Influence of alkaline earth metal on acid–base characteristics of V_2O_5/MO–TiO_2 (M = Ca, Sr and Ba) catalysts

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Abstract

The influence of various alkaline earth metal oxides (CaO, SrO and BaO) on the acid–base properties of TiO_2 and the dispersion behaviour of V_2O_5 over MO−TiO_2 (M = Ca, Sr and Ba) have been investigated systematically. The MO−TiO_2 binary oxides (1:1 molar ratio) were synthesized by adopting a co-precipitation method from the corresponding chloride precursors by in situ hydrolysis with urea and calcined at various temperatures from 723 to 1073 K. A nominal 10 wt.% V_2O_5 was deposited over the calcined (773 K) MO−TiO_2 supports by a wet impregnation method. The synthesized catalysts were characterized using X-ray diffraction (XRD), Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS), thermogravimetry–differential thermal analysis (TG–DTA) and BET surface area techniques. The MO−TiO_2 composite oxides exhibited reasonably high-specific surface area and high-thermal stability retaining titania-anatase phase up to 1073 K treatment temperature. The impregnated V_2O_5 over MO−TiO_2 binary oxides remained in a highly dispersed form. A preferential interaction between the basic MO and the dispersed V_2O_5 lead to the formation of MVO_3 at higher calcination temperatures. The surface acid–base properties of the prepared samples were examined for the conversion of cyclohexanol to cyclohexanone/cyclohexene under normal atmospheric pressure. All the investigated samples were found to exhibit interesting catalytic properties.

1. Introduction

Oxidation catalysts are always the subjects of interest because of their significant role both in the production and destruction of desired and undesired products respectively by oxidation reactions, partial or complete [1–3]. In this context, considerable attention has been focused on the synthesis, characterization and evaluation of various new catalyst systems for increasing newer applications. Among industrial oxidation catalysts, supported vanadium oxides share an important position due to their efficiency in several heterogeneous catalytic processes including *ortho*-xylene partial oxidation, ammoxidation of hetero-aromatic compounds, selective catalytic reduction (SCR) of NO$_x$, oxidative dehydrogenation of alkanes and so on [1–9]. Among supported vanadium oxide catalysts, the V_2O_5/TiO_2 combination has gained paramount importance.

Titania (TiO_2) has been widely studied because of its extensive use as a support as well as catalyst due to its inherent characteristics such as high-dielectric constant, better oxygen sensitivity and photoelectric properties [10,11]. Orthorhombic brookite, tetragonal anatase and tetragonal rutile are the three natural phases reported for titania crystallization [12]. Some properties of TiO_2 are very sensitive to its structure. Anatase phase is chemically and optically active making it suitable for catalysts and supports. Rutile phase is known to bear highest refractive index and UV-absortivity for which it finds uses in paints, pigments and UV-absorbents [12]. For most commercial SCR and selective oxidation applications, TiO_2 has been employed as the support on which the active chemical species including V_2O_5, WO_3 and MoO_3 were impregnated [13,14]. Since anatase is a metastable titania polymorphs, it tends to transform into rutile phase decreasing its surface area thereby inducing a loss of catalytic activity [13]. The anatase to rutile transformation has been reported to be a major cause of deactivation in titania-based catalysts [15]. The stabilization of TiO_2-anatase phase can be achieved by changing its surface or bulk composition by incorporating various additive atoms [12]. Such combination

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catalysts for example, $V_2O_5/Ga_2O_3-TiO_2$, $V_2O_5/La_2O_3-TiO_2$ and $V_2O_5/CaO-TiO_2$ possessing acid–base and redox characteristics were reported to exhibit better catalytic properties for various reactions [16–18]. Addition of CeO_2 and CuO to TiO_2 matrix has also been reported to improve the thermal stability and specific surface area of the titania thereby inducing better catalytic activity [12].

The present investigation was undertaken against the above background. In this systematic study the influence of same group alkaline earth metal oxides namely CaO, SrO and BaO on the phase stability and catalytic properties of TiO_2 has been examined. A homogeneous co-precipitation method was adopted to make the desired $MO-TiO_2$ binary oxide combinations (M = Ca, Sr and Ba; 1:1 molar ratio) and calcined at various temperatures from 723 to 1073 K. A nominal 10 wt.% V_2O_5 was also deposited over the calcined (723 K) $MO-TiO_2$ supports and subjected to various calcination temperatures. Physicochemical properties of all synthesized catalysts were investigated by means of X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, differential thermal analysis and BET surface area techniques. To assess the acid–base properties, conversion of cyclohexanol to cyclohexanone and cyclohexene was performed. The competitive dehydration/dehydrogenation reaction of cyclohexanol is considered as a universal test reaction for evaluation of acid–base properties of various solid catalysts [19–21]. It is a known fact that both surface acid–base characteristics and redox properties of catalysts greatly influence the selective oxidation or oxidative dehydration reactions of commercial significance [22,23].

2. Experimental

2.1. Catalyst preparation

All mixed oxide supports (1:1 molar ratio based on oxides) investigated in the present study were prepared by a homogeneous co-precipitation method using urea as hydrolyzing agent. An appropriate amount of cold $TiCl_4$ (Fluka, AR grade) was initially digested in cold concentrated HCl and subsequently diluted with deionized water. To this aqueous solution the required quantity of $BaCl_2 \cdot 2H_2O$ (Loba Chemie, GR grade) or $SrCl_2 \cdot 6H_2O$ (Loba Chemie, GR grade) or $CaCl_2 \cdot 2H_2O$ (Loba Chemie, GR grade), dissolved separately in deionized water, was added. An excess solid urea (Loba Chemie, AR grade) with a metal to urea molar ratio of 1:2.5 was also added to this mixture solution for better control of pH and heated to 368 K with vigorous stirring. After about 6 h of heating, a white precipitate was gradually formed as the urea decomposition progressed to a certain extent. In order to make sure complete precipitation, the pH of the solution was increased further by adding dilute ammonia externally. The precipitate was heated for 18–24 h and kept aside for 4 days to facilitate aging. The co-precipitate thus obtained was filtered off and washed thoroughly with deionized water until free from anion impurities. The obtained cake was oven dried at 383 K for 12 h and calcined at various temperatures from 723 to 1073 K for 6 h in air atmosphere.

A nominal 10 wt.% V_2O_5 was deposited on various mixed oxide supports by adopting a wet impregnation method. To impregnate V_2O_5, the requisite quantity of ammonium metavanadate (Fluka, AR grade) was dissolved in aqueous oxalic acid solution (2 M). To this clear solution, the finely powdered calcined (723 K) mixed oxide support was added. The excess water was evaporated on a water-bath with constant stirring and the resulting material was oven dried at 383 K for 16 h and subsequently calcined at various temperatures from 723 to 1073 K for 5 h in a closed muffle furnace in flowing oxygen atmosphere. The rate of heating (as well as cooling) was always maintained at 10 K min^{-1}. In the text all the catalysts containing 10 wt.% V_2O_5 were labeled as VCT ($V_2O_5/CaO–TiO_2$), VST ($V_2O_5/SrO–TiO_2$) and VBT ($V_2O_5/BaO–TiO_2$), and the pure supports as CT (CaO–TiO_2), ST (SrO–TiO_2) and BT (BaO–TiO_2), respectively for the sake of convenience during discussion.

2.2. Catalyst characterization

X-ray powder diffraction patterns were recorded on a Siemens D-5000 diffractometer, using monochromated Cu Kα (0.15418 nm) radiation and standard recording conditions. The XRD phases present in the samples were identified with the help of the ASTM powder data files. The Raman spectra were recorded at ambient temperature on a Nicolet FT-Raman 960 spectrometer using the 1064 nm exciting line (~600 mV) of a Nd:YAG laser (Spectra Physics). The wavenumber values obtained from spectra are accurate to within 2 cm^{-1}. The XPS measurements were made on a VG Scientific Lab 210 spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source. Charging of catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. The XPS analysis was done at room temperature and pressures typically in the order of less than 10^{-6} Pa.

The TG–DTA analysis was performed on a Mettler Toledo TG–SDTA apparatus. Uncalcined samples were heated from ambient temperature to 1173 K under nitrogen flow. The sample weight was ca. 12 mg and the heating rate was 10 K min^{-1}. The specific surface areas of the samples were determined on a Micromeritics Gemini 2360 instrument by N_2 physisorption at liquid nitrogen temperature. Before measurements, the samples were oven dried at 393 K for 12 h and flushed in situ with He gas for 2 h.

2.3. Catalytic activity

To study the acid–base properties of various samples, the vapour phase reaction of cyclohexanol to cycohexanone/cyclohexene was investigated under normal atmospheric pressure, in a down flow fixed bed differential micro-reactor, at different temperatures from 623 to 723 K. For each run ~2 g of catalyst sample was secured between two plugs of quartz wool inside the glass reactor and above the catalyst bed filled with glass chips in order to act as preheating zone. The reactor was placed vertically inside a tubular furnace, which can be heated electrically. The reactor temperature was monitored by