ABSTRACT

Chemical industry is one of the most important manufacturing industries. A great variety of products is synthesized in an industry, which can be scaled from simple to complex. The major challenge in the present scenario lies in the development of new methods for clean production of chemicals, which is termed as green chemistry. Microporous zeolites are among the best known and most widely applied catalyst for fine chemical synthesis. Their uniform pore sizes with molecular dimension, good stability, selectivity and activity are due to their crystallinity. The possibility of incorporating heteroatoms into the structure and their ion exchange capacities make zeolites unique materials in catalytic processes. After the first reports on the introduction of M41S family of ordered mesoporous silicas at the beginning of 1990s, the synthesis of advanced mesoporous materials has undergone explosive growth.

MCM-41 possesses a porous system consisting of a hexagonal array of channels with diameter varying from 15 to 100 Å. It has good thermal stability in air and water vapor during hydrothermal treatment. Other M41S family related mesoporous materials such as MCM-48 and MCM-50 possess cubic and lamellar mesostructure respectively. SBA-1 has three dimensional cubic structure of uniform pore size. SBA-15 is a highly ordered, two-dimensional hexagonal mesoporous silica.

KIT-6 is a new type of mesoporous material with 3-D cubic structure. It has large pores with thick wall, high hydrothermal stability, high
surface area and large pore volume. KIT-6 structure consists of interpenetrating bicontinuous network of channels such as those found in MCM-48. In contrast to MCM-48, the intertwined systems of relatively large channels in KIT-6 are connected through irregular micropores present in the mesopore walls analogous to those in SBA-15. These properties have attracted increasing attention for potential use as catalyst, adsorbent, host for nanostructure and hard template for the fabrication of nano-objects. KIT-6 is used as a hard template in the preparation of highly ordered mesoporous carbon, carbon nitride and metal oxides such as CeO₂, WO₃, Co₃O₄, SnO₂ and Cr₂O₃ for many applications. Incorporation of metal ions in the silicate framework becomes necessary for their use in catalysis because of the limited applications of mesoporous silica.

The present work focuses on the synthesis, incorporation, characterization and catalytic evaluation of Al-KIT-6 and Ce-KIT-6 molecular sieves. The catalytic performance of these materials has been evaluated in the liquid phase and in the vapor phase reactions. Mesoporous Al-KIT-6 with Si/Al ratios of 20, 30, 40, 50, 100 and 150 and Ce-KIT-6 with Si/Ce ratios of 5, 10, 20, 50, 100 and 150 were synthesized hydrothermally using tetraethylorthosilicate, aluminium isopropoxide and cerium nitrate as the sources for Si, Al and Ce respectively.

The synthesized materials were characterized by low angle XRD, ICP-AES, FT-IR, TG-DTG, Nitrogen adsorption studies, pyridine adsorbed DRIFT-IR, SEM and HR-TEM techniques. The physico-chemical characterization revealed that the synthesized materials possess good morphology. Mesoporous Al-KIT-6 exhibited good phase purity from XRD
analysis. The unit cell parameters were calculated from XRD data. ICP-AES analysis indicated that Si/Al ratios are close to the expected stoichiometry based on the composition of the synthesis gel. The surface area of the catalysts decreased with increase of aluminium content and it is in the range 667-890 m$^2$/g. The high quality cubic Ia3d silica product was judged by HR-TEM image. The nature and strength of acid sites of the catalysts were probed by pyridine adsorbed DRIFT spectra. The calcined Al-KIT-6 materials showed highly ordered cubic Ia3d mesostructure and possess both Bronsted and Lewis acid sites with medium acidity.

The catalytic activity of Al-KIT-6 materials was examined in the vapor phase acylation of phenol using acetic acid as the acylating agent. The influence of reaction parameters such as reaction temperature, reactant feed ratio, WHSV and time-on-stream was studied over Al-KIT-6 (40) and the results were correlated with physico-chemical characteristics of the catalysts. All the catalysts were found to be active in the formation of phenyl acetate with high selectivity. The formation of coke was not significant at any temperature. The time-on-stream study revealed steady conversion of phenol (80%) and steady selectivity to phenyl acetate (90%) during the entire period. The activity of the catalysts followed the order: Al-KIT-6 (20) > Al-KIT-6 (30) > Al-KIT-6 (40) > Al-KIT-6 (50) > Al-KIT-6 (100) > Al-KIT-6 (150). The selectivity of phenyl acetate was almost the same over all the catalysts but the selectivity of o-HAP over Al-KIT-6 (40) was slightly lower than others.

The catalytic activity of Al-KIT-6 materials with different Si/Al ratios has been evaluated in the acylation of isobutylbenzene with acetic
anhydride in the liquid phase. Acylation of isobutylbenzene over Al-KIT-6 (20) was carried out at 60, 80, 100, 120 and 140 °C with a feed ratio (isobutylbenzene : acetic anhydride) 1:3 for 12 h. The products were 4-AIBB and 2-AIBB. The conversion increased with increase in temperature from 60 to 100 °C but decreased thereafter. The reaction parameters were optimized to obtain high selectivity of the desired product with maximum isobutyl benzene conversion. Al-KIT-6 (20) has shown high conversion (72%) of isobutylbenzene and very high selectivity (94%) of 4-acyl isobutylbenzene.

Ce-KIT-6 with different Si/Ce ratio was synthesized using triblock copolymer P123 as the structure directing agent, n-butanol as co-solute, tetraethylorthosilicate (TEOS) and cerium nitrate as the sources for silicon and cerium respectively. Ce-KIT-6 materials were characterized by low angle XRD, ICP-AES, FT-IR, Nitrogen adsorption studies, TG-DTG, DRS-UV-vis, XPS, SEM and HR-TEM techniques. The small-angle powder XRD patterns of calcined Ce-KIT-6 materials showed a phase that can be indexed to cubic Ia3d. ICP-AES analysis indicated composition of the synthesis gel. The thermal stability of the synthesized materials was evaluated using TG-DTG. The DRS-UV-vis spectra of Ce-KIT-6 samples showed two distinct absorption bands with maximum at 265 and 300 nm corresponding to the charge transfer transition of O²⁻ to Ce³⁺ and Ce⁴⁺ respectively. Their intensity increased with increase in the Ce content of the samples. The FT-IR spectra showed that the band at ca. 962 cm⁻¹ (Si-KIT-6) is shifted towards higher wave number side (970 cm⁻¹) in the case of Ce-KIT-6. The BET surface area was found to be in the range 668 - 837 m²/g. HR-TEM images presented a well ordered cubic 3-D mesoporous channels. The XPS spectra confirmed the presence of Ce³⁺ and Ce⁴⁺ in Ce-KIT-6 materials.
Ce-KIT-6 materials were examined in the liquid phase oxidation of cyclohexane using hydrogen peroxide as a sacrificial oxidant in acetic acid at 70, 80 and 90 °C. The main product was found to be cyclohexanol. This is concluded that cerium planted KIT-6 molecular sieves are effective catalysts for selective formation of cyclohexanol from cyclohexane. Although Ce⁴⁺ is shown to be the main active site to activate H₂O₂ in the reaction, their planting largely on the channel surface is an important observation. Ce³⁺ is not required for cyclohexane oxidation but their presence is unavoidable in the synthesis of Ce-KIT-6. Recyclability without leaching of cerium is also an important characteristic of the catalyst. Acetic acid as a solvent is better than either acetone or methanol, as the former gave high conversion and high selectivity to cyclohexanol. This study concluded that any quadrivalent metal ion in the framework of mesoporous material with high coordination property is capable of oxidizing cyclohexane to cyclohexanol by activating H₂O₂.

Ce-KIT-6 materials were also tested in the vapor phase dehydration of cyclohexanol from 175 to 350 °C. The main products were found to be dicyclohexyl ether and cyclohexene. Among them, the yield of the former was found to be higher than the later. The selectivity to cyclohexene was higher than dicyclohexyl ether at all temperatures illustrating that the acid sites may possess enough strength to catalyse the formation of cyclohexene. Based on the cyclohexanol conversion, the activity of Ce-KIT-6 (5) was found to be higher than others. The effect of time-on-stream on conversion and product selectivity was studied at 300 °C with a flow rate of 3 ml/h. The conversion decreased with increase in time-on-stream due to coke formation but the decrease was slow as the catalyst is mesoporous in nature.