

Supporting Information

Temperature programmed desorption technique

Temperature Programmed Desorption (TPD) technique was used to measure the extent of acidic sites in a set up locally fabricated. In TPD we are determining the amount of ammonia desorbed from a catalyst saturated with ammonia using volumetric titration method. In a typical experiment, the stepwise determination of the amount of acidic sites is carrying out by programming the temperature of the catalyst from 100 to 700° C. After degassing in presence of a carrier gas at 300° C, the sample is allowed to cool to room temperature. A measured quantity of ammonia gas (excess) is then injected to an accurately weighed quantity of a catalyst, which is made into a pellet form, kept in the reactor. In the course of temperature programming, the sample is being kept at each temperature such as 100, 200, 300, 400, 500, 600 and 700° C for a constant period of time. This is to allow the sample to react at that temperature, and the desorbed ammonia gas is then collected in a standardized H₂SO₄ solution kept in a conical flask. This solution is further used for the volumetric determination of the amount of ammonia desorbed by the catalyst. The calculation is as follows.

Undoped titania, 300° C

Wt of catalyst, w	= 1.041g
Normality of NaOH	= 0.0252N
Normality of H ₂ SO ₄	= 0.051N

Standardization of H₂SO₄

$$10 \text{ ml H}_2\text{SO}_4 = 20.25 \text{ ml NaOH}$$

Volume of NaOH (ml)	ΔV (ml)	Amount of ammonia desorbed
at temperatures, °C		$= (N_{\text{NaOH}} \times V) \times 17/w \text{ (mg/g)}$
100	19.45	0.8
200	19.65	0.6
300	19.85	0.4
400	19.95	0.3
500	19.95	0.3
600	19.9	0.35
700	19.85	0.4

Undoped titania, 700° C

Wt of catalyst, w	= 0.971g
Normality of NaOH	= 0.0258N
Normality of H ₂ SO ₄	= 0.0521N

$$10 \text{ ml H}_2\text{SO}_4 = 20.2 \text{ ml NaOH}$$

Volume of NaOH (ml)	ΔV (ml)	Amount of ammonia desorbed
at temperatures, °C		$= (N_{\text{NaOH}} \times V) \times 17/w \text{ (mg/g)}$
100	16.05	4.15

200	17.2	3.0	1.36
300	18.8	1.4	0.63
400	19.55	0.65	0.29
500	19.6	0.6	0.27
600	19.5	0.7	0.31
700	19.45	0.75	0.34

1% lanthana-titania, 300° C

Wt of catalyst, w	= 1.02g
Normality of NaOH	= 0.024N
Normality of H ₂ SO ₄	= 0.0511N

$$10 \text{ ml H}_2\text{SO}_4 = 21.3 \text{ ml NaOH}$$

Volume of NaOH (ml)	ΔV (ml)	Amount of ammonia desorbed	
at temperatures, °C		$= (N_{\text{NaOH}} \times V) \times 17/w \text{ (mg/g)}$	
100	19.65	1.65	0.66
200	19.7	1.6	0.64
300	19.9	1.4	0.56
400	20.6	0.7	0.28
500	20.55	0.75	0.30
600	20.35	0.95	0.38
700	20.45	0.85	0.34

1% lanthana-titania, 700° C

Wt of catalyst, w = 1.016g

Normality of NaOH = 0.025N

Normality of H₂SO₄ = 0.053N10 ml H₂SO₄ = 21.2 ml NaOH

Volume of NaOH (ml)	ΔV (ml)	Amount of ammonia desorbed at temperatures, °C	$= (N_{\text{NaOH}} \times V) \times 17/w \text{ (mg/g)}$
100	17.5	3.7	1.548
200	17.95	3.25	1.359
300	19.25	1.95	0.82
400	19.4	1.8	0.75
500	19.65	1.55	0.65
600	19.4	1.8	0.75
700	19.4	1.8	0.75

2% lanthana-titania, 700° C

Wt of catalyst, w = 1.019g

Normality of NaOH = 0.0258N

Normality of H₂SO₄ = 0.0503N10 ml H₂SO₄ = 19.5 ml NaOH

Volume of NaOH (ml) at temperatures, °C		ΔV (ml)	Amount of ammonia desorbed $= (N_{\text{NaOH}} \times V) \times 17/w$ (mg/g)
100	15.1	4.4	1.72
200	15.5	4.0	1.89
300	15.55	3.95	1.70
400	17.15	2.35	1.01
500	17.35	2.15	0.92
600	16.8	2.7	1.16
700	19.3	2.0	0.86

The proposing La^{3+} site formation

Pure titania possesses terminal surface hydroxy-groups^{33b}, but they are non acidic, and this surface is catalytically unimportant. According to Pauling, the acidity of a catalyst can be tailored by adding cations with a different valence state to a host oxide. In our case, let a trivalent La^{3+} cation substitutes for a tetravalent Ti^{4+} cation in TiO_2 , in such a way that it occupies a tetrahedral Ti site. A net negative charge is then created which must be balanced by a nearby positive charge. This can be an H^+ cation from water molecules, which dissociates to fix a hydroxyl OH on the La^{3+} cation. So this can behave as a Bronsted acid and can give up a proton according to the reaction given below (Scheme I) or it may transform to a Lewis acid by losing a water molecule according to reaction (Scheme II)

*Structural modifications and associated**Sibu et al**Scheme 1 & II*