



Short Communication

Novel analytical method for quality control of molecular sieves at manufacturing sites

Debasish Banerjee*, Ganeshan R., Narayana Rao and Ajay Kumar

Analytical Science, Corporate T&I, SABIC Research & Technology Pvt. Ltd, Bengaluru, India
debasish.banerjee@sabic.com

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Abstract

Molecular Sieves are zeolites (metal aluminosilicates) that are extensively used for drying various fluid streams industrially. They are tailored with precise pore size, and work based on size exclusion, adsorbing only those molecules, which can be fit in the pores. Depending on the pore size, applications can range from drying of unsaturated hydrocarbon streams to separation of normal paraffins from cyclic/branched ones. In this work, we have come up with a novel and easy to implement method to check the quality of molecular sieves before loading a new batch in the reactor. Since tons of these molecular sieves are loaded in the reactors, quality has to be checked beforehand. Any issue with the quality of these materials can be detrimental to the operational efficiency of the drying process, leading to the loss of time and money, if it surfaces after loading the molecular sieves in the reactor. Therefore, it is imperative to have a quality check each time a new batch of molecular sieves is loaded.

Keywords: Molecular Sieve, Aluminosilicates, Pore size, Industrial Drying, ICP-OES.

Introduction

Molecular Sieves are widely used materials for drying various liquids or gaseous streams for industrial operations^{1,2} as well as for the removal of organic pollutants from water³. Generally, these molecular sieves are zeolites⁴ having precise pore sizes. They are synthetically produced hydrated metal aluminosilicates. They can be regarded as an inorganic polymer made up of tetrahedral Silicon (Si) or Aluminum (Al) oxides⁵, where each oxygen (O) atom occupies the corner of the tetrahedron and shared between two Si/Al atoms, thus forming a three-dimensional network containing channels (or pores) of distinct size⁶ (typical range 0.3-20Å).

Molecular sieves work on the simple principle of size exclusion whereas they only adsorb molecules having effective diameter lower than the pore size, excluding bigger molecules⁷. For example, the distillation of ethanol⁸ can only form upto ~96% purity, which is not suitable for fuel grade applications^{9,10}. This is due to an azeotrope formation, which can be easily overcome by using the 3Å type molecular sieve to dry ethanol, yielding upto 99% pure ethanol¹¹. Depending on the pore size, applications can range from drying of unsaturated hydrocarbon streams¹² to separation of normal paraffins from cyclic/branched ones^{13,14}.

In this work we have come up with a novel, quick and easily implementable method (at the manufacturing site level) to check the quality of molecular sieves before loading a new batch in the reactor.

The details of molecular sieve preparation are well documented in literature¹⁵. The powdered molecular sieves are combined with a binding material to form beads, which are then dried at 600-700°F. Initially the 4Å molecular sieves were selected, which contain predominantly sodium (Na) ions in the pores (this information was confirmed by our elemental analysis, Table-1). These beads are then subjected to an ion exchange whereby about 60% of the sodium ions are replaced by potassium ions, which results in a smaller (effective) pore size of about 3Å on an average. A similar procedure is also followed to obtain 5Å molecular sieves from the 4Å ones, where almost half of the sodium ions were exchanged with calcium ions. The 13X molecular sieves¹⁶ have a different crystal structure and they have an average pore size of about 10Å¹⁷. These are extensively used for medical applications, mainly to produce oxygen-enriched air.

Material and Methods

Materials: Molecular sieve 3Å, 4Å, 5Å, 13X were purchased from Sigma-Aldrich. Other reagents were also received from Sigma-Aldrich Chemicals, namely nitric acid, Millipore water, hydrofluoric acid. Multi element ICP standard solution IV from Merck was used along with above-mentioned chemicals for sample preparation and analysis.

Analytical techniques: The various elements like sodium (Na), potassium (K), calcium (Ca), iron (Fe), magnesium (Mg) and aluminum (Al) were estimated by Spectro-Arcos ICP-OES^{18,19}, with 1400 W plasma power, radial torch, Argon coolant of

14L/min flow, Cross flow nebulizer of 0.85L/min and auxiliary flow of 1L/min. Maintaining uniformity is one of the critical processes. Hence, the molecular sieve samples were powdered with help of mortar and pestle. Wet acid digestion was used for the sample preparation. Table-1 illustrates the summary details of the ICP-OES, which was utilized for analysis.

Sample preparation: Open vessel acid digestion with mixture of nitric and hydrofluoric acids were used to dissolve the molecular sieve for the elemental compositional analysis. The powdered sample was accurately weighed (100-120 milligram) in a 100mL glass beaker in triplicate and added 10mL water, 5mL 65% suprapur Nitric acid and 3mL of 48% hydrofluoric acid. It was heated over a hot plate at 100-120°C until all the samples were dissolved. It was then made up to 50mL volume with milliQ water (stock solution). 2mL of the stock solution was diluted to 50mL volume for the measurement of major constituent and stock solution as such for the minor constituent.

Standard solution preparation: 0.5ppm, 2ppm, 5ppm, 10ppm and 15ppm of multi element standard IV were prepared by diluting the required volume of the 100-ppm stock standard to 50mL volume with 2% Nitric acid. 0.25mL, 1mL, 2.5mL, 5mL, 7.5mL of the stock 100-ppm standard was diluted to 50mL volume to get 0.5,2,5,10 and15ppm, respectively.

Method of analysis: The instrument was calibrated with the selected emission lines by spraying all the standards in the sequence as mentioned in the method giving adequate washing with deionized water between the standards. The correlation coefficient for all the analytical lines should be > 0.995. After the calibration, the sample solution was aspirated through auto sampler.

Results and discussions

The 3Å molecular sieves are inert to catalytic activity and hence, they are effectively used for removing moisture (by selective adsorption) in the petrochemical streams. However, on few occasions, it was observed that very high temperature rise occurs during the process, indicating catalytic activity of these molecular sieve samples during the moisture removal process.

The investigation of the samples showed change in the chemical composition in comparison to the standard molecular sieves. In order to qualify the material and to find the root cause of the problem, the Na/K ratio was derived from the compositional analysis of different molecular sieves received from Aldrich. The compositional analysis of various molecular sieve samples was listed in the following Table-1.

Table-1: Compositional analysis.

Sample ID	Na %		K %		Ca %		Na/K	Na/Ca
	Replicate	Average	Replicate	Average	Replicate	Average		
Mole sieve_3A	5.7	5.8	7.11	7.13	0.14	0.16	0.81	36.25
	5.91		7.14		0.17			
Mole sieve 4A	11.43	11.44	0.26	0.25	0.76	0.76	45.29	15.05
	11.46		0.25		0.75			
Molesieve-5A	3.24	3.21	0.11	0.12	3.18	3.19	27.41	1.01
	3.17		0.13		3.2			
Molesieve-13X	8.04	8.24	0.36	0.36	0.19	0.18	22.73	45.78
	8.43		0.36		0.18			

From literature^{11,20-22}, it is well understood that the different molecular sieves differ in their chemical composition. However, molecular sieves being metal aluminosilicates, they have quite complex structures with a number of elements. Hence, we came up with a novel method to determine the ratio of Sodium to Potassium (Na/K) and Sodium to Calcium (Na/Ca) to ascertain the purity and/or contamination of the different molecular sieves. Only molecular sieve 3Å has a higher amount of potassium than sodium and indeed our analysis showed that the ratio of sodium to potassium was close to 0.8. It is because about 60% of Na atoms were exchanged with K atoms, in order to convert the 4Å sieves to 3Å¹¹, whereas in other molecular sieves (4Å and 5Å), the percentage composition of potassium was much lesser, which resulted in much higher sodium to potassium (Na/K) ratio (20-45, depending on the sample). The uniqueness of the 5Å molecular sieves came from the much higher calcium composition than any other molecular sieve samples. This resulted in a sodium to calcium ratio (Na/Ca) close to one (1). This finding was also in line with literature, and is due to the fact that to obtain 5Å molecular sieves from the 4Å ones, almost half of the sodium ions were exchanged with calcium ions.

The specific property of molecular sieve 3Å for moisture absorption is mainly due to the chemicals composition leading to its physical characteristics. Any change in the chemical composition will affect the property of the molecular sieves. The Na/K ratio, obtained from the 3Å molecular sieve standards, fell in the range 0.8-0.9. Hence, aberration from this range indicated some contamination of other molecular sieves in the sample, which resulted in the increase of average pore size and ultimately resulted in some runaway reactions.

Hence we propose a unique, robust and easy to implement (even in the manufacturing site level) analytical methodology to ascertain the purity of molecular sieves. A simple ICP measurement of the sodium and potassium ion concentration and the resultant ratio is a good indicator of the effectiveness of the ion exchange process, which is responsible for the 3Å structure. Similarly, the Na/Ca ratio was found to be an excellent indicator of the purity of the 5Å molecular sieves, any deviation from desired Na/Ca ratio of 1 would indicate incomplete exchange and hence unwanted contamination. This method, if implemented to check the quality of each and every new batch of molecular sieves before loading in the reactors, can save a lot of time, effort and money since poor quality of the molecular sieves can produce different hazards including unwanted side reactions in case of improperly dried hydrocarbon streams.

Conclusion

A novel and robust methodology was developed to evaluate the quality of molecular sieves to differentiate the presence of 4Å molecular sieves in 3Å molecular sieves. This is a cost effective step before charging the reactor for moisture removal purposes

at the manufacturing site. Any issue with the quality of these molecular sieves is detrimental to the operational efficiency of the industrial gas drying operation, which may lead to the loss of time and money, if it appears after loading the molecular sieves in the reactor. Therefore, it is imperative to have a quality check each time a new batch of molecular sieves is loaded. This novel method can be a suitable solution for the in-house quality control of molecular sieves in the industrial scale.

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