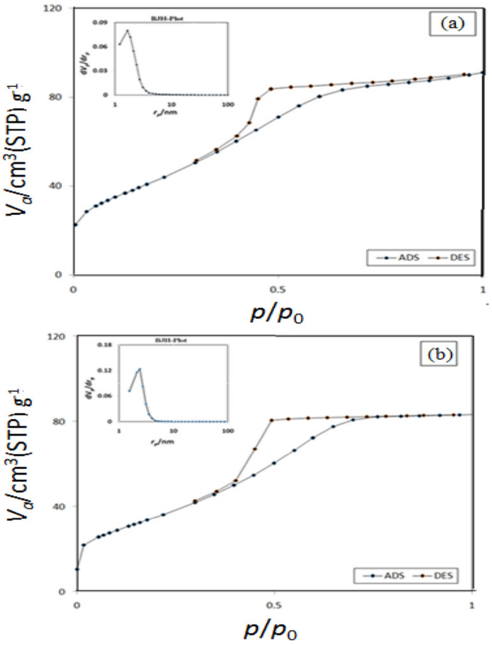
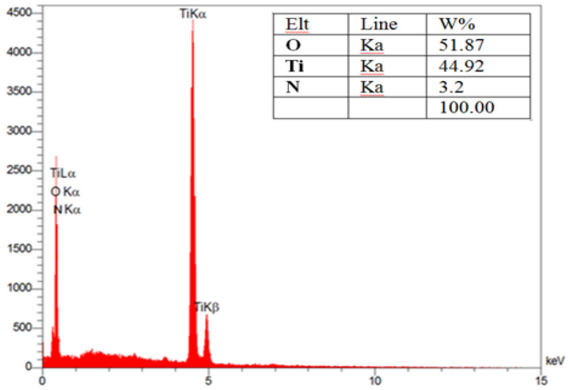


Figure 1: The N_2 adsorption–desorption isotherms of catalysts: a) TiO_2 [7], b) N-TiO_2.



Elt	Line	W%
O	Ka	51.87
Ti	Ka	44.92
N	Ka	3.2
		100.00

Figure 2: EDX analysis of N-TiO_2 nanoparticles

CATALYTIC PERFORMANCES

Figure 3 indicates the performance of two catalysts TiO_2 and N-TiO_2 with 15 weight percent of nitrogen for selective oxidation of H_2S to S with optimized temperature 200 °C and $O_2/H_2S=0.5$ for feed stream 4400 ppm and GHSV 17000 h^{-1}. The results show that conversion 15% N-TiO_2> TiO_2. Moreover, 15% N-TiO_2 catalyst with 99.2% of H_2S conversion and selectivity of 99.4% have activity higher than TiO_2. According to our BET results, nitrogen provides higher surface area for 15% N-TiO_2 in comparison with TiO_2 catalyst. Also, According to our EDX results, presence of nitrogen groups is caused that N-TiO_2 has better performance than undoped TiO_2. Nitrogen species due to their electron density which provides basic centers for H_2S dissociation are the most active sites for H_2S selective oxidation. Also, synergistic effects of TiO_2 and N may be lead to N-TiO_2 better performance than TiO_2. N-TiO_2 exhibits much higher activity in the direct oxidation reaction compare to the undoped TiO_2 due to higher surface area and pore volume. These results show that N-TiO_2 catalyst keeps favorably side reactions during selective oxidation of H_2S at 200 °C and O_2/H_2S ration equal to 0.5.

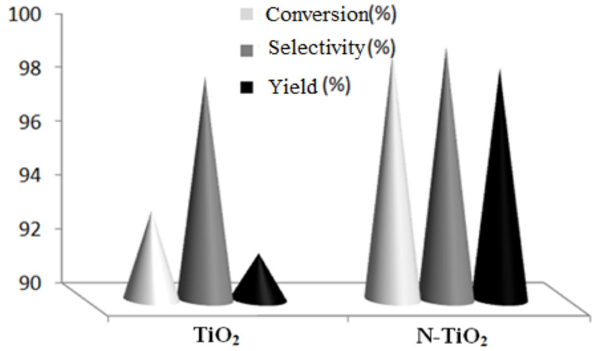


Figure 3: Catalytic performance of catalysts for direct oxidation reaction in 200 °C and O_2/H_2S ratio of 0.5

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