Oxide and zeolitic systems of catalytic importance synthesized from fly ashes from industrial energy sector

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Significance and Relevance

For many decades the conventional energy sector operating worldwide on fossil fuels and biomass to generate energy produces fly ashes (FAs) on a massive scale. One of the most ambitious ways to efficiently manage various FAs, remaining in accordance with principles of circular economy, is their use as anthropogenic raw materials to obtain functional systems such as catalysts, supports, or sorbents. In this work we present how to apply FAs to synthesize oxide phases, active in environmentally relevant reactions, catalytic supports for metals and oxides, or 3D and 2D zeolites. The latter group is particularly interesting from a catalytic viewpoint.

Preferred and 2nd choice for the topic:
Circular economy; Sustainable and clean energy production and transport;
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral preferred or Short Oral

Introduction and Motivations

Due to the diverse composition of the starting fly ashes, obtaining the appropriate structures of the functional materials suitable for catalytic applications is quite challenging. Each synthesis must be preceded by a thorough analysis of parameters characterizing the FAs, such as e.g.: the Si/Al element content ratio, the presence of iron and carbon residues, as well as the mineral and phase compositions. Also, the ratio of the glassy to crystalline phases has to be taken into consideration. Generally, FAs are characterized by relatively high contents of silicon and aluminum. These elements occur in ashes mainly in the form of aluminosilicate glaze, which is a typical building material of spherical grains called cenospheres. Such components can also exist in crystalline form as quartz and mullite. Catalytically useful oxide phases can be extracted from FAs generated from heavy oil combustion. Cenospheres without any specific treatment or after functionalization with transition metals can be used as catalytic supports or even as catalytically active composites. While the synthesis of zeolites with 3D structures from fly ashes is relatively well mastered, obtaining layered systems (2D), with active centers located close to the external surfaces, attractive from the catalytic point of view, also accessible to more spatially demanding molecules, is much more difficult. One of our main goals was to check the possibility of synthesizing layered zeolite structures and to indicate the parameters controlling their type. Obtaining the functional, catalytically useful structures is a significant step towards both efficient fly ash valorization and more sustainable synthesis of an impressive variety of advanced materials.

Materials and Methods

FAs obtained from industrial power plants have been investigated to be applied as precursors for synthesis of catalytic materials mentioned above. All ashes were generated by coal combustion in pulverized-fuel boilers. Additionally, one type of ash generated from heavy oil combustion has also been investigated. Bare oxides, supported oxide systems containing both supports and active phases prepared from fly ashes as well as NaX, MCM-22 and 2D zeolites were synthesized by optimized wet chemistry procedures. Both FAs used for syntheses and the obtained new materials have been in-depth characterized by XRF, XRD, RS, BET, SEM, DRIFT and UV/Vis-DR techniques.

Results and Discussion

As an initial scientific task, key parameters of fly ashes, determining their possible catalytic applications were selected and analyzed in detail [1]. Structural, textural and functional characterization of FAs, chosen as starting materials, promising for synthesis of both oxide systems and zeolites, has been performed with particular attention paid to those features, which can be decisive for preparation of different classes of catalytic materials [2]. The synthetic impact of such parameters as the presence of residual carbonaceous impurities, the content ratios of the glass to crystalline phases or Si to Al have been elucidated and better understood. Moreover, the importance of such textural properties as specific surface areas, particle types and their size distributions have been analyzed in detail. Fly ashes are rich in silicon, aluminum and sometimes also in iron or titanium. Due to their attractive composition, high availability, and relatively low prices, FAs were satisfactorily tested as substrates e.g., for synthesis of NaX zeolites (3D), MCM-22P systems (being precursors of 2D zeolites of MCM-56 type) (see Fig.), as well as of the layered (2D) bifer zeolite structures [3]. Another option, practically verified in our studies, can be the oriented synthesis of heterogeneous oxide catalysts. Especially, the FAs from the combustion of heavy oil fractions, rich in such transition elements as V and Mo, are particularly attractive as precursors of catalytically active phases active in redox reaction of environmental importance. The obtained results clearly confirmed both the complex nature of the fly ashes and their evident potential to be used for synthesis of advanced materials mentioned above. In turn, bare and functionalized cenospheres have been applied as supports for copper and zinc, and tested in such environmentally sound reactions as SCR NO_x and CO_2 hydrogenation to methanol. The presented sustainable pro-ecological approach to FA valorization remains in agreement with principles of circular economy and permits to exploit high potential of fly ashes as anthropogenic raw materials of catalytic relevance.

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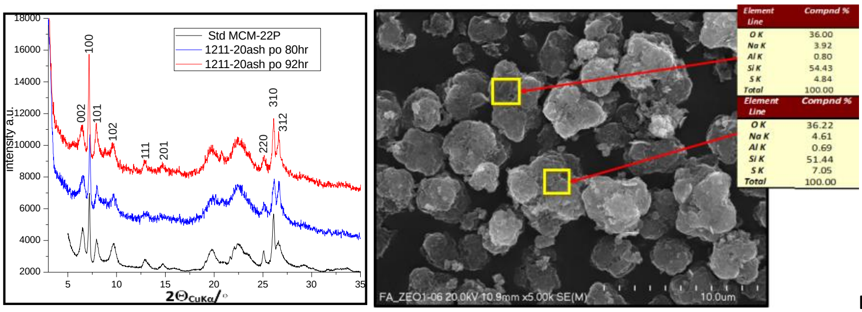

B

Figure. Structure (A) and morphology (B) of MCM-22 materials synthesized from fly ashes together with chemical composition of the selected region determined by EDX.

References

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