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Catalytic activation of OKO zeolite with intersecting pores of 10- and 12-membered rings using atomic layer deposition of aluminium†

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Tetrahedral framework aluminium was introduced in all-silica zeolite -COK-14 using Atomic Layer Deposition (ALD) involving alternating exposure to trimethylaluminium and water vapour. The modification causes permanent conversion of the originally interrupted framework of -COK-14 to a fully connected OKO type framework, and generates catalytic activity in the acid catalysed hydrocarbon conversion reaction.

Yearly, about 1 million tons of synthetic zeolites are produced in industry for catalytic applications.[1] While the Atlas of Zeolite Framework Types[2] counts over 200 framework types, only a limited number of topologies have been implemented in large scale industrial applications, *viz.* FAU, LTL, MOR, BEA, MWW, MFI, FER, AEL and TON.[1] These zeolites have a mono- or multidimensional channel system circumscribed by 12-membered rings of tetrahedra (12-MRs), or 10-MRs. While 10-MR zeolites are particularly attractive for their molecular shape selectivity, the 12-MR zeolites with their larger pores have a wider scope in acid catalysed reactions. Application limiting factors of candidate zeolites are instability and the lack of a trivalent element substituted specimen with cation exchange capacity and Brønsted acidity. Zeolites which combine 10- and 12-MR pores are of particular interest, but their number is even more limited.[3] The new interrupted all-silica -COK-14 zeolite and its fully connected form, COK-14, have such a two-dimensional intersecting 10- and 12-MR pore system (Fig. 1).[4] This zeolite with OKO framework type has been obtained by inverse sigma transformation from the parent germanosilicate UTL zeolite,[5]
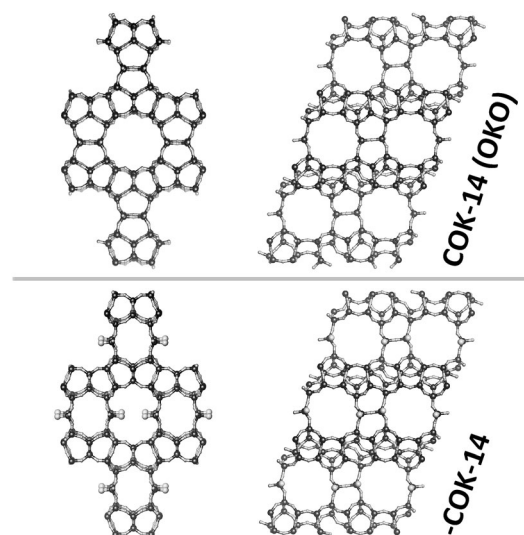

Fig. 1 Framework of COK-14 (OKO framework type) (top) and -COK-14 zeolite (bottom), viewed along the 12-MR pores (left) and 10-MR pores (right). Structural silanol groups in -COK-14 are protruding into the 12-MR channels.

and is probably isostructural to IPC-2, a zeolite made by the ADOR strategy (Assembly, Disassembly, Organization, Reassembly) departing from the same parent zeolite.[6] Degermanation of UTL zeolite to obtain -COK-14 is performed through acid leaching, which impedes aluminium incorporation in the framework because of its amphoteric behaviour.[7] While direct introduction of aluminium during synthesis is often problematic,[8] post-synthesis alumination of zeolites can offer a solution. Strategies such as treatment with an aqueous aluminate solution under hydrothermal conditions, or exposure to aluminium halide vapour have been reported in literature.[9] Among the alternative options, Atomic Layer Deposition (ALD) is gaining importance in catalysis research.[10] ALD is known as an elegant means of applying protective layers on metal nanoparticles, depositing platinum on the surface of graphene nanosheets,

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and for generating photocatalytic activity.[10,11] Aluminium ALD (Al-ALD) has been demonstrated as a method to generate acid sites in nanoporous powders.[11] Alumination of ultrastable Y zeolite and hierarchical Zeotile-4 material by Al-ALD resulted in enhanced acid catalytic activity.[11] Previous attempt to activate 10-MR silicalite-1 zeolite (MFI framework) using Al-ALD was not successful.[11] This is probably due to the pore size of silicate-1 being too narrow for adsorption of the trimethylaluminium (TMA) precursor molecule used in Al-ALD.[11] Here we report the successful introduction of tetrahedral aluminium in the all-silica -COK-14 zeolite by Al-ALD, and demonstrate the catalytic activation of OKO type zeolites for hydrocracking of *n*-decane. This is a first example of generating acid sites in a purely siliceous zeolite by Al-ALD.

The interrupted -COK-14 zeolite framework was prepared by degermanation of UTL zeolite.[4] Al-ALD was performed on -COK-14 in a high-vacuum ALD setup.[12] Experimental details are provided in the ESI.† The Al-ALD treated sample was suspended in 0.5 M NH_4Cl solution and heated under reflux for 90 minutes, washed and dried to obtain the ammonium-exchanged form.

X-ray diffraction (XRD) revealed that Al-ALD did not cause significant changes in the structure and crystallinity, and showed that the interrupted -COK-14 framework was preserved. The interrupted framework of all-silica -COK-14 can be transformed into a fully connected OKO framework of COK-14 zeolite by heating at temperatures of at least 300 °C.[4] The transformation involves reorientation and condensation of silanol groups (Fig. 1). All-silica OKO zeolite is stable only at elevated temperature in the absence of water.[4] Upon hydration and cooling the structure transforms back to the interrupted framework.

For catalytic application, an ammonium-exchanged aluminosilicate zeolite needs to be pretreated at 400 °C to obtain the acid form. XRD revealed that the ammonium-exchanged, Al-ALD treated -COK-14 zeolite after pretreatment at 400 °C was permanently transformed into fully connected COK-14 (Fig. 2a). In contrast with the parent all-silica zeolite COK-14, it did not return to an interrupted framework upon hydration. The aluminosilicate COK-14 zeolite was stable upon storage for 6 months under ambient conditions without special precaution. ^{27}Al MAS NMR revealed a distribution of aluminium coordination in the Al-ALD treated, ammonium-exchanged COK-14 sample of *ca.* 21% tetrahedral Al, *ca.* 19% pentacoordinated or distorted tetrahedral Al, and 60% octahedral extra-framework Al (Fig. 2b). According to EDX the Si/Al atomic ratio was around 50. Combining NMR and EDX data, the framework Si/Al atomic ratio was estimated to be *ca.* 240. Remarkably, introduction of such very low amounts of aluminium *via* Al-ALD is sufficient to stabilise the fully connected OKO framework.

Framework transformation from aluminosilicate -COK-14 to COK-14 has a significant influence on the porosity. Nitrogen adsorption isotherms of aluminosilicate -COK-14 and aluminosilicate COK-14 indicated a pore size enlargement from 7.2 to 7.9 Å (SF method[13]). This widening is ascribed to the annealing of the framework and the elimination of silanol groups pointing into the 12-MR pores (Fig. 1). Framework expansion by aluminium incorporation was considered to contribute less, given the small amount introduced.
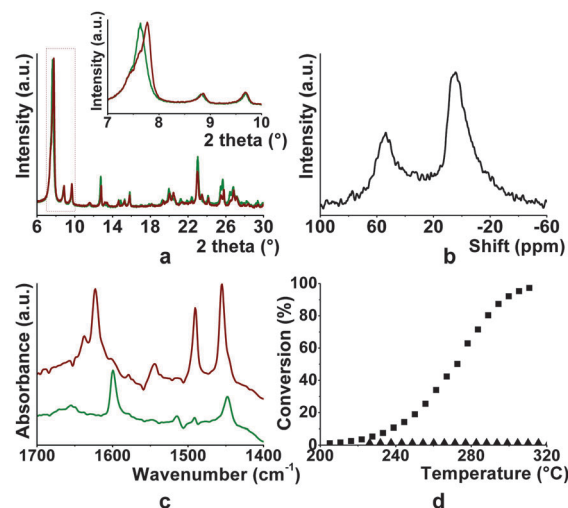

Fig. 2 (a) XRD of hydrated aluminosilicate -COK-14 before (green) and after thermal transformation to aluminosilicate COK-14 (red), (b) ^{27}Al MAS NMR spectrum of aluminosilicate COK-14, (c) FTIR spectra obtained after adsorption of pyridine on all-silica -COK-14 (green) and aluminosilicate COK-14 (red) after evacuation at 150 °C and (d) conversion of *n*-decane against reaction temperature on Pt-loaded all-silica COK-14 (▲) and Pt-loaded aluminosilicate COK-14 (■) (reaction conditions: P_{H2}/P_{C10} = 214, $W/F°$ = 980 kg s mol^{-1}, P = 0.45 MPa).

COK-14 displays a platelet crystal morphology with plates of up to 10 μm and a typical thickness of around 100 nm. The intersecting 10- and 12-MR pores of COK-14 run parallel to the sheets,[4] such that the pore system is accessible only *via* the edges of the platelets. The 10-MRs probably will be too narrow for adsorption of the TMA precursor in the Al-ALD process.[11] TMA molecules are expected to penetrate *via* the 12-MR channels. The presence of Brønsted acid sites was revealed by FTIR spectroscopy after adsorption of pyridine (Fig. 2c). Parent all-silica -COK-14 did not have any Brønsted acid sites retaining pyridine at 150 °C, as expected. In fully connected aluminosilicate COK-14 deammoniated and annealed at 400 °C, the total Brønsted acid site concentration was 6.5 mmol kg^{-1} (retaining pyridine at 150 °C), and the concentration of stronger acid sites retaining pyridine at 200 °C was 5 mmol kg^{-1}. This concentration of Brønsted acid sites probed with pyridine was about one tenth of the concentration of tetrahedral Al, which for a framework Si/Al ratio of 240 is estimated to be *ca.* 70 mmol kg^{-1}. The presence of extra-framework aluminium species, detected using ^{27}Al MAS NMR (Fig. 2b), neutralising framework charges can be responsible.

Ammonium-exchanged aluminosilicate -COK-14 was loaded with 0.5 wt% Pt *via* incipient wetness impregnation with $Pt(NH_3)_4Cl_2$. Transformation to the fully connected OKO framework after pretreatment with oxygen followed by reduction in hydrogen at 400 °C was confirmed by XRD. A uniform distribution of Pt metal particles with sizes of around 6 nm was observed on the external surface of the zeolite crystals using NanoSEM (Fig. 3).

The catalytic activity of Pt-loaded all-silica and Pt-loaded aluminosilicate COK-14 was investigated in the hydroconversion of *n*-decane. The conversion of *n*-decane is plotted against reaction temperature in Fig. 2d. Hydroisomerisation and hydrocracking of
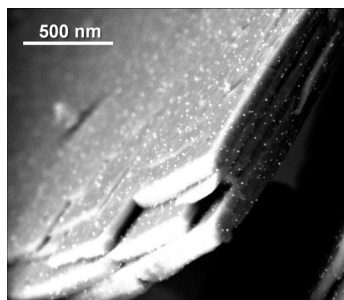
Fig. 3 NanoSEM image of Pt-loaded aluminosilicate COK-14 after catalysis. Pt particles appear as small white spots.

a long *n*-alkane are bifunctional catalytic processes in which the noble metal catalyzes dehydrogenation and hydrogenation, while the carbon–carbon bonds of the *n*-alkane are rearranged on acid sites *via* alkylcarbenium ion chemistry.[14] The parent purely siliceous COK-14 lacking Brønsted acid sites (Fig. 2c) was inactive, as expected. Bifunctional Pt-loaded aluminosilicate COK-14 having Brønsted acid sites was active and reached full conversion of *n*-decane at a reaction temperature of 310 °C. The robustness of this bifunctional OKO catalyst and the absence of deactivation were verified by running the recovered catalyst sample a second time 4 months later.

The significant catalytic activity of this OKO zeolite with a very low concentration of Brønsted acid sites (5 mmol kg^{-1}) is remarkable. The hydroisomerisation selectivity can be used to probe the molecular shape selectivity.[15] On 12-MR zeolites, the refined constraint index (CI°), representing the yield ratio of 2-methylnonane to 5-methylnonane at 5% conversion yield, is in the range 1–2.5, while 10-MR zeolites favour 2-methylnonane formation and have higher CI°. The CI° value of COK-14 is 1.6, confirming the presence of 12-MR pores.

In conclusion, a stable aluminosilicate version of OKO zeolite was obtained by alumination of -COK-14 using Al-ALD, ammonium exchange and deammoniation at 400 °C. Introducing traces of Al through Al-ALD appeared sufficient to stabilise the fully connected OKO framework. Investigation of alternative heteroatom introduction methods to stabilise the fully connected OKO framework and deeper investigation of the origin of this stabilisation using multidimensional NMR and molecular modelling is ongoing. Al-ALD proved to be efficient for generating Brønsted acid sites in OKO zeolite. In this way, a stable aluminosilicate zeolite with 10- and 12-MR pores became available for acid catalysis. ALD originally has been developed for manufacturing of electronic compounds. Although application of ALD for massive catalyst production may be out of reach, it may be considered for preparation of model systems for scientific investigation, and perhaps for medium-scale production since efforts on automation and continuous processing are being made currently.[16]

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