ABSTRACT

Homogeneous catalysts such as sulfuric acid, hydrochloric acid, phosphoric acid, etc., are frequently used in the chemical industry. However these catalysts are environmentally hazardous, toxic, corrosive and non-recyclable. During this adverse situation in the chemical industry, porous materials have emerged as an alternative option for the chemical industry due to their non toxicity, non corrosive nature, possibility of reusing and importantly their ecofriendly nature. However, the use of these porous materials in the chemical industry is limited due to low conversion rate and yield compared to conventional catalysts. Zeolites, crystalline aluminosilicates, emerged as a potential replacement for conventional catalysts due to their acidic nature.

The discovery of aluminophosphate molecular sieves (zeotype materials), known as AlPOs, made many researchers to widen their view in relation to the framework (neutral) flexibility in accommodating metal ions (especially transition metal ions) in order to alter the acidic property of AlPOs for specific catalytic applications. Moreover, isomorphously substituted AlPOs found applications in aerial oxidations of linear and cyclic hydrocarbons using molecular oxygen and as suitable host systems for the fabrication of monosized single-walled carbon nanotubes. Compared to zeolites, AlPO molecular sieves possess a larger variety of acid sites and broader acid sites distribution. Because of these valuable applications, metaloaluminophosphates (MeAPOs) become one of the important materials for research in heterogeneous catalysis and porous materials field. However,
notwithstanding the numerous studies focusing on AlPOs, since their
discovery in early 1980s, the oxidation state of transition metal ions, their
coordination state and framework incorporation in AlPOs are still
controversial. This present study focuses on the synthesis of CoAPO-5,
CoAPO-11, VAPO-5, VAPO-11, FeAPO-5 and TAPO-5. General and
spectroscopic characterization of the above materials was performed for a
better understanding of the surface chemistry and nature of the transition
metal ions focusing on the following: oxidation state, coordination
environment, framework location, isomorphous substitution, acid strength and
nature of the redox centres.

CoAPO-5 and CoAPO-11 were synthesized hydrothermally using
aluminium isopropoxide (CoAPO-5), aluminium oxide hydroxide
(CoAPO-11), phosphoric acid, cobalt nitrate as the precursors for Al, P and
Co respectively. Triethylamine (CoAPO-5) and dipropylamine (CoAPO-11)
were used as structure directing agents. The synthesized materials were
characterized by XRD, TEM, SEM-EDX and volumetric analysis.
Spectroscopic characterization of CoAPO-5 and CoAPO-11 was performed
by DRS-UV-Vis and FT-IR spectroscopy with CO and NO as probe
molecules. The physico-chemical characterization revealed that the
synthesized materials possess good morphology, absence of structural
degradation and non-framework metal oxide species. The presence of
Co$^{2+}$/Co$^{3+}$ redox centres and their reversibility was monitored by means of
DRS-UV-Vis and FT-IR spectroscopy. DRS-UV-Vis spectra support the
hypothesis that only a small fraction of Co$^{2+}$ ions is converted into Co$^{3+}$
during oxidation. The NO interaction also identified unoxidised framework
Co$^{2+}$ sites with strong Lewis character in both samples by using FT-IR
spectroscopy. NO oxidation products were observed on redox treated CoAPO-11, while not in CoAPO-5. The presence of Co\(^0\) metallic clusters (not detectable by TEM) on reduced CoAPO-5 (not in CoAPO-11) was shown by CO adsorption as testified by an intense band at 2047 cm\(^{-1}\), with minor components at 2008 and 1990 cm\(^{-1}\) assigned to the formation of Co\(^0\) (CO)\(_n\) (n = 2 or 4) and (Co\(^0\))\(_n\) CO (n = 2, 3 bridged complexes) respectively. Higher concentration and dispersion of accessible Co\(^{2+}\) ions was found in CoAPO-11 with respect to CoAPO-5.

VAPO-5 and VAPO-11 were synthesized hydrothermally using aluminium isopropoxide (VAPO-5), aluminium oxide hydroxide (VAPO-11), phosphoric acid and vanadyl sulfate as the precursors for Al, P and V respectively. Triethylamine (VAPO-5) and dipropylamine (VAPO-11) were used as structure directing agents. The prepared materials were characterized by XRD, SEM-EDX and volumetric analysis. Spectroscopic characterization of VAPO-5 and VAPO-11 using CO and NO as probe molecules was carried out by DRS-UV-Vis and FT-IR spectroscopy. Raman spectroscopy was also applied to study these materials. High crystallinity, homogeneous morphology and distribution of vanadium ions were found by physico-chemical characterization techniques. Two monomeric Td V\(^{5+}\) ions, that can be reversibly transformed into Td V\(^{4+}\) ions upon reduction, were found by DRS-UV-Vis studies. No evidence was found for the presence of unoxidised species in both samples, which is not the case in other low oxidation state transition metal ion MeAPOs samples. Isolated oxo-vanadate species were observed by Raman spectroscopy, more abundant in the calcined VAPO-5 than in calcined VAPO-11. FT-IR spectroscopy of CO and NO interactions on reduced VAPO-5 and VAPO-11 samples also support the presence of two distinct framework V\(^{4+}\) sites that transform into V\(^{5+}\) upon oxidation. Neither
CO (at 85 K) nor NO (at RT) adsorb on the oxidized sample because of the coordinative saturation of V$^{5+}$ ions and the covalent character of the V$^{5+}$=O bond. Di-nitrosylic complexes were found in the ranges 1905-1756 and 1835-1693 cm$^{-1}$ (1906-1752 and 1832-1681 cm$^{-1}$ on VAPO-11) on two distinct V$^{4+}$ sites. Carbonyl bands were found at 2192 and 2184 cm$^{-1}$ due to the formation of carbonyl complexes on two different V$^{4+}$ sites. No evidence was found for the presence of V$^{3+}$ ions in neither VAPO-5 nor VAPO-11 upon reduction. More accessible and dispersed V sites are evident in VAPO-11 as compared to VAPO-5.

FeAPO-5 was synthesized hydrothermally using aluminium oxide hydroxide, phosphoric acid and ferrous acetate as the precursors for Al, P and Fe respectively, with triethylamine as the structure directing agent. The synthesized FeAPO-5 was characterized by XRD, SEM-EDX and volumetric analysis. Spectroscopic characterization of FeAPO-5 was performed by DRS-UV-Vis and FT-IR spectroscopy with CO and NO as probe molecules. XRD data of FeAPO-5 were consistent with the corresponding AlPO-5 structural patterns and indicated that the material was well crystallized. SEM-EDX studies showed homogeneous nature and distribution of Fe ions. Volumetric analysis displayed high surface area in agreement with previous reports. The state of Fe ions in FeAPO-5 was studied with DRS-UV-Vis and FT-IR spectroscopy using CO and NO as probe molecules. DRS-UV-Vis spectra and the slightly reddish colour of the calcined sample support the presence of a small amount of extra framework Fe$_x$O$_y$ clusters. The presence of redox centres (Fe$^{2+}$/Fe$^{3+}$) and the reproducibility of the cycle was evident from DRS-UV-Vis studies. NO adsorption studies using FT-IR spectroscopy confirmed the presence of two distinct Fe$^{2+}$ sites (framework and/or defective framework) in the sample. Bands related to di-nitrosylic complexes with two
distinct $\text{Fe}^{2+}$ ions were found at 1900-1797 and 1840-1737 cm$^{-1}$. CO interaction leads to the formation of $\text{Fe}^{3+}(\text{CO})$ and $\text{Fe}^{2+}(\text{CO})$ adducts at 2225 and 2177 cm$^{-1}$ respectively. The formation of nitrosyl and carbonyl complexes with Fe centres with coordinative vacancies was also evident by DRS-UV-Vis spectroscopy with NO and CO as probe molecules. Presence of a fraction of unoxidised $\text{Fe}^{2+}$ ions in FeAPO-5 was apparent during spectroscopic characterization.

TAPO-5 was synthesized hydrothermally using aluminium oxide hydroxide, phosphoric acid and titanium isopropoxide as the precursors for Al, P and Ti respectively. Triethylamine was used in the synthesis as the structure directing agent. The synthesized materials were characterized by XRD, SEM-EDX and Volumetric analysis. Spectroscopic characterization of TAPO-5 was carried out by DRS-UV-Vis and FT-IR spectroscopy with CO and NO as probe molecules. XRD patterns and SEM images revealed the well ordered structure and homogeneous nature of the crystals and aggregates without any detectable extra phase. High surface area and homogeneous distribution of Ti ions in the material were accounted by volumetric and EDX analysis of TAPO-5. DRS-UV-Vis spectra disclosed the presence of symmetrical Td $\text{Ti}^{4+}$ sites and small Ti oligomers and/or dimers. The existence of redox centres ($\text{Ti}^{4+}/\text{Ti}^{3+}$) in TAPO-5 was also ascertained for the first time by DRS-UV-Vis studies. FT-IR spectroscopy identified the presence of strong $\text{Ti}^{4+}$ Lewis acid centres in TAPO-5 using CO and CD$_3$CN as probe molecules. CO interaction leads to the formation of bands at 2188 and 2185 cm$^{-1}$ related to $\text{Ti}^{4+}$ and $\text{Ti}^{3+}$ sites. On the contrary the observed band at 2310 cm$^{-1}$ related to CD$_3$CN adsorption was assigned to CN interaction with $\text{Ti}^{4+}$ Lewis acid sites in TAPO-5, providing no information about the presence of $\text{Ti}^{3+}$ sites. CO is thus found to be an useful probe in monitoring the oxidation state of transition metal ions in TAPO-5.