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Short communication

Influence of transition metals on the surface acidic properties of titania prepared by sol–gel route

N.B. Shali, S. Sugunan *

Department of Applied Chemistry, Cochin University of Science and Technology, Cochin-22, Kerala, India

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Abstract

A series of titania catalysts containing chromium, molybdenum as well as tungsten has been prepared by colloidal sol–gel route using metatitanic acid as the precursor. Structural characterization of the prepared catalysts was done with Energy dispersive X-ray analysis, X-ray diffraction, BET surface area and pore volume measurements. The influence of different transition metals like chromium, molybdenum and tungsten on the surface acidic properties of titania is investigated in detail. Two independent methods have been used to study the surface acidity of these catalyst systems: temperature programmed desorption of ammonia which is a measure of total acidity and thermodesorption studies using 2,6-dimethyl pyridine which is a measure of Bronsted acidity. Cumene cracking reaction is carried out over the prepared systems for further characterizing the acidity of the prepared catalysts. Remarkable enhancement in the surface acidity is observed after transition metal incorporation. The catalytic activity of the prepared catalysts was tested towards the dehydrogenation of cyclohexane.

Keywords: Titania; Transition metals; Sol–gel route; Surface acidity; Cyclohexane dehydrogenation

1. Introduction

The replacement of liquid acids by solids is now considered as highly desirable in order to design clean processes for better protection of the environment [1]. Most of the solid acid catalysts used in various chemical transformations are based on inorganic oxides. In most cases, these oxides are to be modified chemically or physically so as to get the desired catalytic activity for a particular reaction. Oxides, because of their ability to take part in the exchange of electrons, protons or oxide ions are used as catalysts in both redox as well as acid base catalysis [2]. In metal oxides, coordinative unsaturation is principally responsible for the ability towards adsorption and catalysis of various reactions. The exposed cations and anions of the metal oxide surfaces form acidic and basic sites as well as acid–base pairs. Besides this, the variable valency of the cation results in the ability of the oxides to undergo oxidation and reduction. The catalytic activities of the solid acids are not only related to the surface concentration of acid sites, but also depends on their nature (i.e. Bronsted or Lewis type) and strength [3].

Titania is now the object of increasing interest in the field of heterogeneous catalysis. The interactions between metal oxides and the oxide supports have attracted much attention because of the wide application of the supported metal oxide systems. It is well known that the supported oxides of transition metals are widely used as catalysts for

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* Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595.
E-mail address: ssg@cusat.ac.in (S. Sugunan).

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various reactions. There are three common titania polymorphs—anatase, brookite and rutile. Both anatase and rutile have been extensively studied for photocatalytic applications with the former found to be the most suitable for photocatalytic reactions [4]. One of the most important applications of the sol–gel method can be found in the field of catalysis. The properties of catalysts and support materials strongly depend on the preparation procedures [5–11]. The high porosity and large specific surface area of materials prepared by sol–gel route make them very attractive from a catalytic point of view. The relatively low surface area as well as poor stability of titania structure at high temperature is the main disadvantage of titania while using as a catalyst or a catalyst support [12]. The sol–gel synthesized titania and its modification with other metals overcomes these limitations.

The aim of the present work is to prepare titania and their transition metal modified analogues through colloidal sol–gel route and to characterize its structure using various physico-chemical techniques. Furthermore, a detailed investigation on the surface acidic properties of the prepared catalysts is also carried out using different independent techniques.

2. Experimental

Transition metal modified titania catalysts (2, 6 and 10 wt. %) were prepared by sol–gel method. The precursor used is metatitanic acid i.e., hydrated titania (Travancore Titanium Limited, Kerala). Titanyl sulphate is obtained by dissolving the precursor in concentrated sulphuric acid. Ammonia is added to this until complete precipitation of titanium hydroxide occurs. The sulphate freed precipitate is suspended in hot water and added 10% HNO_3 drop wise until a stable sol is obtained at a pH of around 1.5. Calculated amounts of the metal to be incorporated is added to the clear sol before gelation. Gelation is done chemically by slightly perturbing the pH of the sol by the addition of drops of ammonia. The gel is oven dried at 383 K for 12 h and subsequently calcined at 773 K for 5 h in air atmosphere. The catalysts are denoted as Ti*Xy* where X is the symbol of the incorporated metal and *y* is its corresponding weight percentage.

XRD patterns of the samples were recorded between 10° and 70° 2θ on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu Kα radiation source (λ = 1.5406 Å). The BET surface area and pore volume measurements were carried out by nitrogen adsorption at 77 K using a Micromeritics Gemini-2360 surface area analyzer. The precalcined samples were outgassed for 4 h at 400 °C in nitrogen atmosphere prior to the sorption measurement. EDX spectra of the samples were recorded in an EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si-Li detector). To determine the total acidity of the catalysts, temperature programmed desorption was done using NH_3 as the probe molecule. Prior to the experiment, the catalysts were activated inside the reactor at 300 °C for 30 min with continuous flow of nitrogen. After cooling to the room temperature, a specific volume of ammonia was injected in the absence of the carrier gas and allowed to attain equilibrium. Excess physisorbed ammonia was removed by the flow of nitrogen. Then the temperature program is done from room temperature to 600 °C in a stepwise manner. The ammonia desorbed at each interval of 100 °C was collected in a known volume of dilute sulfuric acid and estimated volumetrically by titration with standardized NaOH. 2,6-Dimethyl pyridine (2,6-DMP) adsorbs strongly on Bronsted acid sites and forms weak bonds with Lewis acid sites. The 2,6-dimethyl pyridine weakly bound to the Lewis acid sites get desorbed below 300 °C. Hence thermodesorption study of 2,6-dimethyl pyridine adsorbed sample beyond 300 °C can give the measure of Bronsted acid sites. The samples were activated at 500 °C for 1 h and kept in a dessicator saturated with 2,6-dimethyl pyridine for 48 h. It is then subjected to TG analysis at a heating rate 20 °C/min. in nitrogen atmosphere. The percentage of weight loss in the temperature region 300–600 °C is divided into weak (300–400 °C), medium (400–500 °C) and strong (500–600 °C) acid sites. Gas phase cumene cracking reaction is carried out in a vertical down flow glass reactor under the flow of nitrogen using 0.5 g of the catalyst. The catalysts were placed in the reactor and supported on either side with a thin layer of glass wool and ceramic beds. The reactor was heated to the reaction temperature with help of a tubular furnace provided with a temperature controller. The catalyst was activated at 500 °C for 2 h before the catalytic runs. Reactants were fed into the reactor using a syringe pump. The bottom of the reactor was connected to a coiled condenser and receiver to collect the products. The products obtained in the first hour were discarded and the products collected after different times-on-stream was analyzed. The activities and selectivities considered for comparison of the behaviour of the different catalysts are those obtained after 2 h. The same reaction set up is used for the catalytic dehydrogenation of cyclohexane. The products were analyzed by gas chromatography (Chemito GC 1000) using BP1 capillary column (12 m × 0.32 m) with FID detector.

3. Results and discussion

The crystalline phases of the catalysts were investigated using XRD analysis. The main peaks at 2θ of 25.2, 37.9, 47.8, and 53.8, which represent the indices of (1 0 1), (0 0 4), (2 0 0) and (1 0 5) planes respectively are ascribed to structure of anatase titania. It is evident that the catalyst systems structurally contained pure anatase phase. After being modified with transition metals like chromium, molybdenum and tungsten, the XRD pattern is shown in Fig. 1. However, the presence of diffraction peaks corresponding to the incorporated transition metal oxides could not be observed, probably due to the smaller content on a relative mass basis and high dispersion degree. Besides, the diffractogram also shows that the crystallinity of titania reduces upon transition metal modification. The crystallite size of titania in the prepared catalysts as determined from the Scherrer equation using the broadening of (1 0 1) anatase reflection peak is calculated [13,14]. The chemical composition of the calcined samples is given in Table 1. The expected amount of molybdenum and tungsten is not incorporated into titania and this may be attributed to the loss of those species as soluble ammonium molybdate and tungstate, respectively. The surface area of titania increases upon metal incorporation. Addition of transition metal species causes a further setback to the crystallization and sintering process, which is evident from the higher surface area of the samples in comparison with pure titania. The metal oxide species along with incorporated ones prevent the agglomeration of titania particles resulting in a higher surface area.

Ammonia TPD method is widely used for characterizing the surface acidity. Being a small molecule, it has greater accessibility to almost all acidic sites including the weak ones [15–18]. The acid site distribution pattern can be classified into weak (desorption at 100–200 °C), medium (200–400 °C) and strong (400–600 °C) acid sites. Total acidity is also shown as the sum of amount of ammonia desorbed from the entire temperature region. The amount of ammonia desorbed at 100 °C may contain some amount of physisorbed ammonia too. From Table 2, it is revealed that pure titania possesses comparatively lower amount of acid sites. Considerable enhancement in the surface acidity was observed upon metal modification. The TPD data of transition metal modified systems show a gradual increase in the

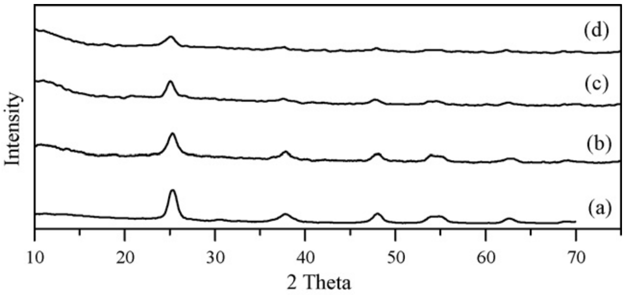

Fig. 1. XRD profiles of (a) Ti, (b) TiCr2, (c) TiCr6 and (d) TiCr10.

Table 1
Surface parameters of the prepared systems

Catalyst	Composition (at.%)		BET surface area (m^2/g)	Pore volume ($\times 10^{-6}$ m^3/g^{-1})	Crystallite size ($\times 10^{-9}$ m)
	Ti	Metal			
Ti	100		79	0.11	8.6
$TiMo_2$	99.0	1.0	104	0.13	9.0
$TiMo_6$	96.1	3.9	117	0.24	7.7
$TiMo_{10}$	94.1	5.9	117	0.17	6.7
$TiCr_2$	97.0	3.0	91	0.17	8.6
$TiCr_6$	90.9	9.1	102	0.23	7.4
$TiCr_{10}$	86.6	13.5	112	0.21	6.0
TiW_2	99.0	1.0	111	0.25	9.5
TiW_6	97.1	2.9	112	0.28	8.5
TiW_{10}	96.5	3.5	120	0.28	6.2

Table 2
Influence of transition metal on the acid site distribution of titania

Catalyst	Amount of ammonia desorbed (mmol/g)			
	Weak (100–200 °C)	Medium (200–400 °C)	Strong (400–600 °C)	Total (100–600 °C)
Ti	0.20	0.12	0.03	0.27
$TiMo_2$	0.19	0.23	0.08	0.42
$TiMo_6$	0.60	0.33	0.13	0.89
$TiMo_{10}$	0.57	0.52	0.20	1.13
$TiCr_2$	0.26	0.18	0.14	0.48
$TiCr_6$	0.33	0.20	0.31	0.69
$TiCr_{10}$	0.43	0.05	0.27	0.73
TiW_2	0.19	0.09	0.12	0.39
TiW_6	0.17	0.23	0.20	0.45
TiW_{10}	0.45	0.13	0.12	0.64

acidity with the increase of the percentage of the metal incorporated. The combination of titania with transition metals probably generates stronger acid sites and more acidity as compared with the separate components. The nature of acid sites is greatly altered by the nature of the ions incorporated into the lattice. The change in the distribution may be a coupled effect of the crystalline as well as structural changes. The change in the acid strength distribution for the different systems may be related to the interaction of the added metal cations with titania.

The thermodesorption study of 2,6-dimethylpyridine was carried out with an intention of obtaining a comparative evaluation of the Brönsted acidity in the samples. Upon thermal treatment, 2,6-DMP gets desorbed at different temperature ranges depending on the strength of the acidic sites on which they are adsorbed. 2,6-dimethyl pyridine cannot coordinate to Lewis acid sites because of steric hindrance [19]. From Table 3, it can be concluded that the relative amounts of Bronsted acid sites increases by the incorporation of transition metals into the crystal lattice of titania. Thus a clear relationship was found between the metal content and the acid strength as well as density; both increased with the increase of metal content. The highest Bronsted acidity is shown for molybdena incorporated titania systems. A Bronsted acid site also requires a hydroxyl group, and it is postulated that the number of sites was limited by the availability of hydroxyl species.

Cumene cracking reaction is a test reaction for the simultaneous determination of Bronsted as well as Lewis acidity (Fig. 2). The major reactions occurring during cumene conversion may be grouped into dealkylation (cracking) and dehydrogenation. Dealkylation of cumene yields benzene and propene whereas dehydrogenation gives α-methyl styrene [20]. Another possibility is the cracking of the alkyl chain to give ethylbenzene. Ethylbenzene on dehydrogenation give styrene. The cumene conversion reaction can be schematically represented as shown in Fig. 3. On all the prepared catalysts, cumene conversion resulted in the formation of dehydrogenation as well as cracking products. Table 4 represents the conversion and selectivity of different products obtained from dehydrogenation and cracking of cumene. It is observed that the selectivity to α-methyl styrene decreases with the percentage of the metal

Table 3
Influence of transition metals loaded on Bronsted acid site distribution of titania from 2,6-DMP desorption studies

Catalyst	Relative weight (%) loss of 2,6-DMP desorption			
	Weak (300–400 °C)	Medium (400–500 °C)	Strong (500–600 °C)	Total (300–600 °C)
Ti	0.56	0.38	0.09	1.03
$TiMo_2$	3.50	3.62	0.41	7.53
$TiMo_6$	0.74	3.43	3.93	8.10
$TiMo_{10}$	3.54	3.64	0.95	8.13
$TiCr_2$	2.71	2.77	0.50	5.98
$TiCr_6$	3.57	3.57	0.42	7.56
$TiCr_{10}$	3.72	2.83	0.49	7.04
TiW_2	2.53	1.37	0.52	4.78
TiW_6	3.16	2.73	0.19	6.08
TiW_{10}	2.78	1.92	1.28	5.98

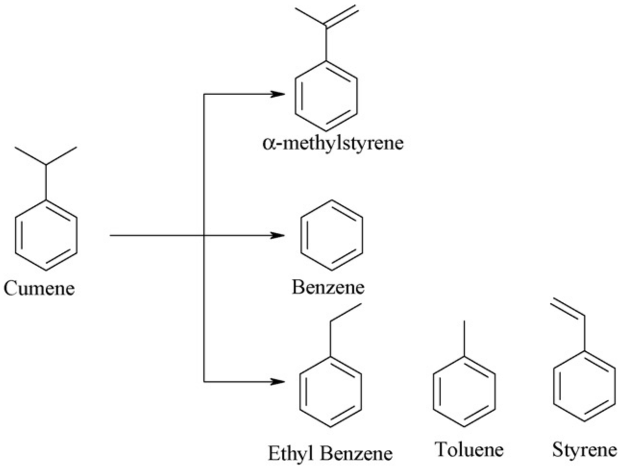

Fig. 2. General scheme of cumene cracking reaction.

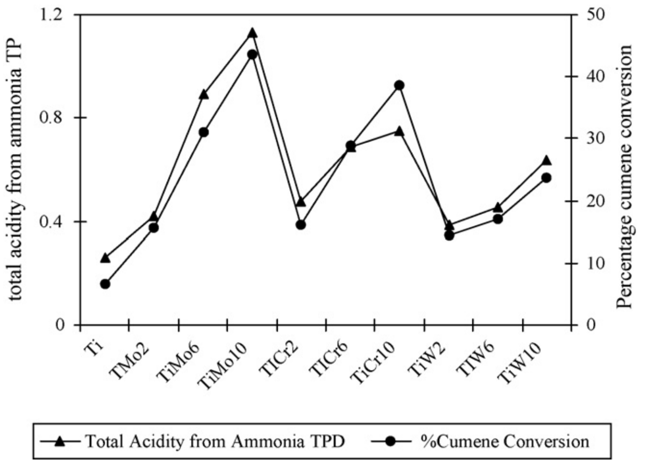

Fig. 3. Correlation between total acidity obtained from ammonia TPD and percentage cumene cracking reaction.

Table 4
Influence of transition metals in the cumene conversion

Catalyst	Conversion of cumene (wt%)	Selectivity (%)	
		α-Methyl styrene	Benzene
Ti	6.6	35.4	8.0
$TiMo_2$	15.6	17.5	77.8
$TiMo_6$	31.0	12.1	84.6
$TiMo_{10}$	43.6	7.5	86.4
$TiCr_2$	16.0	47.0	52.0
$TiCr_6$	29.0	41.6	55.4
$TiCr_{10}$	38.7	41.1	59.4
TiW_2	14.5	48.2	50.8
TiW_6	17.2	38.2	61.7
TiW_{10}	23.6	36.8	62.1

Amount of the catalyst: 0.5 g, temperature: 400 °C, duraton: 2 h, flow rate: 4 ml/h.

incorporated. The cracking products are maximum over the catalyst having the highest percentage of the incorporated metal, indicating the presence of more Bronsted acid sites.

From 2,6-dimethyl pyridine desorption studies, it is seen that molybdena incorporated systems are having comparatively high abundance of Bronsted acid sites. This results support the benzene selectivity obtained from cumene cracking reaction. There is a direct relationship between the percentages of metal incorporated as well as the percentage cumene conversion. As the percentage of the metal loaded increases, a regular increase in the percentage benzene selectivity with a concomitant decrease in the α-methyl styrene selectivity is observed. Thus good correlations obtained between the acidity of the catalysts measured via independent techniques, which is shown in Figs. 3 and 4.

In the catalytic dehydrogenation of cyclohexane, benzene and minor amounts of cyclohexene is obtained. A very small percentage of other products like methyl cyclopentenes are also formed besides the selective formation of benzene. From Table 5, it is revealed that pure titania gave only a very low conversion under the specified reaction conditions. An interesting observation is the enhanced benzene selectivity of the reaction. Titania alone is efficient enough to give a good selectivity of benzene during the reaction. Among the various metal incorporated systems, a notable observation was the increase in percentage conversion with the increase in the metal content. Among the different transition metals, molybdenum incorporated systems are having highest catalytic activity in dehydrogenating cyclohexane with a better selectivity of benzene. This can be attributed to the enhanced amount of acidic sites present in the catalyst systems. A good correlation is obtained between the total acidity obtained from ammonia TPD and the percentage cyclohexane conversion among the various catalyst systems. Fig. 5 illustrates that the total acidity plays a decisive role in the dehydrogenation of cyclohexane.

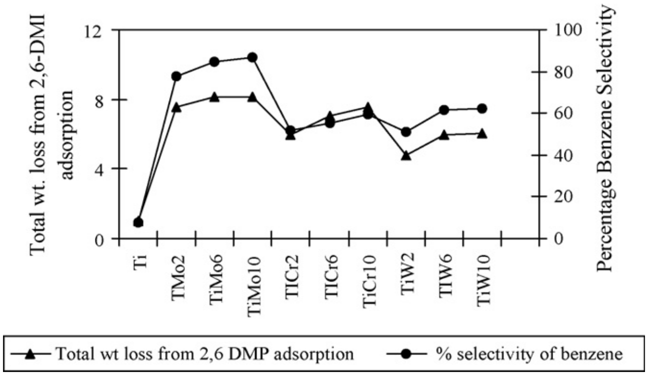

Fig. 4. Correlation between Bronsted acidity obtained from thermodesorption of 2,6-DMP and percentage benzene selectivity from cumene cracking reaction.

Table 5
Influence of transition metals on the dehydrogenation of cyclohexane

Systems	% cyclohexane conversion	Selectivity (%)		
		Benzene	Cyclohexene	Others
Ti	11.0	91.4	7.6	1.0
$TiMo_2$	22.7	95.4	4.1	0.6
$TiMo_6$	40.4	93.3	5.7	1.0
$TiMo_{10}$	55.3	95.6	3.0	1.4
$TiCr_2$	29.6	95.3	3.0	1.7
$TiCr_6$	35.3	92.1	6.7	1.2
$TiCr_{10}$	68.0	96.2	2.1	1.7
TiW_2	22.2	80.5	18.4	1.1
TiW_6	25.5	77.4	19.0	3.6
TiW_{10}	30.3	71.0	25. 6	3.4

Catalyst weight: 0.5 g, duration: 1 h, flow rate: 3 ml/h, temperature: 475 °C.

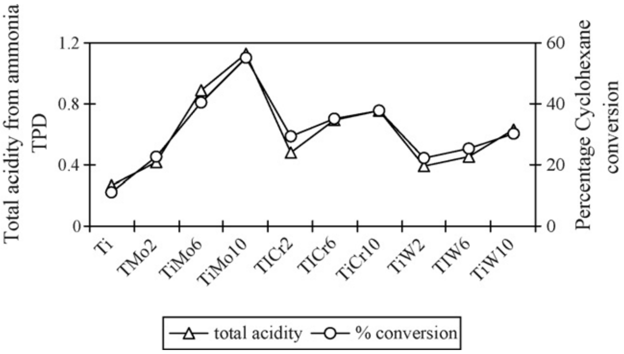

Fig. 5. Correlation between the percentage cyclohexane conversion and total acidity obtained from NH_3 TPD in transition metal modified TiO_2.

4. Conclusions

Experimental results in this work demonstrate that the type of precursor plays an important role in the preparation of titania as well as their transition metal modified analogues. The preparation of the catalysts through colloidal sol–gel route overcomes the limitation of the sol–gel technique, which is mainly the high cost of alkoxide precursor. The anatase is the predominant phase in both pure as well as transition metal modified titania systems. There is a considerable enhancement in the surface acidity upon transition metal incorporation. The results obtained from the different techniques used in the determination of surface acidity such as temperature programmed desorption of ammonia, thermodesorption studies using 2,6-dimethyl pyridine and test reaction such as cumene cracking correlate fairly well. This highlights the reliability of the different techniques. The total surface acidity of the prepared catalyst systems plays an important role in determining the catalytic activity towards the dehydrogenation of cyclohxane.

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