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Original article

Evidence for the catalytic properties of ultramarine pigment

Kokkie Schnetz^{a,*}, Alessa A. Gambardella^b, Roel van Elsas^c, Joost Rosier^c, Edgar E. Steenwinkel^d, Arie Wallert^b, Pieter D. Iedema^a, Katrien Keune^{a,b}

^a University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands

^b Rijksmuseum Amsterdam, Museumstraat 1, Postbus 74888, 1070 DN, Amsterdam, The Netherlands

^c Vrije Universiteit, De Boelelaan 1105, 1081 HV, Amsterdam, The Netherlands

^d Virent, 3571 Anderson Street, Madison, WI 53704, USA

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ABSTRACT

Ultramarine blue paint layers in oil paintings can be affected by ultramarine ‘disease’ or ‘sickness’: a phenomenon described by a grey appearance and a loss of detail in the artwork. An explanation for this phenomenon is an interaction between the organic binder network and ultramarine pigment, with the pigment acting as a catalyst for the breakdown of the network. This breakdown results in micro-cracks in the paint film, which influences the appearance of the artwork. To investigate the possible catalytic property of ultramarine pigment, a test reaction – the dehydration of methanol to dimethyl ether – was carried out, with and without ultramarine pigment present in a micro-reactor with in-line gas chromatography mass spectrometry. It was observed that a higher yield of dimethyl ether was obtained in the presence of ultramarine pigment, confirming that ultramarine pigment possesses catalytic properties similar to commercial zeolitic silica-alumina catalysts.

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1. Introduction

Ultramarine pigment has been used as a blue pigment in oil paintings since medieval times. Traditionally it was produced from lapis lazuli rock, until the invention of synthetic ultramarine in the early 19th century. Nowadays, both types of ultramarine pigments are used. Over time, oil-based ultramarine paint layers have been found to be impacted by an undesirable phenomenon often referred to as ‘ultramarine sickness’ or ‘ultramarine disease’. This phenomenon was identified by Pettenkofer as early as the late 19th century [1], when he described the phenomenon as a loss of detail and a discoloration with a grey blue appearance of the paint layer (an example of the phenomenon can be found in Fig. 1). Over the years, many theories have been proposed and they generally fall into two main categories. The first category attributes the discoloration of the paint layers to the loss of color of pigment particles themselves [2,3] and has been identified as a mechanism for fading of ultramarine pigment in fresco paintings [4]. The second explanation

focuses on formation of micro-cracks between ultramarine pigment particles and the organic binder, causing scattering of incoming light. The light scattering results in a loss of transparency, while the particles themselves still retain their color [1,5,6]. The susceptibility of ultramarine paint layers to these cracks has generally been attributed to poor affinity of hydrophilic ultramarine particles with the organic, more hydrophobic binder [6]. However, as the crystalline structure of the particles shares resemblance to the structure of materials used in industrial catalysts, this paper proposes that the particles play a more active role in the degradation of the organic binder. This study investigates the potential role of ultramarine pigment as a heterogeneous catalyst for degradation of the binder in ultramarine paint layers. Confirming this would provide support for the explanation for the presence of both micro-voids and micro-cracks as found by Klaas [6].

The brilliant blue color of ultramarine pigment originates from the mineral lazurite ((Na,Ca)₈(AlSiO₄)₆(SO₄,OH,S,Cl)₂), which is present in lapis lazuli rock: a blue opaque semi-precious stone, historically found and mined in current Afghanistan [7]. Lazurite has the same crystal structure as the mineral sodalite, Na₈[(AlSiO₄)₆]Cl₂, which is a feldspathoid group mineral with a zeolite structure [8], having so-called sodalite or β-cages (chemical formula (Al₃Si₃O₁₂)^{3−}) as framework (Fig. 2a). The sodalite cages are three-dimensional structures, composed of eight hexagons and six tetragons with Al³⁺ and Si⁴⁺ on the corner points, connected by

* Corresponding author.

E-mail addresses: kokkieschnetz@gmail.com (K. Schnetz), a.gambardella@rijksmuseum.nl (A.A. Gambardella), r.van.elsas@vu.nl (R. van Elsas), j.c.rosier@vu.nl (J. Rosier), edgar.steenwinkel@virent.com (E.E. Steenwinkel), a.wallert@rijksmuseum.nl (A. Wallert), P.D.Iedema@uva.nl (P.D. Iedema), k.keune@rijksmuseum.nl (K. Keune).

Fig. 1. ‘Woman scouring Metalware’, Jan Steen, c. 1650–1660, oil paint on panel, inventory number SK-A-391, Rijksmuseum Amsterdam. The blue skirt has lost most of its modelling and clearly stands out as anomalous: An example of “ultramarine sickness”. (For interpretation of the references to colour in the text and figure legend, the reader is referred to the web version of this article.)

Fig. 2. Schematic overview of a β -cage, with every corner an alumina or silica tetrahedron (a). 3-D structure of alumina or silica tetrahedron (b), crystal structure of lazurite (c), S_3^- radical inside β -cage (d) graphics made with Jmol [32].

oxygen atoms. Each corner point is a tetrahedron with a net formula of AlO_4^- or SiO_4 (Fig. 2b). In lazurite, the cages are closely packed and form channels with diameters smaller than 2.8 Å (Fig. 2c). The negative charge of the framework, due to Al, is counterbalanced by non-framework Na and Ca cations. The β -cages are not empty: They often contain anionic species, and in case of lazurite most cages contain sulfate. Besides sulfate, more reduced sulfur species are also present in lazurite, such as paramagnetic S_2^- and S_3^- radical anions (Fig. 2d). These species are chromophores and give lazurite its blue color [9].

These radicals are unstable but are stabilized within the β -cages [10].

The β -cage structure of lazurite is also found in commercial catalysts, based on synthetic aluminosilicates, such as zeolite X, zeolite Y and Faujasite [11], where Lewis and Brønsted acid sites are responsible for their catalytic activity (Fig. 3). The activity of commercial aluminosilicate catalysts can be enhanced or decreased by pre-treatment of the catalyst. To enhance the catalytic activity, cations are exchanged by protons, which lead to more acidic sites,

Fig. 3. Schematic representation of creation of Brønsted acid sites (hydrogen ions) on heterogeneous silica alumina acid catalysts (upper) and schematic representation of the conversion of Brønsted acid sites into Lewis acid sites (incompletely coordinated aluminum ions) (lower).

while the activity can be decreased when ammonium is absorbed onto acidic sites [11,12].

Indications for catalytic degradation of ultramarine-pigmented paint layers can be found in earlier work. In a comparative study by Keune et al. [13], paints prepared from traditional pigments in linseed oil were subjected to accelerated aging, by exposure to artificial light and high humidity. After aging, the oil-paint reconstruction containing ultramarine pigment became extremely powdery, compared to other traditional pigments. Subsequent pyrolysis gas chromatography mass spectrometry (py-GC-MS) and electrospray mass spectrometry (ESI-MS) analyses of the degraded sample revealed a highly oxidized and hydrolyzed oil binder. Compared to the other paints, the highly oxidized nature of the ultramarine reconstructed paint suggests a catalytic breakdown of the binder and, in turn, a structural failure of the paint layer. More recently, similar degradation was described by de la Rie et al. [14] in paint containing synthetic ultramarine in linseed oil-based paint and urea-aldehyde resins. After accelerated aging by exposure to light, they observed rapid erosion of the linseed oil binder when ultramarine pigment was incorporated in the paint layer.

The catalytic activity of natural lazurite has not been widely investigated; however the presence of synthetic ultramarine pigment has been related to increased perfume degradation [15]. Fukui et al. investigated the influence of several pigments on the conversion rate of linalool using a micro-reactor at 178 °C in combination with off-line GC-MS analysis. The results show that synthetic ultramarine blue and ultramarine violet exhibit high catalytic activity towards the dehydration reaction, consistent with the observed odor change of the samples. They propose a degradation mechanism of linalool, involving formation of intermediate carbonium ions on Brønsted acid sites of the ultramarine. Similarly, in a study by Ogbohe and Ossai [16] accelerated degradation of high-density polyethylene (HDPE) was observed upon exposing HDPE pigmented with synthetic ultramarine to daylight. They proposed that photo-excited ultramarine reacts with oxygen to give singlet oxygen. In the presence of water, the singlet oxygen converts to H₂O₂, which is capable of attacking the polymeric chains.

This paper investigates the potential catalytic activity of both natural lazurite and synthetic ultramarine, by measuring the conversion of methanol to dimethyl ether in the presence of ultramarine/lazurite powder. This dehydration reaction of methanol is known to be catalyzed by aluminosilicate-based catalysts [17–20]. The conversion of methanol to dimethyl ether can be determined by analyzing the ratio of product to reactant using in-line gas chromatography mass spectrometry (GC-MS) with the inlet of the GC functioning as a micro-reactor [21,22]. This in-line GC-MS based micro-reactor method is applied to investigate the catalytic activity of natural lazurite and synthetic ultramarine. In addition, the effect of pre-treatment on the catalytic activity is investigated.

2. Experimental

2.1. Extraction of the low, mid and high-density lapis lazuli samples

Three natural fractions (low-density, mid-density, and high-density lapis lazuli fraction) were extracted from lapis lazuli rock, originating from the Sar-e-Sang region in Afghanistan (provided by P. P. van Pothoven, The Netherlands, 2009). These fractions were separated with a heavy liquid separation procedure developed by IJlst at The Vrije Universiteit, Amsterdam [23]. First, the lapis lazuli rock was cut into smaller pieces using a diamond circular saw. Subsequently, the pieces were crushed to a particle diameter smaller than 200 μm, in a jaw crusher and the fraction bigger than 200 μm milled in a vibrating cup mill. The powder was then sieved with water over a sieve of 20 μm, to remove any very fine dust present. The 20–200 μm fraction was treated with a heavy-liquid procedure in a laboratory overflow centrifuge (LOC 50 separator). Mixtures of diiodomethane and dichlorobenzene with densities of 2.38 g cm⁻³ and 2.45 g cm⁻³, respectively, were used to prepare three lapis lazuli fractions: low-density ($d < 2.38 \text{ g cm}^{-3}$), high-density ($d > 2.45 \text{ g cm}^{-3}$), and mid-density ($2.38 \text{ g cm}^{-3} < d < 2.45 \text{ g cm}^{-3}$), the density range given for natural lazurite [24].

2.2. Sample preparation for enhancement and deactivation of acid sites in synthetic ultramarine

Enhancement of the acidic properties of non-coated synthetic ultramarine (average diameter 9 μm) (FineArtStore, Rochester U.S.) was achieved by decationization. 10 g of synthetic ultramarine was suspended in 500 mL of 0.3 mol L⁻¹ ammonium bicarbonate (ammonium bicarbonate (>99.0%), Sigma Aldrich) solution of pH 9.2 for two hours at 70 °C to replace cations with ammonium. This was followed by heat treatment at 400 °C for two hours to desorb ammonia from most active sites. The procedure was repeated three times to ensure maximum cation removal.

To study the deactivation of the natural lazurite by ion-exchange with ammonium, low-density lapis lazuli sample (0.05 mg) was exposed to a 250 mL ammonium hydroxide solution of pH 9.4 ($2.5 \times 10^{-5} \text{ mol L}^{-1}$) at 70 °C followed by rinsing with de-ionized water and drying in an oven overnight at 50 °C.

2.3. Gas-chromatography mass spectrometry-based micro-reactor experiments

The conversion of methanol to dimethyl ether was performed and monitored in the presence of either synthetic ultramarine or natural lazurite samples (30–60 μm fractions) using a Shimadzu GC-17A-Shimadzu QP 5000 (University of Wisconsin, Madison,

Fig. 4. Extracted ion chromatograms recorded during injection over quartz sand (left). Extracted ion chromatograms recorded during injection over natural mid density lapis lazuli fraction/quartz sand mixture (right). In both graphs the red trace is m/z 32 amu representing the methanol feed and the blue trace is m/z 45 amu representing the produced dimethyl ether. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)

USA) gas chromatography mass spectrometer (GC–MS), with an electron ionization of 110 eV. Each sample (0.05 g) was mixed with inactive quartz sand (0.15 g; 50–70 mesh, Sigma Aldrich) and held between plugs of quartz wool in the quartz inlet liner (3.5 mm inner diameter) of the GC. Inactive quartz sand without ultramarine/lazurite (0.20 g) was used as a blank. The temperature of the inlet was kept at 280 °C, unless otherwise specified. After equilibrating the sample for 30 min, an excess amount of methanol (>99.9%, Sigma Aldrich) (0.2 μ L) was injected into a helium gas stream fed to the inlet liner at a flow rate of 114 mL/min with a split ratio of 1:100. The gaseous reaction mixture was then fed into the GC column (Restek RTX-5ms), kept at 150 °C, and the amount of methanol converted to dimethyl ether was determined in-line by MS. As an excess of methanol was injected, no separation of the methanol and dimethyl ether peaks could be achieved, therefore extracted ion chromatograms were used. The base peak of dimethyl ether at m/z 45 and the molecular ion of methanol at m/z 32 were used to determine the relative amount of dimethyl ether formed, as both are unique markers in this mixture. Data processing was performed with *GCMS solution v1.1* software by determining the peak area of the extracted ion chromatograms. The peak area was integrated from the onset of the response to 0.5 min to include for peak tailing. All measurements have been performed by injecting methanol at least in triplicate over a given sample. To test the repeatability of the method, the in-line GC–MS procedure was carried out in duplicate using synthetic ultramarine and decationized synthetic ultramarine, as these samples were available in abundance.

2.4. Scanning electron microscopy/wavelength dispersive X-ray microanalysis (SEM/WDS)

For wavelength dispersive X-ray microanalysis (WDS) analysis, particles from the three lapis lazuli fractions and synthetic (Kremer, Pigment blue 29) ultramarine particles were imbedded in Technovit 2000 LC mounting resin, a one-component methacrylate that polymerizes under visible blue light (Heraeus Kulzer GmbH, Germany). The embedded samples were subsequently dry polished with Micro-mesh® polishing cloths (final step 12,000 mesh). The analyses were executed using a JEOL JXA-8530F Hyperprobe Field Emission Electron probe micro analyzer, which was equipped with 5 WDS spectrometers, SDD ED system, CL panchromatic and xCLent systems (University Utrecht, The Netherlands). The electron microprobe analyzer was operated at 15 keV, 1 nA and a beam diameter between 3 and 5 μ m, depending on the size of the particles. On average, 3–4 grains were analyzed for each sample with 3–4 spots

per grain. To avoid beam damage, which can cause evaporation of sodium and also in particular sulfur, minimal exposure times and beam current were deployed. To obtain semi-quantitative EDS data (mean calculated values and standard deviations) the counts were converted to oxidic weight percentages by applying ZAF correction.

2.5. X-ray powder diffraction (XRD)

Characterization of the crystalline phases in the natural lapis lazuli fractions was established by XRD measurements, using a Bruker AXS D8 Discover diffractometer (Cultural Heritage Agency of The Netherlands, Amsterdam, The Netherlands). The diffractometer contains a Cu K α tube (40 kV, 30 mA, equipped with a flat graphite monochromator) X-ray source, and a 2D HiStar detector. The fractions were ground to approximately 10 μ m in diameter before measuring to diminish effects of heterogeneity. Data was collected in two frames (16.2–44 and 40–68 2-theta) for 1200s each, with the detector located 20 cm from the samples. Corresponding GADDS software was used to integrate the acquired 2D images into 1D diffraction patterns with chi angles from -100° to -81° . For each sample, four acquisitions were obtained at different locations and averaged.

3. Results and discussion

3.1. Catalytic activity of natural lapis lazuli fractions and synthetic ultramarine with GC–MS-based micro-reactor experiments

The extracted ion chromatograms of methanol (m/z 32) and dimethyl ether (m/z 45) in the presence and absence of mid-density lapis lazuli fraction (natural lazurite) in the micro-reactor are shown in Fig. 4. In the presence of this fraction, dimethyl ether yield is significantly higher, indicating a conversion due to the presence of natural lazurite. To quantify this activity, the ratio of the peak area of m/z 45 over m/z 32 was calculated (Tables 1a and 1b). When mid-density lapis lazuli is present in the micro reactor, this ratio is 7.29%, whereas the blank experiment with only quartz sand resulted in a ratio of 0.61%. This significant increase of conversion shows that natural lazurite is catalytically active. An overview of the conversion ratios of all samples measured is given in Table 2. Table 3 shows that the in-line GC–MS based micro-reactor method is reproducible (assuming a 90% confidence interval).

To confirm that no other products were formed in significant amounts, the total ion chromatograms from m/z 15 to m/z 250 were also recorded, but no additional products were detected. The

sample and the quartz wool holding the samples were also visually inspected after the measurement to detect formation of solid carbonaceous deposits often referred to as 'coke'. The quartz wool did not discolor, indicating that no significant coke formation occurred during the experiment.

Because the presence of strong acid sites should lead to coke formation, a lack of coke formation suggests that the tested samples contain weak to medium strength acid sites [18]. This is also

in accordance with the general theory that a high alumina concentration (low silica to alumina ratio) leads to the presence of weak to medium strength acid sites [11]. Lazurite has a very low silica to alumina ratio ($\text{Si}/\text{Al} \approx 1$) compared to a frequently used commercial solid acid catalysts as zeolite Y with a $\text{Si}/\text{Al} > 2.5$ [11].

3.2. Comparison of the catalytic activity of synthetic ultramarine and mid-density lapis lazuli fraction (natural lazurite)

To make a fair comparison between the catalytic activity of natural mid-density lapis lazuli fraction (natural lazurite) of 11.95 with the catalytic activity of synthetic ultramarine of 13.26, the difference in surface area should be taken into account. The calculated average particle size of all the tested natural lapis lazuli fractions is $45 \mu\text{m}$ (the average of the $30\text{--}60 \mu\text{m}$) and for synthetic ultramarine the average particle size is $9 \mu\text{m}$ as provided by the supplier. Assuming spherical shaped particles, the surface area of the synthetic ultramarine samples is 5 times higher compared to the natural fractions tested in this study. Correcting the catalytic activity of the synthetic ultramarine sample for the difference in surface area results in a catalytic activity of 2.66. The natural mid-density lapis lazuli fraction shows a higher catalytic activity (4.5 times higher), compared to the synthetic one (Table 2). We attribute this higher catalytic activity of the tested natural mid-density lazurite fraction to a larger concentration of non-framework calcium cations in naturally occurring lazurite compared to synthetic ultramarine as synthetic ultramarine is industrially made from China clay ($\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4$), sulfur, sodium carbonate in contact with a reducing agent [9] with low amount of calcium present as an impurity. SEM/WDS analysis confirmed that the tested synthetic ultramarine contains less calcium cations: only 1.8% versus 7.3% in the natural pigment used in this study (Table 4). Bryant showed that a partial exchange (75%) of sodium with calcium enhances the conversion of ethanol to diethyl ether and ethylene by a fac-

Table 1a

Conversion of methanol to dimethyl ether when injected over inactive quartz sand.

Measurement	Peak area m/z 45	Peak area m/z 32	Ratio *1000
Blank: sand injection 1	3.27E+03	5.83E+06	0.56
Blank: sand injection 2	4.20E+03	5.47E+06	0.77
Blank: sand injection 3	3.00E+03	5.21E+06	0.57
Blank: sand injection 4	3.55E+03	5.15E+06	0.69
Blank: sand injection 5	4.80E+03	5.86E+06	0.82
Blank: sand injection 6	3.54E+03	5.39E+06	0.66
Blank: sand injection 7	3.25E+03	5.50E+06	0.59
Blank: sand injection 8	2.52E+03	5.38E+06	0.47
Blank: sand injection 9	1.94E+03	5.07E+06	0.38
Average	3.34E+03	5.43E+06	0.61
SD	8.46E+02	2.75E+05	0.14

Table 1b

Conversion of methanol to dimethyl ether in the presence of medium density lapis lazuli fraction (lazurite fraction).

Measurement	Peak area m/z 45	Peak area m/z 32	Ratio *1000
Lazurite injection 1	2.65E+05	4.77E+07	5.56
Lazurite injection 2	3.18E+05	5.06E+07	6.28
Lazurite injection 3	3.65E+05	4.94E+07	7.38
Lazurite injection 4	4.06E+05	4.79E+07	8.48
Lazurite injection 5	4.12E+05	4.88E+07	8.43
Lazurite injection 6	3.94E+05	5.17E+07	7.63
Average	3.60E+05	4.93E+07	7.29
SD	5.80E+04	1.57E+06	1.17

Table 2

Overview of catalytic activity of the samples – for ease of comparison the term catalytic activity is introduced. This is the ratio of the peak areas of m/z 45 and m/z 32 of the sample divided by the ratio of peak area of m/z 45 and m/z 32 for quartz sand (blank). A value >1 for catalytic activity is the result of a higher conversion than expected and catalytic activity of the sample is probable.

Sample	Number of injections (n)	Ratio 45/32 peak area *1000	SD	Catalytic activity [a.u.]
Quartz sand	9	0.61	0.14	1.00
Natural mid-density lapis lazuli fraction	6	7.29	1.17	11.95
Natural low-density lapis lazuli fraction	5	36.78	2.57	60.30
Natural low-density lapis lazuli fraction treated with ammonium (injection 1)	1	1.84	n/a ^a	3.02
Natural low-density lapis lazuli fraction treated with ammonium (injection 9)	1	4.91	n/a ^a	8.05
Natural low-density lapis lazuli fraction treated with ammonia after stabilization at 325 °C	4	5.00	0.22	8.20
Natural high-density lapis lazuli fraction	5	1.72	0.12	2.82
Synthetic ultramarine	13	8.09	1.43	13.26 (2.66 ^b)
Synthetic de-cationized ultramarine	12	39.73	6.62	65.13 (13.07 ^b)

^a Only one injection, so no standard deviation is available. The difference in activity between injection 1 and 9 indicates that desorption of ammonia is taking place during the measurement.

^b Corrected catalytic activity to reflect the difference in surface area between the synthetic ultramarine tested and the natural fractions tested.

Table 3

Repeatability of test procedure – equivalency was tested in a 2-Sample t test with $\alpha = 0.05$ [28] and assuming normality. The alternative hypothesis posed was that mean (test 1) $>$ mean (test 2). P values > 0.05 indicate the alternative hypothesis is untrue and therefore there is not enough evidence to conclude that the means differ at the 0.05 level of significance.

Experiment	Number of injections (n)	Mean of multiple injections	Standard deviation of multiple injections	Probability values (P value)
Quartz sand 1	4	0.6486	0.098	0.331
Quartz sand 2	5	0.6123	0.138	
Synthetic ultramarine 1	5	8.468	1.558	0.336
Synthetic ultramarine 2	8	8.089	1.434	
Decationized synthetic ultramarine 1	6	39.726	6.618	0.616
Decationized synthetic ultramarine 2	6	38.649	5.665	

Table 4
Overview of WDS results on the various density fractions retrieved from natural lapis lazuli and synthetic ultramarine with n being the number of total spot analyses over the number of particles (p) investigated.

Oxide (wt%)	Mid-density lazurite fraction n = 10, p = 4 (sd)	Low-density lazurite fraction n = 12, p = 3 (sd)	High-density lazurite fraction n = 11, p = 3 (sd)	Synthetic ultramarine n = 2, p = 3 (sd)
Na ₂ O	20.37 (0.42)	19.42 (1.23)	19.43 (0.59)	12.23 (3.67)
SiO ₂	34.78 (0.67)	34.08 (0.92)	34.27 (0.56)	30.53 (1.60)
SO ₃	19.53 (2.21)	17.27 (2.18)	19.36 (0.98)	23.71 (1.94)
CaO	2.89 (0.18)	2.65 (0.23)	3.11 (0.30)	0.26 (0.00)
K ₂ O	0.20 (0.12)	0.13 (0.13)	0.30 (0.08)	0.60 (0.16)
Al ₂ O ₃	26.20 (0.81)	26.68 (0.77)	26.29 (0.38)	19.82 (2.16)
MgO	0.03 (0.02)	0.02 (0.03)	0.06 (0.17)	0.18 (0.04)
FeO	0.02 (0.03)	0.02 (0.03)	0.02 (0.02)	0.00 (0.00)
Normalized atomic %				
Na	32.05 (0.67)	31.57 (1.48)	31.08 (0.79)	24.25 (4.13)
Si	28.23 (0.38)	28.59 (0.63)	28.28 (0.48)	31.74 (2.57)
S	11.89 (1.26)	10.88 (1.45)	11.99 (0.48)	18.49 (0.95)
Ca	2.51 (0.17)	2.38 (0.18)	2.74 (0.22)	0.29 (0.04)
K	0.20 (0.12)	0.14 (0.13)	0.24 (0.09)	0.78 (0.10)
Al	25.07 (0.97)	26.39 (0.68)	25.58 (0.60)	24.19 (0.58)
Mg	0.03 (0.03)	0.03 (0.04)	0.08 (0.20)	0.28 (0.10)
Fe	0.01 (0.02)	0.02 (0.02)	0.02 (0.02)	0.00 (0.00)
Total	100	100	100	100
Atomic fraction based on 12 framework cations (Al + Si) ^a				
Na	7.22 (0.15)	6.89 (0.38)	6.93 (0.29)	5.24 (1.18)
Si	6.36 (0.14)	6.24 (0.10)	6.30 (0.05)	6.81 (0.17)
S	2.68 (0.33)	2.38 (0.32)	2.67 (0.13)	3.96 (0.02)
Ca	0.57 (0.04)	0.52 (0.04)	0.61 (0.06)	0.06 (0.00)
K	0.05 (0.03)	0.03 (0.03)	0.05 (0.02)	0.17 (0.03)
Al	5.64 (0.14)	5.76 (0.10)	5.70 (0.05)	5.20 (0.17)
Mg	0.01 (0.01)	0.01 (0.01)	0.02 (0.05)	0.06 (0.02)
Fe	0.00 (0.00)	0.00 (0.01)	0.00 (0.00)	0.00 (0.00)
Non-frame work cations (Na, Ca, K, Mg, Fe)	7.84 (0.14)	7.46 (0.41)	7.62 (0.34)	5.53 (1.19)
Charge of non-framework cations ^b	8.42 (0.14)	7.99 (0.44)	8.25 (0.40)	5.65 (1.17)

^a Compositions are recalculated on the basis of 12 framework cations (Al + Si) per formula unit. The $(At \%_{Al} + At \%_{Si})/4.44 = 12$, the atomic fraction of the other cations can be calculated by $At \%_{Me}/4.44$.

^b To calculate the charge of non-framework cations, the following formal charges were used: Na 1, Ca 2, K 1, Mg 2 and Fe 2.

tor 6–12 [25]. The enhancement by calcium on catalytic activity is also shown more recently by Xu et al. [26].

3.3. Catalytic activity of the natural lazurite fractions

During the testing of the various density fractions of the lapis lazuli (low-density, mid-density, and high-density natural lapis lazuli fractions) separated by the heavy liquid separation procedure it was noted that the different fractions exhibit different catalytic activities. The GC-MS-based micro-reactor conversion data showed that the natural low-density fraction was a factor 5.05 more active than the natural mid-density lazurite fraction (Table 2). The XRD patterns of the low- and mid-density fraction (Fig. 5) revealed that in both fractions lazurite is the main crystalline component. The XRD patterns also indicated a small difference between the two fractions. In the natural low-density lapis lazuli fraction, some traces of sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$, with exactly the same crystal structure as lazurite) are present, probably contributing to the catalytic activity of the sample in the same way as lazurite. Furthermore, the quantitative elemental composition established with SEM/WDS analyses of the two fractions show subtle differences in the lazurite composition (Table 4). To assess these subtle differences between the fractions, a comparison is made based on the cell formula of lazurite $(\text{Na,Ca})_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4,\text{S,Cl})_2$ [27]. The aluminum content for the natural low-density and natural mid-density fraction is 5.76 ± 0.10 and 5.64 ± 0.14 per 12 framework cations, respectively. Also, the positive charge of the sum of non-framework cations (Na, Ca, K, Mg, Fe) is 7.99 ± 0.44 per

12 framework cations for the natural low-density fraction and 8.42 ± 0.14 per 12 framework cations for the natural mid-density fraction (Table 4). From this data it can be inferred that the natural low-density fraction probably has a slightly higher aluminum content and a slightly lower non-framework cation content. Statistical equivalency testing shows that the means differ at the 0.05 level of significance under the assumption that the data has a normal distribution [28]. As observed in literature these differences might affect catalytic activity. Migliori et al. showed that a higher alumina content can increase the catalytic activity, although this was identified in a different silica-alumina framework (MFI framework ZSM-5) [19]. We would speculate that similar effects can be at play here too. The relative lower amount of non-framework cations in the natural low-density fraction indicates a higher degree of decationization and could thus result in a higher level of catalytic activity [33]. However, we cannot rule out that other factors may also play a role here (e.g. particle size).

The natural high-density lapis lazuli fraction shows only minimal increase in catalytic activity of a factor 2.82 with respect to the quartz sand sample. XRD analysis shows that for the natural high-density fraction – in contrast to the natural low- and natural mid-density lapis lazuli fractions – the main crystalline fraction is diopside, with minor contributions of lazurite and sodalite and possible a trace of pyrite and an unidentified mineral (Fig. 5). The presence of a small amount of lazurite in the natural high-density fraction was also confirmed by SEM/WDS measurements. Quantitative elemental composition data from these measurements indicate that the aluminum ratio of lazurite particles in the high-density

Fig. 5. XRD pattern of (a) low-density, (b) mid-density, and (c) high-density fractions extracted from lapis lazuli rock. Each pattern is the average of 4 patterns acquired in different regions of a given prepared sample.

lapis lazuli fraction is statistically not different from the aluminum ratio of the lazurite in the mid density lapis lazuli fraction (Table 4). The residual catalytic activity of this fraction could be explained by the presence of small amounts of lazurite of similar composition as found in the mid density lapis lazuli fraction and sodalite in the sample.

3.4. Enhancement and deactivation of acid sites in synthetic ultramarine

The influence of exchange of cations by protons (de-cationization) on the catalytic activity was determined with synthetic ultramarine, as this material was available in abundance. The catalytic activity of the de-cationized synthetic ultramarine increased by a factor of 4.91 compared to the non-treated version of the sample (Table 2). As with commercial silica alumina catalysts, de-cationization of ultramarine leads to an increase in catalytic activity by creating more acidic sites. However, when comparing the activity of de-cationized synthetic ultramarine with commercial catalysts, it is evident that the conversion level for the dehydration reaction of methanol to dimethyl ether is a factor 100 lower than for commercial catalysts. Commercial catalysts typically have conversion levels of 40%–85% at temperatures between 277 °C to 320 °C [29]. An explanation for the low conversion is the small pore structure of synthetic ultramarine and natural lazurite for methanol to get into the cage (Fig. 2c). Larger pore sizes in commercial catalysts allow organic molecules to diffuse inside and interact with the large reactive surface, which has a surface area typically in the range of 1–1000 m² g^{−1} [30]. In comparison, the synthetic ultramarine fraction used in this experiment has a reactive surface area that equals 0.28 m² g^{−1} (based on an average particle size of 9 μm and with only an outer surface accessible for reactions, and the assumption of spherical particles). This is a factor of up to 4000 lower than commercial catalysts.

Deactivation of acid sites was studied on the natural low-density lapis lazuli fraction, because of its high natural activity as shown in the previous section. By exchanging protons for ammonium, a decrease in catalytic activity by more than a factor of 11.0 was observed. During subsequent injections over the treated catalyst the activity of the catalyst increased from 3.02 to 8.05 (from injection 1 to 9; see Table 2), which is an indication that ammonia was probably desorbing from the sample due to the temperature in the micro reactor of 280 °C. An additional pre-treatment of heating the sample to 325 °C before injecting methanol over the micro reactor at 280 °C resulted in a stabilization of the activity at 8.20. The sample did not regain its complete catalytic activity of 60.30 probably due to the fact that at a temperature of 325 °C, most active sites are still blocked by ammonium [31].

4. Conclusion

The possible catalytic property of ultramarine/lazurite pigment as a cause for a phenomenon known as 'ultramarine sickness' in paint layers pigmented with ultramarine/lazurite pigment, was studied by using a gas-phase test reaction to show that ultramarine/lazurite can exhibit catalytic activity. The experiments clearly showed that both natural lazurite and synthetic ultramarine can act as an aluminosilicate catalyst, as demonstrated by the increase in dimethyl ether yield in the presence of both natural lazurite and synthetic ultramarine. As such reactions are known to be catalyzed by weak to medium strength acid sites, it can be inferred that these types of acid sites are present in these pigments.

Ongoing research focuses on studying the catalytic effect of ultramarine/lazurite pigment on the binder network, at lower temperatures, including room temperature. These studies include model systems representative for linseed oil binder as well as on complete oil paint reconstructions.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.culher.2020.04.002>.

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